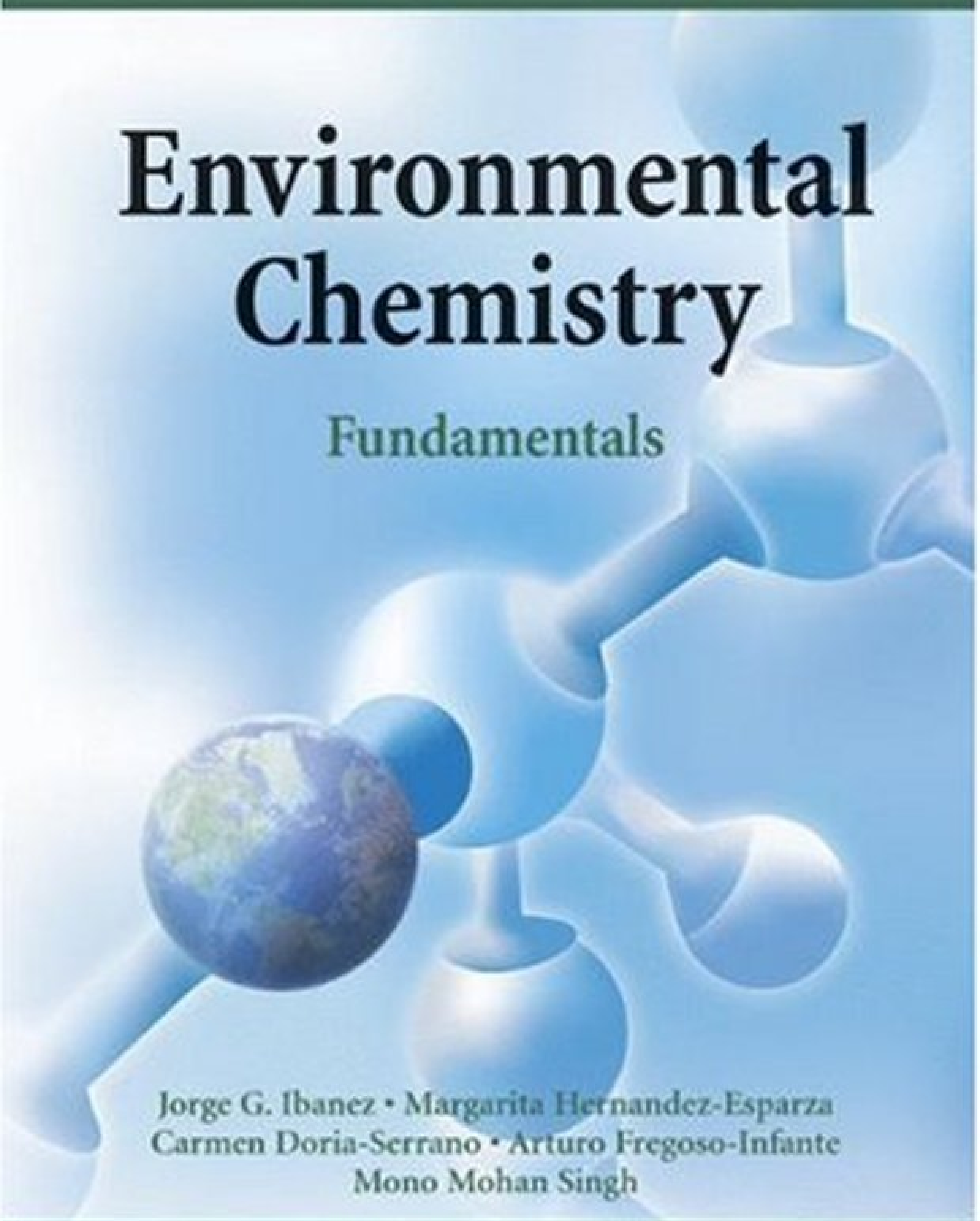
Environmental Chemistry

Fundamentals



Jorge G. Ibanez • Margarita Hernandez-Esparza
Carmen Doria-Serrano • Arturo Fregoso-Infante
Mono Mohan Singh

Springer

Environmental Chemistry

Environmental Chemistry

Fundamentals

Jorge G. Ibanez
Margarita Hernandez-Esparza
Carmen Doria-Serrano
Arturo Fregoso-Infante
Mexican Microscale Chemistry Center
Dept. of Chemical and Engineering Sciences
Universidad Iberoamericana—Mexico City

Mono Mohan Singh
National Microscale Chemistry Center
Merrimack College—North Andover, MA

Springer

Library of Congress Control Number: 2007920054

ISBN-13: 978-0-387-26061-7
eISBN-13: 978-0-387-31435-8

Printed on acid-free paper.

9 8 7 6 5 4 3 2 1

springer.com

Foreword

When I was about eight years old, the beautiful wetland that stretched out beside my home was destroyed and was replaced by a large office park. My father, upon seeing how upset I was, said to me, "If you care about something, you care enough to learn about it." This event perhaps more than anything else caused me to dedicate my life to sustaining our environment, our world, through the power of chemistry. And perhaps, more than anything else, this is also the lesson of this excellent textbook, Environmental Chemistry: Fundamentals and Microscale Experiments. It is the knowledge and perspective contained in this textbook that allows all of us as scientists to understand the way our environment functions on a molecular level and how to identify potential threats to human health and the environment that need to be addressed. But it does more than that. It also gives us the fundamental basis for ensuring that those problems never arise by using the Principles of Green Chemistry that emphasize avoiding hazards through innovations in chemistry.

For much of the history of the environmental movement, the scientific community has sought to identify and quantify environmental problems. If we were able to identify the problems, we then sought ways to clean them up sometimes elegantly, sometimes expensively, sometimes both. Because of the knowledge and fundamentals presented in this textbook we are able to build on those historical approaches and incorporate the principles of sustainable design into the chemical products and processes of tomorrow. The authors deserve tremendous credit for their extraordinary efforts that have resulted in this comprehensive and much needed volume. This book will provide an excellent resource for those aspiring scientists to understand that the way to protect the Earth is through intimately and rigorously understanding the Earth.

Paul T. Anastas
Yale University
December, 2006

Preface

Modern science is not straightforward. Intricate relationships exist among the different disciplines involved in the understanding of virtually every scientific issue and phenomenon. The days of the Renaissance, when a single person could master a large portion of the knowledge then available, are long gone. This is not due to a lack of individual capacity, but rather to the explosion of knowledge, characteristic of our times.

Environmental Science—and more specifically, Environmental Chemistry—finds itself completely immersed in such a scenario. In this regard, a book written by several authors having complementary backgrounds and interests appeared to be an appropriate project to pursue. On the other hand, multiauthored undergraduate textbooks run the risk of lacking smoothness and continuity in the presentation of ideas and concepts. The present project involved many meetings and cross-checking among the five authors. This is why we perceive this finished task as valuable, and we hope that the reader finds a flowing progression and fair treatment of the various subjects.

The book is written with sophomore or junior college students in mind (i.e., undergraduate students in their second or third year). However, issues are often presented in such a way that General Chemistry students—and even graduate students—can find subjects of interest applicable to their level. The book consists of a theoretical section (12 chapters) and a companion book with an experimental section (24 experiments). A brief description now follows (initials of the main authors of each chapter and experiment appear in parentheses).

The beginning of the theoretical section comprises a general introduction to Environmental Chemistry (Chapter 1, MH), and a summary of the main background concepts that a student of Environmental Chemistry ought to know (Chapter 2, JI; Chapter 3, JI, AF, MS). We assume that the students have the minimum background in Organic Chemistry and in Biochemistry necessary for Environmental Chemistry. Subsequent chapters discuss the composition and characteristics of the natural chemical processes that occur in the atmosphere (Chapter 4, AF), the lithosphere (Chapter 5, JI), and the hydrosphere (Chapter 6, MH and JI). This discussion concludes by examining natural biochemical processes and introducing the organisms in the biosphere (Chapter 7, CD). Chapters that follow then analyze the effects of many pollutants (Chapter 8, JI, CD and MS; Chapter 9, CD), their treatment (Chapter 10, JI and CD; Chapter 11, CD), and the minimization and prevention of pollution, emphasizing Green Chemistry (Chapter 12, CD). Each chapter also contains a list of educational experiments in the literature related to its subject and a list of other useful references.

The experiments are rather varied, ranging from the characterization of aqueous media to pollutant-treatment schemes. For increased safety, savings, and environmental awareness, as well as for reduced costs, wastes, and environmental damage, we present our experiments at the *microscale* level (sometimes also called *small-scale*). Such experiments typically use microliters or micromoles of at least one of the reagents. The main authors of each experiment are as follows: Experiments 1–4, MH; 5, 6, JI; 7, AF and JI; 8, JI; 9, MH; 10, AF;11,12, JI; 13,14, JI and MS; 15, JI; 16, JI and AF; 17, JI and MH; 18–20, JI;

21, JI (from an experiment by Viktor Obendrauf); 22–24, CD. The answers to selected problems from the various experiments are given in the book's website at www.springer.com. Many open-ended projects are suggested in the *additional related projects* section of each experiment.

The possibilities for accidents or personal injury while performing these experiments are fairly small. However, owing to the incalculable number of variables involved when many individuals perform experiments in separate places with different materials and reagents, we cannot accept any responsibility in such unlikely events. In the same vein, we cannot accept responsibility for any possible consequences when performing the *additional related projects* described above.

The book contains 240 questions, problems, and examples; of these, over 100 are solved in the text. It also contains more than 150 figures, 70 tables, and 1300 references to the literature (almost 50% of these references are related to educational environmental activities and experiments). Lastly, 80 *additional related projects* are suggested in the experimental section.

Further technical notes are in order:

(a) Even though the IUPAC (International Union for Pure and Applied Chemistry) has advised using the symbol e (for the electron) without its negative charge as superscript, we have circumvented this rule for didactic purposes since, in our experience, students are less confused when balancing charges in redox equations when they *actually* see the minus sign of the electron charge.
(b) Physical states are written here as subscripts just below the participants in chemical reactions, except for aqueous species. A few years ago, such physical states started to be written as normal letters rather than subscripts; however, we use the traditional convention here for the sake of clarity. In addition, following the usage set forth by perhaps the most referenced book worldwide in Aquatic Environmental Chemistry (Stumm and Morgan), we adhere in this text to the practice that aqueous species are to be understood as such, even when they appear without the corresponding physical state as subscript. This undoubtedly improves the readability of a large number of reactions. A similar idea applies to the gases in Chapter 4, where it would be cumbersome to write their physical states.
(c) Some chapters and subjects lend themselves more naturally than others to exercises (shown as examples).
(d) Old and new styles of writing references have been combined in this book. Most of the references appear only with initials of the authors, as in the traditional manner. However, other references are written according to an emerging trend that includes entire names.
(e) Equations and figures in the worked examples are not numbered, unless they need to for a practical reason.
(f) A plethora of Environmental Chemistry experiments are performed throughout the world. As this book presents merely a few of these subjects, each chapter also has references to other experimentation found in the literature. The reader is encouraged to inform the authors of any omissions, so that future editions may be as complete as possible.
(g) Environmental Analytical Chemistry is of the utmost importance in understanding a large number of environmental issues, and there are many excellent textbooks and laboratory manuals dealing with this area of interest. Unfortunately, this rather extensive subject requires a stronger background than that assumed for readers of the present book. Furthermore, the methods and techniques involved often call for somewhat sophisticated equipment not available in all schools. It is for these reasons that we have chosen to emphasize other aspects in the present text, and thus urge the readers to seek key references in this field elsewhere. With such a thought in mind, a comprehensive list of Environmental Chemistry experiments that give prominence to analysis—and that require instrumentation beyond that used in the present book—is given in the Appendix.

Jorge Ibanez first conceived the idea for this book. Zvi Szafran (New England College, USA) induced us into making this a full textbook and not simply a laboratory manual. Margarita Hernandez was the architect and Jorge Ibanez the main driving force behind the project—they weaved the threads from the different chapters into an orderly whole. In addition, Carmen Doria endowed this book with her expertise in the Life Sciences and Green Chemistry, Arturo Fregoso in the Atmospheric Sciences, and Mohan Singh in Microscale Chemistry. In addition, all the authors participated in and reviewed other chapters as well.

Work on the book greatly benefited from comments and suggestions made by Hugo Solis (Universidad Nacional Autonoma de Mexico–Universidad Autonoma Metropolitana – Azcapotzalco, Mexico) and Mario Avila (Ecole Nationale Superiure de Chimie de Paris, France – Universidad de Guanajuato, Mexico). In addition, Dara Salcedo (Massachusetts Institute of Technology, USA – Universidad Autonoma del Estado de Morelos, Mexico), Pedro F. Zarate-Del Valle (Universite Pierre et Marie Curie, France – Universidad de Guadalajara, Mexico), Sergio Gomez-Salazar (Syracuse University, USA – Universidad de Guadalajara, Mexico), Martin Adolfo Garcia-Sanchez (ITESO – Guadalajara), and Lorena Pedraza-Segura (Universidad Iberoamericana) also helped reading some portions.

Andrea Silva-Beard gave the book the final administrative "push" for its completion. Rosa Maria Noriega provided the magic touch to the use of language through editing English grammar and style in most of the manuscript. Aida Serrano, Patricia Hernandez-Esparza, Marcela and Daniela Delgado-Velasco revised some parts of the book. Juan Perez-Hernandez (PROVITEC) helped in getting all the authors together for meetings, and Elizabeth Garcia-Pintor tested most of the experiments. Alberto Sosa-Benavides, Adriana Canales-Goerne, Gabriela Castañeda-Delgado, and Alejandro Correa-Ibargüengoitia transformed many of our rough sketches into understandable figures. The cover was developed after an idea first conceived by Carmen María Tort-Oviedo (Universidad Iberoamericana).

We are especially thankful to Ken Howell (Springer) for believing in us, and for his patience and encouragement. We also thank the many other co-authors and experimenters from other institutions that participated at different stages: Zvi Szafran (Merrimack College – Georgia Technical University, USA), Ronald M. Pike (Merrimack College – University of Utah, USA), Patricia Balderas-Hernandez (Universidad Nacional Autonoma de Mexico – Universidad Autonoma del Estado de Mexico), Bruce and Susan Mattson, Michael P. Anderson, Jiro Fujita, and Trisha Hoette (Creighton Jesuit University, USA), Alejandro Alatorre-Ordaz (Universidad de Guanajuato, Mexico), Viktor Obendrauf (Graz Pedagogical Academy, Austria), Michael W. Tausch and Michael Seesing (Universität Duisburg-Essen, Germany), Rodrigo Mayen-Mondragon (CINVESTAV-Queretaro, Mexico), Maria Teresa Ramirez-Silva (Universidad Autonoma Metropolitana – Iztapalapa, Mexico), Christer Gruvberg (University of Halmstad, Sweden), Alanah Fitch (Loyola University-Chicago, USA), and Adolfo de Pablos-Miranda (Institut Quimic de Sarria, Spain).

Also, many thanks are in order for extensive experimental assistance in some cases and exceptional clerical help in others, to colleagues and students at Universidad Iberoamericana: Samuel Macias-Bravo, Veronica Garces-Castellanos, Sebastian Terrazas-Moreno, Rodrigo Mena-Brito, Carlos Navarro-Monsivais, Ignacio Gallo-Perez, J. Clemente Miranda-Treviño, Jose Topete-Pastor, Luis C. Gonzalez-Rosas, Iraida Valdovinos-Rodriguez, Maria Lozano-Cusi, Ana Lozano-Cusi, Enrique Lopez-Mejia, Jose A. Echevarria-Eugui, Karla Garcia, Juan Jose Godinez-Ramirez, Fernando Almada-Calvo, Leticia Espinoza-Marvan, Rosa Margarita Ruiz-Martin, Juan Jose Arrieta, Alejandro Moreno-Argüello, and Denise Salas.

Funding was—without a doubt—of paramount importance for the development of experiments through projects and research stays at diverse stages. This was kindly provided by Universidad Iberoamericana (Mexico), the International Business Office of CONACYT (Mexico), Merrimack College (USA), the National Microscale Chemistry Center (USA), the National Science Foundation (USA), the Fulbright Program of the Department of State (USA), the Linnaeus – Palme Program of the Swedish Agency for International Development (Sweden), the Alfa Program of the European Commission (Belgium), Loyola University of Chicago (USA), Creighton Jesuit University (USA), the University of Halmstad (Sweden), and the University of Guadalajara (Mexico).

Above all, we thank our families for their gift of patience and understanding during the seemingly unending and highly demanding hours that this book required.

We are convinced that among the most important issues in Environmental Science are the appreciation and knowledge of the different phenomena involved in our environment, and the on-going need to participate in its care. We are hopeful that through this book we are contributing with a grain of sand to such an end.

Our environment is undoubtedly part of a greater, transcendental reality—it is in this sense that we dedicate the present book ***ad majorem Dei gloriam***.

(Note: Names of the authors appear below followed by the institutions where they did graduate work, then by their present affiliations).

Margarita Hernandez-Esparza (Stanford University). Universidad Iberoamericana, Mexico City.

Ma. del Carmen Doria-Serrano (Universidad Nacional Autonoma de Mexico). Universidad Iberoamericana, Mexico City.

Arturo Fregoso-Infante (University of Missouri-Kansas City). Universidad Iberoamericana, Mexico City.

Mono Mohan Singh (St. Petersburg Institute of Technology). Merrimack College, MA, USA.

Jorge G. Ibanez (University of Houston). Universidad Iberoamericana, Mexico City.

Mexico City and North Andover, MA, USA
Spring of 2007

Contents

Part 1 Introductory Concepts

Part 2 The Chemistry of Natural Environmental Processes

Part 3 Effects, Treatment and Prevention of Pollution

Part 1

Introductory Concepts

1

Introduction to Environmental Chemistry

When we see the words "Environmental Chemistry," several questions come to mind.

- What do we understand as Environmental Chemistry?
- Why is it important that we understand and know Environmental Chemistry?
- What areas of knowledge are related to Environmental Chemistry, and how can we use this concept?

In this chapter we consider these questions and try to explain what many scientists have come to agree on, as to the meaning of Environmental Chemistry. It is clear that Environmental Chemistry encompasses a number of fields of chemistry and chemical processes that take place in soil, water, air, and living systems.

1.1 Chemistry of the Natural Processes in the Biosphere

Our Earth is a reaction vessel, in which complex reactions take place. It can also be considered a closed system, in which atoms and molecules are neither created nor destroyed, and a balance is maintained. The atoms and molecules are always located in some environmental compartment, combined in different compounds, present in different physical states, or accumulated in organisms. They are transported through

- Local, regional and global mass flow
- Horizontal and vertical mass transfer in the atmosphere, hydrosphere, and lithosphere, following different pathways and exchange mechanisms among different environmental compartments
- Complex spatial and temporal physical phase equilibria
- Chemical transformations of biotic and abiotic nature, using air and water as their mobile phases and equilibrating media

All the chemical reactions that take place in the environment—and that are directly related to the natural cycling and transformation of the elements on Earth—are identified as Environmental Chemistry. Likewise, the transformations or chemical interactions and processes of (a) substances introduced by human activity into the environment, (b) natural compounds, or (c) living organisms are included in this concept.

In the natural cycles of elements and molecules, the biochemical and chemical transformations have been recycling the elemental compounds for millennia, maintaining a balance and a cycling rate that allows natural ecosystems and organisms to coexist. Originally, the concept of Environmental Chemistry focused on

- Reactions related to the "biogeochemical cycles"
- Reactions that may affect the growth of plants and the sustainment of organisms
- Reactions and processes that involve geochemical formations and transformations

However, the ever-increasing complexity of biochemical and chemical processes has changed this focus, and a wider range of views and new aspects are incorporated into the concept. Examples of some natural reactions and transport phenomena

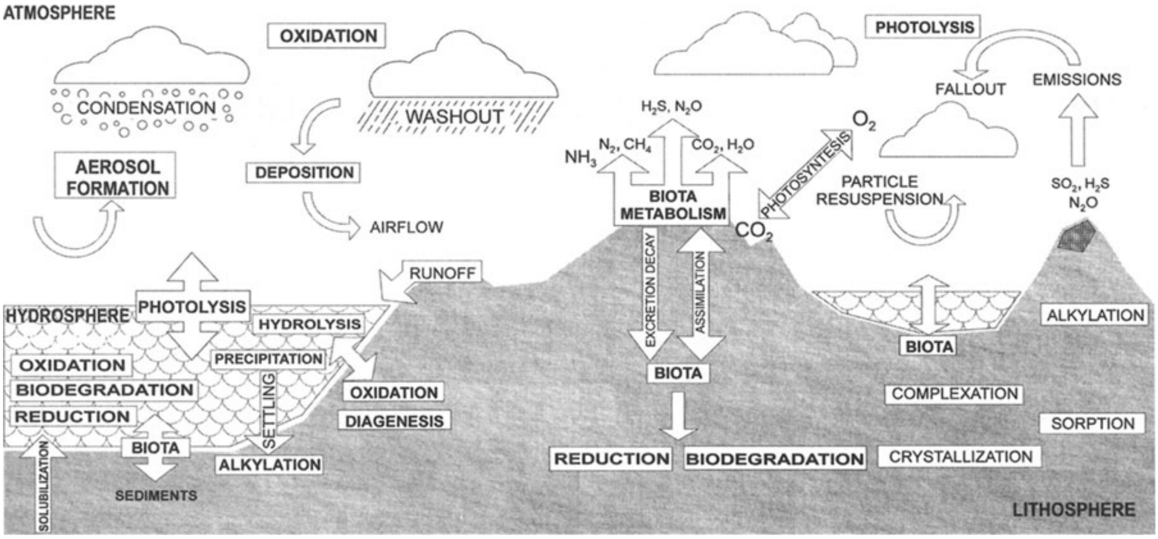


FIGURE 1.1. Reactions and transport of substances in the environment.

involved in the cycling of the elements are shown in Figure 1.1.

1.2 Chemistry Associated with Pollution Processes

Mankind—with its exponential population growth and its ever-changing and -expanding activities and demands for products and services—has increased the discharge of substances and extraction of resources, thereby increasing the pollution of the environment. Many of these contaminating substances are the same as those found in nature, but in higher concentrations. Therefore, cycling of the natural chemical species has been altered by human action through the discharge into environmental compartments of excessive amounts of compounds that cannot be assimilated, moved, or transformed at the same rate as before. This has resulted in an environmental and health impact due to the high concentrations of natural compounds and elements in a given environmental compartment, phase, site, or organism. Such high concentrations may exceed toxicity levels or the tolerance limits of organisms, or give rise to the inordinate reproduction of one organism over others; this, in turn, modifies the reproduction rates, the food chains, and the energy and mass balances in the ecosystems.

In addition, a number of natural elements and molecules have been combined through human inventiveness into synthetic compounds that are particularly beneficial to mankind and its present quality of life, many of which are *xenobiotic* substances (i.e., substances not found in nature). Some of these substances have been introduced into the environment deliberately, like pesticides; others have been discharged into the environment either by accident or as wastes, owing in part to the lack of awareness of the possible negative environmental and human impact in the long, or even the short, term; or of the dispersion and transformations that such compounds may undergo. This is known as the *Law of Ignored or Unexpected Consequences.*

An example of how human activity has affected or contributed to the alteration or modification of the natural biogeochemical cycles is depicted in Figure 1.2.

The pollutants discharged into the environment, may, in the best case, undergo abiotic or biotic transformations, resulting in innocuous compounds that may not represent an immediate health hazard. However, many of the xenobiotic compounds are toxic and may undergo partial transformations that result in even more toxic derivatives. This process is known as *activation.*

In the polluting process, the original compounds themselves or their derivatives are transported through the biosphere and may then be partially

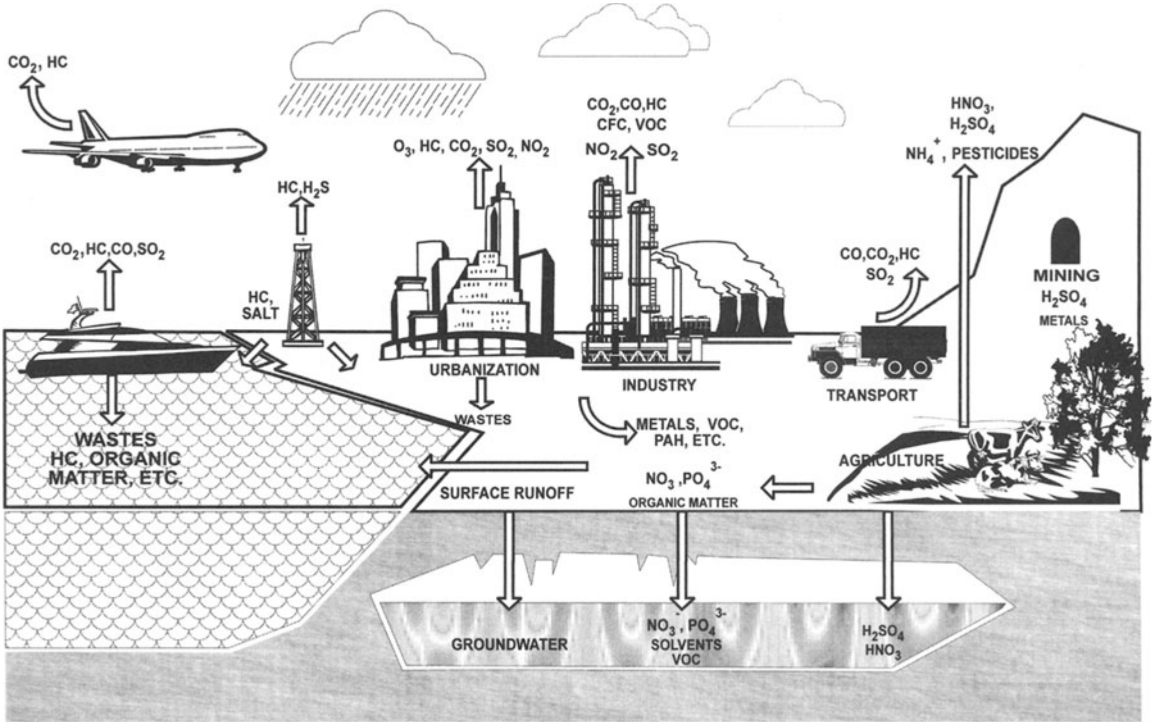


FIGURE 1.2. Contributions of human activity to the environmental load, modifying the biogeochemical cycles.

degraded or totally *mineralized* (i.e., converted into small, relatively innocuous inorganic molecules) and excreted, or else they may be transformed and accumulated in organisms. Many of the products that accumulate in organisms (*bioaccumulation*) or are metabolized have *genotoxic effects* (i.e., they affect cellular reproduction) and may even cause death. Many of these transformations or activations can be brought about by microorganisms under aerobic or anaerobic conditions, or carried out through the metabolic processes in animals and humans.

Some examples of biotic and abiotic transformations of toxic substances and contaminants that do not result in mineralization or detoxification, but result in products sometimes even more toxic than the original ones, are listed in Table 1.1.

An example in which a biotic transformation of a man-made pollutant generates a nontoxic product is the metabolic biotic transformation of the dodecylsulfate detergent into acetoacetic acid. On the other hand, an example of the generation of a toxic substance due to human chemical treatment is the generation of chloroform (or other organochlorine compounds or *trihalomethanes*) in treated water, through the chlorine disinfection process that entails the reaction of chlorine with a biodegradation product of organic matter.

Other xenobiotic compounds are more stable and may be transported, without major changes, through global mass transfer to sites very far from the original discharge point, and exposed to unpredictable conditions that may produce a serious environmental or health impact. Such is the case of the pesticide DDT and the CFCs (chlorofluorocarbons). In the case of DDT, although it has been banned in the United States and other countries since 1972, its negative effects are still present; for example, it has been detected in the Arctic Circle where no DDT was ever applied. In the case of CFCs, their high volatility and low reactivity allow their movement to the stratosphere and the destruction of the protective ozone layer through an initial photolytic reaction caused by ultraviolet (UV) radiation.

Therefore, the principles of atmospheric, water, and soil chemistries along with those of organic, inorganic, and biochemistry are a basic part of Environmental Chemistry. Moreover, they are essential for understanding (a) the fate and transformation

TABLE 1.1. Transformation and characteristics of different toxic pollutants

Parent compound	Dangerous characteristics	Biotic and abiotic transformations	Final products	Dangerous characteristics of final or intermediate products
(RDX) 1,3,5-Cyclotrimethylene nitroamine or "cyclonite" (used as an explosive)	Explosive, neurotoxicant, possible carcinogen	Anaerobic reduction and photolysis	1,1-Methylhydrazine, 1,2-Dimethylhydrazine	Possible carcinogens and mutagens, neuro-, nephro-, and hepatotoxicants
Benzo(*a*)pyrene (found in cigarette smoke)	Carcinogen	Metabolic oxidation	Benzo(*a*)pyrene-hydroquinone	Highly carcinogenic
Hg^0 (used in industrial processes)	Toxic vapor (neuro- and nephrotoxicant)	Abiotic oxidation and microbial transformation in aerobic or anaerobic conditions	Hg^{2+} and methyl mercury	Toxic compounds, nephro- and neurotoxicants, affect reproduction and digestive processes, probable carcinogens
(DDT) Dichlorodiphenyl trichloroethane (pesticide)	Neuro- and hepatotoxicant, causes reproductive alterations, probable carcinogen	Photolysis and microbial transformation	Dichlorodiphenyl dichloroethylene (DDE)	Neurotoxicant, reproductive alterations, probable carcinogen

reactions of the compounds discharged into the environment, (b) the decomposition reactions of wastes, and (c) the alteration of biogeochemical cycles.

An understanding of the chemistry involved in the abiotic and metabolic processes, and of the biochemistry in the biotic processing of xenobiotic compounds and natural compounds, may lead to important considerations. For example, this understanding can help to determine which chemicals can be employed that are not only safe for the environment and human health, but also beneficial for human use, and which ones, if used, are dangerous and carry a high risk for humanity.

The following example presents some of the possible movements and transformations that may result from the discharge of a pollutant (which may imply a risk to human beings or animals upon exposure). Perchloroethylene is a pollutant that can be discharged into the atmosphere from dry-cleaning processes and industrial degreasing of parts, or from seepage from a leaking storage tank in an industrial site. Its vapors will move along with air and can be transported by rainfall into land and surface water. Seepage from a storage tank will partially vaporize, and the rest can seep into groundwater or surface water. If retained in the groundwater or in the sediments of aquatic bodies, it can undergo sequential anaerobic biotic transformations or cometabolic dechlorination. In other media, it can undergo abiotic elimination reactions that will result in other compounds, all of them toxic. Such transformations are summarized as:

$$\text{PCE (perchloroethylene)} \rightarrow \text{TCE (trichloroethylene)} \rightarrow \text{DCE (dichloroethylene)} \rightarrow \text{vinyl chloride}$$

Such a transformation process will affect its mobility and increase its toxicity. This we can see in the corresponding data, reported in Table 1.2 [i.e., the *carcinogenic potential* or *slope factor*, the *reference dose for oral and inhaled intake* (*RfD*), its solubility, and its vapor pressure]. If these pollutants reach a certain exposure level for a community who breathes contaminated air or consumes polluted water, its members will be at risk.

1.3 Chemistry Applied to the Analysis of Pollutants and Natural Compounds

When people want to know more about the environment where they and their families live, their concerns are: What is the quality of the water that we drink or of the air that we breathe? How clean is the water in the lake? What types of toxic wastes are there in a nearby dumpsite or in an aquifer, and what are their concentration levels? What causes certain

TABLE 1.2. Risk characteristics of compounds derived from environmental transformations of perchloroethylene

Compound	Reference dose (mg/kg·d)	Carcinogenic slope factor [(mg/kg·d)$^{-1}$]	Solubility (mg/L at 25°C)	Vapor pressure (mm Hg at 25°C)
Perchloroethylene (tetrachloroethylene)	0.171 (inh) 0.01 (oral)	0.175 (inh) 0.052 (oral)	150 (at 20°C)	18.47
Trichloroethylene	0.01 (inh) 0.0003 (oral)	0.4 (inh) 0.011 (oral)	1366	74
1,1-Dichloroethylene	0.057 (inh) 0.05 (oral)	0.175 (inh) 0.6 (oral)	2500	591
Vinyl chloride	0.0286–0.01 (inh) 0.003 (oral)	0.03 (inh) 1.5 (oral)	2763	2660

Sources: http://www.atsdr.cdc.gov/toxprofiles/, EPA Toxic Profiles.
http://www.epa.gov/iris/subst/, IRIS (EPA Integrated Risk Information System).
http://www.epa.gov/ttn/atw/hlthef/, EPA Technology Transfer Network Air Toxics Website.
http://risk.lsd.ornl.gov/cgi.bin/tox/, RAIS (EPA Risk Assessment Information System).

algae blooms for the death of fish? How safe is it to eat fish from a body of water (for example, from Chesapeake Bay or Lake Michigan)? Do the fruits and vegetables we eat contain pesticides?

In order to have this information, the parameters that define the level and type of pollution need to be evaluated. Therefore, scientists and technicians have to find the best chemical analytical tools that identify potential and existing pollutants. They also need to determine their properties, particularly those affecting the fate, transport, bioavailability, toxicity, and stability/degradation of the chemical constituents in a sample. Tools such as these may be considered a part of Environmental Chemistry.

Thus, Environmental Chemistry is related to the methods required to determine, in a complex sample, the presence of pollutants and their transformation products, from high to very dilute or trace concentrations. This chemistry, focused on the analysis of environmental contaminants or natural compounds, has special concerns:

a. It should have a truly representative environmental sample.
b. It should identify and avoid possible sources of sample contamination.
c. It often needs a highly effective method of extraction or separation, and concentration to reach detection levels, especially when measuring extremely low concentrations or trace amounts of the analyte.
d. It should separate or identify a target compound from an array of a complex mixture of compounds or matrix, taking into account innumerable interactions with other compounds present in the sample and considering that they may interfere with the method.
e. Because many of the analyses have to be normalized, it is almost certain that validation of the results will be necessary.

An example of an extraction and reaction sequence of a soil matrix sample analysis is presented in Figure 1.3.

The following is an example of a typical chemical process (in a schematic form) used for the analysis of a wastewater sample in order to determine the presence of organic matter or oxidizable fraction through the measurement of the *chemical oxygen demand* (COD), a very common parameter in the evaluation of water pollution:

(a) Digestion of the sample with dichromate in acid media:

$$\text{Organic matter } (C_aH_bO_c) + Cr_2O_7{}^{2-} + xH^+ \longrightarrow aCO_{2(g)} + 2Cr^{3+} + yH_2O_{(l)} \quad (1.1)$$

(b) Titration in the excess dichromate with Fe^{2+} (as ammonium ferrous sulfate), after the carbon oxidation in organic matter:

$$Cr_2O_7{}^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O_{(l)} \quad (1.2)$$

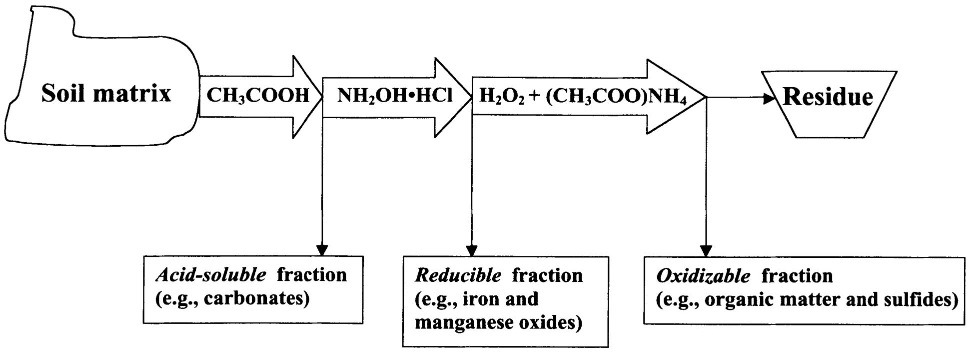


FIGURE 1.3. Representative line of analysis for environmental soil samples.

These are chemical reactions typically used in environmental analysis.

1.4 Chemistry Applied to the Treatment and Remediation of Pollution

Environmental Chemistry can also be applied to treat wastes, and to prevent and reduce the impact of certain discharges into the environment. A basic knowledge of chemistry will allow for a more-detailed understanding of processes such as water and wastewater treatment, air pollution control, and waste management.

Chemistry is one of the essential tools available to mankind for the transformation of dangerous and toxic wastes into less aggressive substances, or for separating these toxic, dangerous, or sometimes valuable substances. The purpose of such waste segregation is either to recover the waste for further reuse or recycling or to make it insoluble through a precipitation reaction or through a fixation or solidification process in order to reduce its mobility and lessen the risk of human contact.

Chemistry is also used to transform complex, although biodegradable, wastes into simpler products that can be easily incorporated in the biogeochemical cycle of the elements. It is often used to mimic natural chemical or biochemical processes under human-controlled circumstances. In optimal conditions these processes are kinetically favored, achieve high efficiencies, and completion of the reactions in shorter times as compared to the corresponding natural rates of change. This ideally leads to discharges that can be easily assimilated by natural webs and cycles.

When a leaking tank has contaminated a site or an aquifer, or an accidental spill occurs, the only option is remediation, that is, cleaning-up the site or any other environmental space that has been polluted. This remediation will often be performed by applying chemical processes to transform those undesirable substances either on- or off-site (e.g., by normal extraction and treatment techniques) using biochemical reactions with microorganisms, chemical oxidation, stabilization, or other advanced technologies.

In further reference to our previous example, a chemical process for the remediation of perchloroethylene- and trichloroethylene-contaminated sites is the oxidation of these pollutants with potassium permanganate, hydrogen peroxide, or ozone. The final products will be CO_2, Cl^-, Cl_2, and H_2O, which upon reaction will give HClO and HCl, plus Mn^{2+} and MnO_2 (as byproducts of the permanganate oxidation). Such products represent a much smaller risk (or no risk at all) than the original pollutants.

1.5 Green Chemistry

Many of the undesirable situations described above can be avoided by a judicious selection of more environmentally friendly processes. This is where Green Chemistry becomes an essential and important issue.

What is Green Chemistry? Green Chemistry is the chemical tool used to design a reaction, a process, or a new material benign to the environment. It is the chemistry applied in pollution prevention and waste minimization.

In the design and development of new products and processes, key environmental requirements that should be observed or are a priority in Green Chemistry are:

- utilization of reusable or recyclable materials, thus avoiding consumption of nonrenewable natural resources as material inputs
- reduction and replacement of some of the traditionally harmful reagents and solvents in industry
- reduction in energy consumption
- reduction in dissipative loss of waste materials, aiming for zero discharges
- lessening of threats to the ecology and to human health
- lowering of safety risks

A sustainable chemical industry is characterized by *green chemical processes*, where all of the above concerns are taken into account, or where there is a total recycling of intrinsically toxic or hazardous materials and substances, and an almost total recycling of other nonhazardous materials (e.g., water, plastic, or metals) that may constitute an environmental problem through resource depletion and pollution, as well as additional energy consumption.

A major challenge for Green Chemistry lies in the large percentage of chemical products such as coatings, pesticides, pigments, flocculants, detergents, fuels, and others, where recycling is inherently unfeasible due to chemical, economical, or technical reasons.

Wasteful processes can be made more economical and environmentally compatible by applying new green technologies. For example, the use of biosynthesis or catalytic transformations, with biocatalysts or other catalysts that are highly selective, which occur under mild reaction conditions is possible; they save energy and provide high structural selectivity, thereby reducing byproducts.

The importance of waste reduction through the use of a chemical catalyst can be exemplified by the use of *N*-methylimidazole as a catalyst in the leaching step of gold extraction from ores in the mining industry. Cyanide, a toxic substance that poses a major health threat, has traditionally been used for these processes. A sample case is the 1999 leak in a Rumanian facility from a cyanide storage tank into the Rhine River that killed thousands of fish. A hopeful sign is that DuPont scientists have been able to considerably reduce the amount of sodium cyanide and the reaction time required in the gold leaching process, by using a few parts per million of the imidazole activator that dramatically boosts the recovery rates.

In some cases, green reactions are based on feedstocks derived from renewable resources that produce highly pure compounds. Another green option is the use of supercritical fluids that are more benign substances (e.g., water, carbon dioxide, and light nonhalogenated hydrocarbons); such fluids can be used as solvents for separations or as media for reactions, and can be easily recovered from the product mixture and recycled. We can also include here the use of ionic systems of nonvolatile salts that are molten at ambient temperature, and that act as solvents or even have a dual role (as catalysts and solvents), without the risk of unwanted vapors. These ionic solvents replace the more hazardous, volatile, and expensive organic solvents used traditionally.

Other technologies that are applied in pollution prevention include electrochemical processes, which normally take place under mild reaction conditions and can be highly selective. They are usually cost-effective for low-volume, high-value products, although their overall competitiveness in high-volume processes needs to be analyzed as each case may require.

Another "green" alternative is the use of photocatalytic processes, which involve photochemical activation of semiconductors working as catalysts for redox processes that efficiently transform organic or inorganic pollutants into less dangerous substances.

1.6 Importance of Environmental Chemistry

As indicated above, knowledge of Environmental Chemistry is essential for understanding what happens in nature and for predicting the fate and the chemical reactions that natural compounds and artificial pollutants may undergo; for understanding their interactions, and for predicting what may happen to certain compounds if discharged into the environment, and if organisms (human or not) come into contact with them. It is also fundamental to know what are the abiotic transformations, the metabolic pathways, or other biotic transformations carried out by microorganisms that take place under different environmental conditions (e.g., aerobic or anaerobic).

Reactions such as dissolution, hydrolysis, precipitation, photolysis, adsorption/desorption, oxidation–reduction, ion exchange, complexation, biodegradation, polymerization, and others taking place in the environment, may affect the solubility of pollutants and therefore their mobility, speciation, and toxicity. This, in turn, can define to a great extent the dispersion, bioavailability, and risk associated with them.

Examples of the above include the following:

- The solubility of Fe(II) and Mn(II) compounds can be greatly decreased by oxidizing them to Fe(III) and Mn(IV), respectively.
- The bioavailability and toxicity of copper, selenium, and arsenic for some aquatic organisms is higher in their inorganic form, but not in the presence of certain chelating ligands or metal–organic complexes.
- The toxicity of Cr(VI) compounds can be greatly decreased by simply reducing it to a lower oxidation state, Cr(III).
- Iron oxides in minerals or in deposits can be dissolved by the action of light in the presence of certain compounds (ligands), but not in their absence.

These and other examples are further discussed throughout this book.

Environmental Chemistry also provides data input for risk assessment and treatability studies, and determines the required level of environmental quality or control needed in a system. All of these factors are particularly important when making cost-effective decisions about discharge treatments or risk-management decisions, or in determining environmental-impact mitigation or remediation measures.

In the following chapters we will explore, from the chemical point of view, what are the main reactions taking place in the processes mentioned above. This will help us understand what is happening in and to our environment, with and without human intervention.

References and Further Reading

Alloway, B. J.; Ayres, D. C. *Chemical Principles of Environmental Pollution*, 2nd ed.; Chapman & Hall: London, 1997.

Ballschmitter, K. "The Globe as a Reaction Vessel," *Sci. Spectra* **1997**, *11*, 18–23.

Butcher, Samuel, S.; Charlson, Robert J.; Orians, Gordon H.; Wolfe, Gordon V. *Global Biogeochemical Cycles*; Academic Press: San Diego, 1992.

Freemantle, Michael. "Green Applications of Ionic Liquids." *Chem. Eng. News*, March 30, 1998, pp. 32–33.

McEldowney, Sharon; Hardman, David J.; Waite, Stephen. *Pollution: Ecology and Biotreatment*, Longman Scientific & Technical: Essex, UK, 1993.

Turner II, B. L.; Clark, William C.; Kates, Robert W.; Richard, John F.; Mathews, Jessica T.; Meyer, William B. *The Earth as Transformed by Human Action: Global and Regional Changes in the Biosphere over the Past 300 Years*; Cambridge University Press: Cambridge, UK, 1993.

Wilkinson, Sophie L. "Green is Practical, even Profitable", *Chem. Eng. News*, Aug. 4, 1997, pp. 35–43.

2

Chemistry Fundamentals, Part A

From the overview given in Chapter 1 it is clear that many chemical principles are involved in the discussion of environmental phenomena. The next two chapters are devoted to several of these principles, namely: chemical equilibria, acid–base reactions, redox reactions, complexes and complex formation, chemical kinetics, photochemical processes, and radioactivity. The first three are dealt with in this chapter and the rest in the next chapter.

2.1 Chemical Equilibria

Chemical transformations can be of a reversible or irreversible nature. In the irreversible case, reactions may be simply written as follows:

$$\mathrm{aA + bB \rightarrow cC + dD} \tag{2.1}$$

where a, b, c, d are the stoichiometric coefficients of each species as they participate in the reaction (A and B are the reactants, C and D are the products). The reversible case occurs when the reaction proceeds as above, and then the products "react back" to yield the reactants. This can be written as

$$\mathrm{aA + bB \rightleftarrows cC + dD} \tag{2.2}$$

The two arrows here indicate bidirectionality of the reaction. All the species involved in this equilibrium react back and forth until the system reaches its natural equilibrium (i.e., until the Gibbs free energy of the reactants and the products becomes equal). At this point a dynamic equilibrium is achieved, because the overall reaction does not stop but the forward and backward reaction rates become equal. It has been found experimentally that regardless of the initial concentration of the reactants or products, the system will always reach equilibrium in ideal solutions (see below) when the product of the molar concentrations of the products (raised to their stoichiometric coefficients), divided by the product of the molar concentrations of the reactants (also raised to their stoichiometric coefficients) becomes constant. This ratio is called the ***equilibrium constant***, *K*. In an aqueous solution of dissolved species this constant is given for reaction 2.2 by the expression

$$K = [\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}}/[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}} \tag{2.3a}$$

or, in general,

$$K = \frac{\prod_i [P]^p}{\prod_j [R]^r} \tag{2.3b}$$

where the symbol Π indicates multiplication of all the ith and jth concentration terms involved, and $[P]$, $[R]$ represent the molar concentrations of the products and reactants, respectively, raised to their corresponding stoichiometric coefficients.

As mentioned above, this *K* is defined for ideal solutions (i.e., those solutions in which the participating species behave as if little or no interactions existed among them, nor with the solvent). A measure of the "departure" from ideality is the activity coefficient, γ. The closer it is to unity, the more "ideally" the solution behaves. The product of this coefficient and the molar concentration is called *activity* (a_i) of the ith species, and is given by

$$a_i = \gamma_i [i] \tag{2.4}$$

If the solution is non-ideal, a new K (called K') is defined for the equilibrium described in equation 2.2 as

$$K' = \frac{a_C^c a_D^d}{a_A^a a_B^b} \tag{2.5a}$$

or, in general

$$K' = \prod_i \frac{[a_P^p]}{[a_R^r]} \tag{2.5b}$$

where a_P^p, a_R^r represent the activities of the products and reactants, respectively, raised to their stoichiometric coefficients. It then follows that

$$K' = \frac{\gamma_C^c[C]^c\gamma_D^d[D]^d}{\gamma_A^a[A]^a\gamma_B^b[B]^b} = \left(\frac{\gamma_C^c\ \gamma_D^d}{\gamma_A^a\ \gamma_B^b}\right)\cdot\frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{2.6}$$

It can be noted that the last term on the right is equal to K. The preceding term contains the activity coefficients (γ), and depends on the concentration, charge, and nature of the species involved. In solutions where strong interactions among the dissolved species occur, the value of these coefficients drops significantly below unity. For example, in seawater the following activity coefficients (in parentheses) have been evaluated: (a) monovalent ions, Na^+ (0.76), $HCO_3{}^-$ (0.68); and (b) divalent ions, Ca^{2+} (0.26), $CO_3{}^{2-}$ (0.20). To simplify, we will assume ideal conditions for the reactions described throughout this book. However, the reader is by now aware of the deviations from ideality that can be encountered, and of the kind of errors that can be made by using this simplified approach. Better (and somewhat more complicated) approximations can be used; the reader is referred to more advanced books if such calculations are desired (see, for example, the books by Ramette, 1981 or Stumm and Morgan, 1996). K' is then a constant whose value depends on these factors, i.e., a *conditional constant.*

2.1.1 Equilibrium Values and Calculations

To give an idea of the possible magnitude of K, we can cite some extreme values it can acquire: for example, from 10^{-120} (as in the gas-phase decomposition of N_2 to atomic nitrogen) to 10^{+79} (as in the formation of an Ag complex with six thiosulfate ligands). In aqueous solutions the most common values for K are in the range $\sim 10^{-30}$ to 10^{+30} (e.g., solubility products, complex formation, dissociation constants, etc.). The magnitude of K signifies the extent of a reaction.

When solids or gases are present in a reaction either as products or reactants, mole fractions and partial pressures (respectively) are normally used as a measure of their concentration. If the solid is a pure, one component phase, its mole fraction is used and its value is unity. Likewise, the solvent mole fraction (which is practically unity in very dilute solutions) is used as a measure of its concentration.

In this book we use the convention that those ions for which the phase is not specified are in the aqueous phase.

When the values of the concentrations of the species that appear in the equilibrium expression are known, the calculation of the equilibrium constant is an easy task. Likewise, when the equilibrium constant is known, the equilibrium concentrations can often be obtained. See Examples 2.1–2.4.

Example 2.1 Write the equilibrium expression for the reaction systems below.

1. Solubility of calcite

$$CaCO_{3(s)} \rightleftarrows Ca^{2+} + CO_3^{2-}$$

Answer

$$K = [Ca^{2+}][CO_3^{2-}]$$

$CaCO_{3(s)}$ is a solid; therefore, its mole fraction is unity and it is not included in the equilibrium expression. K is called here the solubility product, K_{sp}.

2. Dissolution of goethite in acidic water

$$FeOOH_{(s)} + 3H^+ \rightleftarrows Fe^{3+} + 2H_2O_{(l)}$$

Answer

$$K = [Fe^{3+}]/[H^+]^3$$

Because water is the solvent, its mole fraction is considered unity. Because FeOOH is a solid, the same rule applies.

3. Dissolution of atmospheric ammonia

$$NH_{3(g)} + nH_2O_{(l)} \rightleftarrows NH_3$$

Answer

$$K = [NH_3]/[NH_{3(g)}]$$

When the partial pressure of ammonia gas (p_{NH_3}) is used instead of its molar concentration, this expression is also called Henry's constant (see Chapter 6).

4. Reaction between a metal ion (electron-pair acceptor, Lewis acid) and a Lewis base (electron-pair donor). For example, complex formation (see Chapter 3):

$$Fe^{3+} + 4Cl^- \rightleftarrows FeCl_4^-$$

Answer

$$K = [FeCl_4^-]/[Fe^{3+}][Cl^-]^4$$

This is a complexation constant.

5. Autodissociation (autoionization, self-ionization) of water

$$H_2O_{(l)} \rightleftarrows H^+ + OH^-$$

(As discussed below, we will use H^+ in this book to designate the solvated proton, which in reality exists mainly as the hydronium ion, H_3O^+).

Answer

$$K = [H^+][OH^-]$$

This is called the water dissociation constant, K_w (its value at 25°C is approximately 1×10^{-14}).

Example 2.2 Calculate the equilibrium concentration of $[OH^-]$ in a water sample where $[H^+] = 10^{-5}$ M.

Answer

$$K_w = 10^{-14} = [H^+][OH^-] \qquad [OH^-] = 10^{-14}/[H^+] = 10^{-9}\text{ M}$$

Example 2.3 Calculate the solubility of $CaSO_{4(s)}$ assuming that the dissolution equilibrium is the only equilibrium present in this water/salt system. Here, $K_{sp} = 10^{-5.9}$.

Answer

$$CaSO_{4(s)} \rightleftarrows Ca^{2+} + SO_4^{2-}$$

$$K_{sp} = 10^{-5.9} = [Ca^{2+}][SO_4^{2-}]$$

Because the concentration of the cation and the anion is the same (let us call it x), then

$$K_{sp} = x^2, \text{ and } x = 10^{-2.95} = 0.00112\text{ mol/L}$$

Example 2.4 Calculate the solubility of atmospheric ammonia in water, knowing the value of Henry's constant, $K_H = 10^{1.75}$ (for partial pressure in atmospheres and aqueous concentration in moles/L). The partial pressure of atmospheric ammonia can be taken as 5×10^{-9} atm.

Answer

Because $NH_{3(g)} + nH_2O_{(l)} \rightleftarrows NH_3$,

$$K = K_H = [NH_3]/p_{NH_3}$$

Then

$$[NH_3] = K_H p_{NH_3} = 10^{1.75}(5 \times 10^{-9})$$
$$= 2.8 \times 10^{-7}\text{ M}$$

2.1.2 Exchange Reaction Equilibria: Systems of the Type $ML_n/ML_{n-1}/\cdots/ML/M$

Aqueous systems where one chemical species (say, L) is "exchanged" are quite common, and the study of the equilibria involved is crucial to understanding their behavior. For example, when a monoprotic acid is dissolved in water, the following equilibrium exists:

$$HA \rightleftarrows H^+ + A^- \qquad (2.7)$$

(For a discussion on the aquation of H^+, see reaction 2.9c).

The acid (HA) is called the *donor*, the base (A^-) is the *acceptor*, and H^+ is the *exchanged species* or *exchanged particle.* Owing to the wide range of concentrations in which the exchanged particles can be found, a logarithmic definition is commonly used. In general, if the exchanged particle is X, then

$$pX = -\log a_x \qquad (2.8)$$

where a_X is the activity of the exchanged particle. As discussed earlier, we will use molar concentrations instead of activities. Then we get

$$pX = -\log [X] \qquad (2.9a)$$

Perhaps the most common application of such a definition is the hydrogen potential or pH, defined as

$$pH = -\log [H^+] \qquad (2.9b)$$

Note that H^+ reacts with H_2O to form H_3O^+ (proton aquation) as follows:

$$H^+ + H_2O_{(1)} \rightleftarrows H_3O^+ \qquad K_{aq} = [H_3O^+]/[H^+] \qquad (2.9c)$$

Because the equilibrium concentrations of H^+ and H_3O^+ are known to be the same (see Stumm and Morgan, 1996) and the activity of H_2O in dilute solutions (and its mole fraction) is essentially unity, then $K_{aq} = 1$. Thus, *in this book we follow the convention of using $H^+_{(aq)}$, or more simply, H^+ to represent the aquated hydrogen ion.*

The exchange equilibrium discussed above also applies to metal complexes where a generalized reaction occurs between a metal ion, M, and a ligand, L, e.g., OH^-, NH_3, Cl^- (see definition of metal complexes in next chapter). This reaction can be written as

$$ML \rightleftarrows M + L \qquad (2.10)$$

In the same manner as above, ML is the donor, M is the acceptor, and L is the exchanged particle. The handling of the equilibrium involved is the same as that discussed earlier.

However, when the donor and the acceptor can exchange more than one particle, the following situation arises (all species are assumed to be in the aqueous phase):

$$M + L \rightleftarrows ML \qquad K_1 = \frac{[ML]}{[M][L]} \qquad (2.11)$$

$$ML + L \rightleftarrows ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]} \qquad (2.12)$$

$$ML_2 + L \rightleftarrows ML_3 \qquad K_3 = \frac{[ML_3]}{[ML_2][L]} \qquad (2.13)$$

$$\vdots \qquad\qquad \vdots$$

$$ML_{n-1} + L \rightleftarrows ML_n \qquad K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \qquad (2.14)$$

Here, the constants represent *complex formation equilbrium constants.* The equilibrium resulting from this series can also be regarded as a *global equilibrium.* For example, if three L particles are exchanged

$$M + 3\,L \rightleftarrows ML_3 \qquad K_{G3} = \frac{[ML_3]}{[M][L]^3} \qquad (2.15)$$

Here, the equilibrium constant is a global constant, K_{G3}. Global constants are also symbolized as betas (in this case it would be written as β_3). How can these be calculated from the individual equations?

If one adds the first three equilibria, this global equilibrium is obtained. Then the individual constants must be multiplied (not added!). In other words, $K_{Gk} = \prod_k K_i$. For this case, $K_{G3} = K_1K_2K_3$.

The generalized equation corresponding to the series described above is

$$ML_i + (j-i)L = ML_j \quad \text{for } i \in 0, 1, 2, \ldots (j-1) \quad \text{and} \quad j \in (1, 2, \ldots n) \qquad (2.16)$$

and the corresponding equilibrium constant is

$$K_{ML_j}^{ML_i,(j-i)L} = \frac{[ML_j]}{[ML_i][L]^{j-i}} \tag{2.17}$$

where the sub index in the constant refers to the complex formed by the reaction, and the super index contains the starting species and the number of participating ligands. The values of the equilibrium constants define the distribution of species in the aqueous solution.

In other words, species with large formation constants will predominate, whereas those with small constants may not exist at all. One can find the value of ligand concentration needed to obtain any desired complex ratio (or the complex ratio that is obtained with a given ligand concentration) by simply taking logs on both sides, and solving for the ligand concentration function (pL) as follows:

$$pL = \frac{1}{j-i}\log\left(K_{ML_j}^{ML_i,(j-i)L}\right) + \frac{1}{j-i}\log\left(\frac{ML_i}{ML_j}\right) \tag{2.18}$$

A graphical representation of the equilibria involved in this type of systems is a plot of the distribution of the species containing M vs pL. This is called a *chemical species distribution diagram*; it can be calculated by defining the equations of the distribution fractions, f, of the species of M as a function of the concentration of L as follows:

$$f_M = \frac{[M]}{[M]+[ML]+[ML_2]+\cdots+[ML_n]} \tag{2.19}$$

$$f_{ML} = \frac{[ML]}{[M]+[ML]+[ML_2]+\cdots+[ML_n]} \tag{2.20}$$

and

$$f_{ML_j} = \frac{[ML_j]}{[M]+[ML]+[ML_2]+\cdots+[ML_n]} = f_M K_{ML_j}^{M,jL}[L]^j \tag{2.21}$$

for $j \in (1, 2, \ldots, n)$.

These functions are monotonic (i.e., increasing or decreasing in a continuous fashion) with respect to [L] (or to pL) for the first and last species in the equilibria involved; they show a maximum for the intermediate species (called *ampholytes*). The resulting chemical species distribution diagrams can easily be constructed by introducing these equations in a spreadsheet (e.g., Excel). See Examples 2.5 and 2.6. Typical examples can be found in the educational literature, and several programs are available for these calculations (see, for example, Kim, 2003).

Example 2.5 (a) Derive the two equations to calculate f_M and f_{ML} as functions of only [L] for a system where only one product (ML) of M and L is formed. (b) Select a monoprotic acid as an example and find its corresponding acid dissociation constant (Analytical Chemistry textbooks are normally good initial sources). (c) Plot the results for pL = 0 to pL = 14. Note that in this example, pL = pH.

Answer

(a)

$$M + L \rightleftarrows ML \qquad K = \frac{[ML]}{[M][L]}$$

$$f_M = \frac{[M]}{[M]+[ML]} = \frac{[M]}{[M]+K[M][L]} = \frac{[M]}{[M](1+K[L])} = \frac{1}{(1+K[L])}$$

If $K[L] = x$, then

$$f_M = \frac{1}{(1+x)}$$

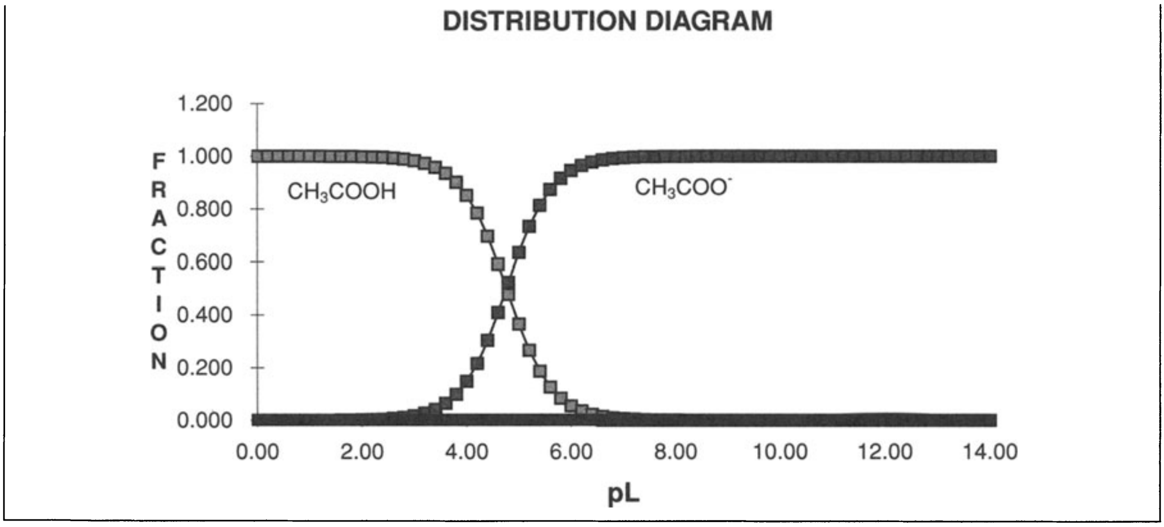
Likewise,

$$f_{ML} = \frac{[ML]}{[M]+[ML]} = \frac{K[M][L]}{[M]+K[M][L]} = \frac{K[M][L]}{[M](1+K[L])} = \frac{K[L]}{(1+K[L])} = \frac{x}{(1+x)}$$

Note that at any point, $f_M + f_{ML} = 1$.

(b) Let us take acetic acid, CH_3COOH (abbreviated as AcOH), as an example. It has a $pK_a = 4.76$.

(c) Calculating and plotting $f_M = f_{AcO^-}$ and $f_{ML} = f_{AcOH}$ one gets the diagram below. (Note that the two functions cross at exactly 0.5, since $f_{AcO^-} + f_{AcOH} = 1$).



2.2 Acid–Base Reactions

The autoionization of pure water occurs due to the collision of two water molecules:

$$2H_2O_{(1)} \rightleftarrows H_3O^+ + OH^- \qquad (2.22)$$

As discussed above, in this book we follow the convention of using $H^+_{(aq)}$, or more simply, H^+ to represent the aquated hydrogen ion. Then, to simplify equation 2.22 we often write:

$$H_2O_{(1)} \rightleftarrows H^+ + OH^- \qquad (2.23)$$

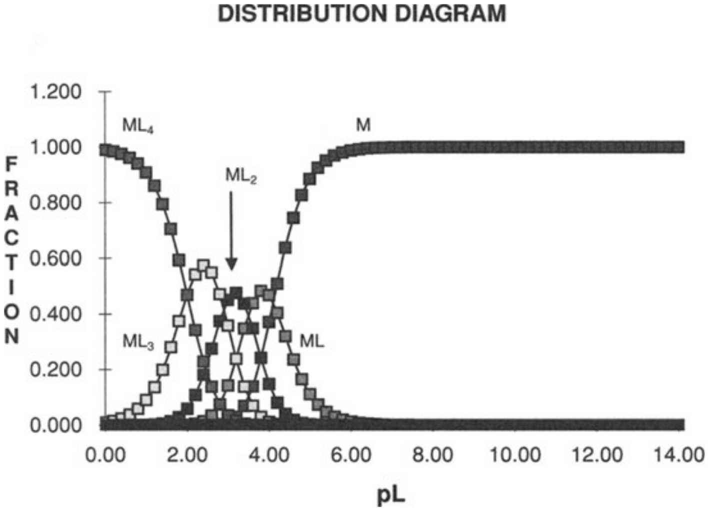
with an associated dissociation constant defined as

$$K_w = [H^+][OH^-] \qquad (2.24a)$$

At 298 K (25°C), its value is 1×10^{-14}. Because $[H^+] = [OH^-] = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7}$,

Example 2.6 Calculate and draw the chemical-species distribution diagram for the Cu(II)–NH_3 system, using the following log values of the global constants for the four sequential equilibria involved: 4.10, 7.60, 10.50, and 12.50. Here, pL = pNH_3, and $M = Cu^{2+}$.

Answer



Example 2.7 Several physicochemical parameters vary with temperature. For example, at 100°C the pH of pure water is approximately 6. Under these conditions,

(a) Calculate $[H^+]$.
(b) Calculate $[OH^-]$.
(c) Is water at 100°C acidic, neutral or basic? Why?
(d) Why is pH not 7.00?

Remember that $K_w = [H^+][OH^-] = 10^{-14}$ at 25°C.

Answer

(a) $pH = -\log[H^+] = 6$. Then, $[H^+] = 10^{-6}$
(b) $K_w^{100} = [H^+][OH^-] = 10^{-12}$
Since $[H^+] = 10^{-6}$, then $[OH^-] = 10^{-12}/10^{-6} = 10^{-6}$
(c) Since $[H^+] = [OH^-]$, then water is still neutral.
(d) pH is not 7.00 because at a higher temperature more bonds are broken, resulting in a higher $[H^+]$ (and $[OH^-]$) concentration.

one gets

$$pH = -\log[H^+] = 7 \qquad (2.24b)$$

At higher temperatures, the collision of water molecules is facilitated and the equilibrium constant increases. However, the concentration of hydrogen ions remains, by necessity, equal to that of hydroxyl ions.

2.2.1 Acid–Base Characteristics of Common Chemical Species

Pure water is never found in nature. It will generally contain different chemical species, which in turn modify its characteristics. The pH of an aquatic system is determined by the type and concentration of the predominant species present in water (acidic, basic, or neutral).

Acids and bases (strong or weak) obviously contribute according to their nature to the acidity/basicity of aqueous media. Salts may also contribute depending on their composition, as shown in the following tables.

Note: The conjugate bases are the anions generated by the acids when they dissociate according to their equilibrium reactions. The stronger the acid, the weaker its conjugate base; the opposite holds for a strong base. Also, small and highly-charged aquated cations (like $Al(H_2O)_6^{3+}$) attract electron density from the oxygen in water; as a result, the H-O bond is weakened and the proton may be released, acidifying the solution.

Thus, several combinations can occur in a salt as shown in Tables 2.1 and 2.2.

2.2.2 Buffers

It is often necessary to prevent large pH changes during certain processes. A buffer solution resists such changes when H^+ or OH^- are added to it. They typically contain either a weak acid and it conjugate base (i.e., one of its salts), or a weak

TABLE 2.1. Contribution of cations and anions to the acid/base characteristics of aqueous solutions

			Affinity for		Produces		
Type	Characteristic	Example	H^+	OH^-	H^+	OH^-	Contribution to pH
CATION	Conjugate of a strong base	Na^+	NO	NO	NO	NO	Neutral
	Conjugate of a weak base	$NH_4{}^+$	NO	YES	YES	NO	Acidic
	Highly charged metal ion	$Al(H_2O)_6^{3+}$	NO	YES	YES	NO	Acidic
ANION	Conjugate of a strong acid	Cl^-	NO	NO	NO	NO	Neutral
	Conjugate of a weak acid	$C_2H_3O_2^-$ (acetate)	YES	NO	NO	YES	Basic

TABLE 2.2. Salts and their effect on the pH of aqueous solutions

Cation	Example	Anion	Example	Salt	Contribution from the Cation	Contribution from the Anion	Resulting solution
Conjugate of a strong base	Na^+	Conjugate of a strong acid	Cl^-	NaCl	N	N	N
Conjugate of a strong base	Na^+	Conjugate of a weak acid	$C_2H_3O_2^-$	$NaC_2H_3O_2$	N	B	B
Conjugate of a weak base	NH_4^+	Conjugate of a strong acid	Cl^-	NH_4Cl	A	N	A
Conjugate of a weak base	NH_4^+	Conjugate of a weak acid	$C_2H_3O_2^-$	$NH_4C_2H_3O_2$	A	B	*
Highly charged metal ion	$Al(H_2O)_6^{3+}$	Conjugate of a strong acid	Cl^-	$[Al(H_2O)_6]Cl_3$	A	N	A
Highly charged metal ion	$Al(H_2O)_6^{3+}$	Conjugate of a weak acid	$C_2H_3O_2^-$	$[Al(H_2O)_6]\,[C_2H_3O_2]_3$	A	B	*

Notes: A = Acidic, B = Basic, N = Neutral.
*Depends on the relative magnitudes of the dissociation constants K_a and K_b as follows:
If $K_a > K_b$, the resulting solution is acidic.
If $K_a < K_b$, the resulting solution is basic.
If $K_a = K_b$, the resulting solution is neutral.

base and its conjugate acid (i.e., one of its salts) and are used as acid or base buffers, respectively. Examples include acetic acid + sodium acetate and ammonia + ammonium chloride. The pH at which the buffer exerts its action can be easily calculated, as shown in the following example.

Example 2.8a One liter of a buffered solution is prepared with 0.1 M acetic acid (AcH) + 0.2 M sodium acetate (AcNa).

(a) Calculate its pH.
(b) Calculate the new pH when 0.01 mol of gaseous HCl is added to the initial (buffered) solution. Compare this pH to that obtained in (a) (i.e., calculate ΔpH = pH final −pH initial).
(c) Calculate the pH when 0.01 mol of gaseous HCl is added to 1 L of pure water. Calculate ΔpH and compare this pH change to that obtained in (b).
(d) Calculate the new pH when 0.01 mol of solid NaOH is added to the initial (buffered) solution. Compare this pH to that obtained in (a) (i.e., calculate ΔpH).
(e) Calculate the pH when 0.01 mol of solid NaOH is added to 1 L of pure water. Calculate ΔpH and compare this pH change to that obtained in (d).

You may assume that in every case the volume of solution remains approximately constant at 1 L, that $T = 25°C$, and that $[H^+] = [OH^-] = 10^{-7}$ in pure water.

Answer

(a) The *predominant* species are AcH, Ac^-, H^+, Na^+, OH^-. In this case, Na^+ ions do not participate in determining the pH. AcH is a weak acid and as such it is little dissociated. AcNa is a salt, and we will assume that it is completely dissociated. H_2O is a molecule that is very little dissociated. Then, the predominant species in solution are AcH, Ac^-, Na^+, and H_2O. Because Na^+ is very stable as such, and H_2O is almost completely undissociated, these species do not participate in determining the pH of the solution, which then depends on AcH and Ac^-. Consequently, the target equilibrium is

$$AcH \rightleftarrows Ac^- + H^+ \qquad K_A = 1.8 \times 10^{-5} = \frac{[Ac^-][H^+]}{[AcH]}$$

	AcH	Ac^-	H^+
Initial	0.1	0.2	10^{-7}
Change	$-y$	y	y
Equil.	$0.1 - y$	$0.2 + y$	$10^{-7} + y$

$$1.8 \times 10^{-5} = \frac{[y + 0.2][y + 10^{-7}]}{[0.1 - y]}$$

Assuming that $[y + 0.2] \approx 0.2$, $[y + 10^{-7}] \approx y$, and $[0.1 - y] \approx 0.1$ then, $1.8 \times 10^{-5} \cong 0.2y/0.1$

$$y \approx 0.9 \times 10^{-5} = [H^+] \rightarrow pH = 5.04$$

(b) Upon addition of 0.01 mol HCl, the HCl reacts with the Ac^- from AcNa (assume that this goes to completion):

	Ac^-	+	H^+	=	AcH
Initial	0.2		0.01		0.1
Change	−0.01		−0.01		0.01
Equil.	0.19		0		0.11

Then, the only H^+ present will come from the *dissociation* equilibrium of AcH:

$$K_A = \frac{[Ac^-][H^+]}{[AcH]}$$

$$pK_A = pH - \log\frac{[Ac^-]}{[AcH]}$$

$$pH = pK_A + \log\frac{[Ac^-]}{[AcH]}$$

$$= 4.74 + \log\frac{0.19}{0.11} = 4.98$$

$$\Delta pH = pH_{fin} - pH_{init} = 4.98 - 5.04 = -0.06$$

This is a *small* pH change.

(c) If HCl is added,

$$HCl + H_2O_{(l)} \rightleftarrows H_3O^+ + Cl^-$$

Because HCl is a very strong acid, this reaction goes essentially to completion, and

$$[H_3O^+] = 0.01\ M, pH = 2\ \therefore$$

$$\Delta pH = pH_f - pH_i = 2 - 7 = -5$$

This is a *much larger* pH change than that obtained in (b).

(d) Upon addition of 0.01 mol NaOH

	AcH	+	OH^-	=	Ac^-	+	H_2O
Initial	0.1		0.01		0.2		—
Change	−0.01		−0.01		0.01		—
Equil	0.1 − 0.01		0		0.2 + 0.01		—

Then

$$pH = pK_A + \log\frac{0.21}{0.09} = 5.11$$

$$\Delta pH = 5.11 - 5.04 = 0.07$$

This is a *small* pH change.

(e) Because NaOH is a very strong base, it dissociates completely and $[OH^-] = 10^{-2}$ M, Then,

$$[H^+] = 10^{-12}\ M, \text{and } pH = 12$$

$$\Delta pH = 12 - 7 = 5$$

This is a *much larger* pH change than that obtained in (d).

In summary, one can see that buffering helps to prevent large pH variations upon the addition of acids or bases to an aqueous solution.

Buffering can also occur in the following cases:

(a) When a base and a slightly soluble salt are present (e.g., bicarbonate ions and calcium carbonate). The reaction taking place when an acid is added, is

$$CaCO_{3(s)} + H^+ \rightleftarrows Ca^{2+} + HCO_3^- \qquad (2.25)$$

(The reader may wish to write the reaction that would take place if a *base* were added instead.)

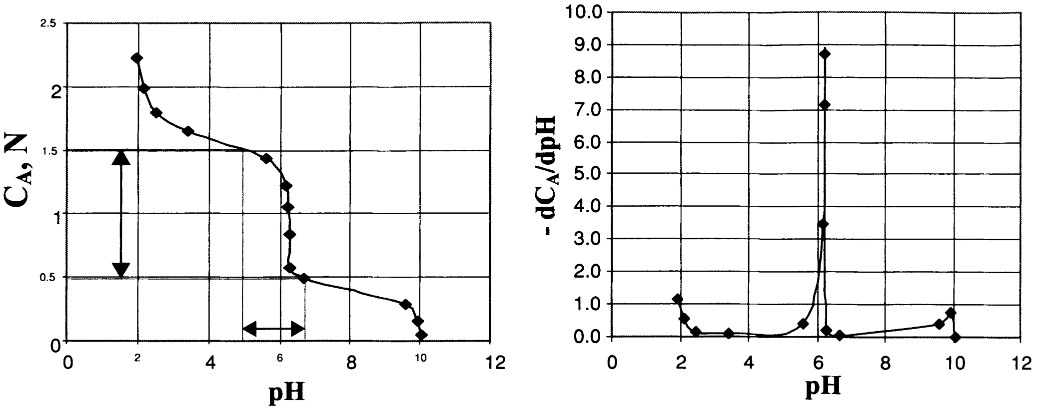
(b) When the intermediate ions of polyprotic acids are present (i.e., $H_2PO_4^-$ and HPO_4^{3-}).

(c) When the conditions of the system are strongly acidic or basic. In this case, even if an ion pair were not present, the pH variation with small additions of acid or base is not noticeable. These conditions correspond to the initial/final regions of a titration curve.

From the example above one can see that the pH of a buffered medium depends on the pK of the main buffer and is independent of its concentration. However, the concentration of each ion-conjugate pair will determine the *buffering capacity*, that is, the amount that can be buffered or tolerated by reacting immediately without a significant change in pH. The buffering capacity in the environment is discussed in Section 6.3.1.

Mathematical Definition of Buffer Capacity

This quantity gives the capacity of an aqueous system to resist pH changes upon addition of an acid or a base. When one plots the amount of acid A (or base B) added per liter of solution (C_A, C_B) vs. pH change, the *slope* of the resulting curve (or titration curve) is the *buffering index* or *buffer*



a) Raw titration plot **b) First derivative**

FIGURE 2.1. Experimental measurement of the buffering capacity of a water sample.

intensity, ß:

$$\beta = -\frac{dC_A}{dpH} = \frac{dC_B}{dpH} \qquad (2.26)$$

In Figure 2.1 we see how the buffering index or buffering intensity of a sample is experimentally determined from titration-like data. It is clear that the β value in this particular plot is very large at pH 6.2, since there is a large change in the slope. That is, at this point the system has a large capacity to accept an acidic input without undergoing a significant pH alteration.

Because (dC_A/dpH) is always a negative quantity whereas (dC_B/dpH) is always positive, the former is used with a negative sign so as to have a positive ß in both cases. We will now derive the expression for ß in a (simple) buffer system in terms of the total concentration of buffer, C_T, the constant for the main equilibrium, K, and $[H^+]$. We will use a buffer composed of a weak acid, HA and its conjugate base, A^-.

$$HA \rightleftarrows H^+ + A^- \qquad (2.27)$$

$$K_A = \frac{[H^+][A^-]}{[HA]} \qquad (2.28)$$

Since

$$C_T = [HA] + [A^-] \qquad (2.29a)$$

then,

$$K_A = \frac{[H^+](C_T - [HA])}{[HA]} \qquad (2.29b)$$

$$K_A[HA] = [H^+]C_T - [H^+][HA] \qquad (2.29c)$$

and

$$[HA](K_A + [H^+]) = [H^+]C_T \qquad (2.29d)$$

$$[HA] = \frac{C_T\,[H^+]}{K_A + [H^+]} \qquad (2.29e)$$

$$C_T - [A^-] = \frac{C_T\,[H^+]}{K_A + [H^+]} \qquad (2.29f)$$

$$[A^-] = C_T - \left(\frac{C_T\,[H^+]}{K_A + [H^+]}\right) \qquad (2.29g)$$

$$= C_T\left\{1 - \frac{[H^+]}{K_A + [H^+]}\right\}$$

$$= C_T\left(\frac{K_A + [H^+] - [H^+]}{K_A + [H^+]}\right) \qquad (2.29h)$$

and then

$$[A^-] = \frac{C_T K_A}{K_A + [H^+]} \qquad (2.29i)$$

If a base (BOH) is then added to this system, (dC_B/dpH) can be calculated in this manner. First, the charge balance condition must be satisfied:

$$[B^+] + [H^+] = [A^-] + [OH^-] \qquad (2.30)$$

Using $[B^+] = C_B$, $[OH^-] = \dfrac{K_w}{[H^+]}$ and equation 2.29i, one gets

$$C_B = \frac{C_T K_A}{K_A + [H^+]} + \frac{K_w}{[H^+]} - [H^+] \qquad (2.31)$$

In order to calculate the buffering index, ß, we can do

$$\beta = \frac{dC_B}{dpH} = \frac{dC_B}{d[H^+]} \cdot \frac{d[H^+]}{dpH} \qquad (2.32)$$

To calculate the first term, we derive equation 2.31 with respect to $[H^+]$:

$$\frac{dC_B}{d[H^+]} = C_T K_A \frac{d}{d[H^+]}\left(\frac{1}{K_A + [H^+]}\right) + K_W [H^+]^{-2}\frac{d[H^+]}{d[H^+]} - \frac{d[H^+]}{d[H^+]} \qquad (2.33)$$

$$= -C_T K_A (K_A + [H^+])^{-2}\frac{d[H^+]}{d[H^+]} - \frac{K_W}{[H^+]^2} - 1 \qquad (2.34)$$

Then,

$$\frac{dC_B}{d[H^+]} = -\left(\frac{C_T K_A}{(K_A + [H^+])^2} + \frac{K_W}{[H^+]^2} + 1\right) \qquad (2.35)$$

The second term of equation 2.32 is calculated very easily:

$$pH = -\log[H^+] = -\left(\frac{1}{2.3}\right)\ln[H^+] \qquad (2.36)$$

$$dpH = -\left(\frac{1}{2.3}\right)\left(\frac{1}{[H^+]}\right)d[H^+] \qquad (2.37)$$

and

$$d[H^+]/dpH = -2.3\,[H^+] \qquad (2.38)$$

Then, equation 2.32 becomes

$$\beta = \frac{dC_B}{dpH} = -\left(\frac{C_T K_A}{(K_A + [H^+])^2} + \frac{K_W}{[H^+]^2} + 1\right) \times (-2.3[H^+]) \qquad (2.39a)$$

and finally,

$$\beta = 2.3\left(\frac{C_T K_A [H^+]}{(K_A + [H^+])^2} + \frac{K_W}{[H^+]} + [H^+]\right) \qquad (2.39b)$$

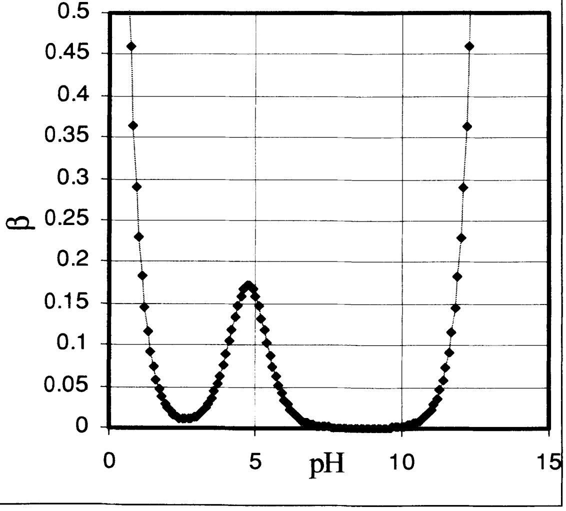
which is a very convenient form of ß. since all the quantities involved are usualy known.

Example 2.8b One liter of a buffered solution is prepared with 0.1 M acetic acid (AcH) + 0.2 M sodium acetate (AcNa). Plot ß vs. pH for the interval 0 < pH < 14. (See data from Example 2.8a, where this buffering action is further explained.)

Answer
Using

Ct	0.3
Ka	0.000018
Kw	1.00*E*-14

we plot equation 2.39b and get



2.2.3 Acid/Base Character of Oxides

For a large number of cases and applications, a metal oxide is more important than the metal itself. Many oxides are found native in nature or are formed spontaneously (e.g., TiO_2, which is used in white paint and in the whitening of paper), while others are artificially produced from the metal itself (e.g., Al_2O_3, which protects aluminum from surface mechanical damage and corrosion; it is produced by an electrolytic industrial process, and it also occurs in nature as the mineral corundum).

Given that oxygen represents approximately 50% by weight of the elements that form the Earth's crust, and that many elements react with it to form oxides, some reactions of oxide production will be studied in this section together with other reactions in which oxides are reduced to the metallic state in order to produce the corresponding metal.

Soluble binary oxides can be classified according to their acid–base character as acidic, basic, and amphoteric, depending on the nature of the resulting solution from their reaction with water. Thus, K_2O reacts with water to produce the base KOH as follows:

$$K_2O_{(s)} + H_2O_{(l)} \rightleftarrows 2K^+ + 2OH^- \qquad (2.40)$$

and therefore, it is considered a *basic* oxide; on the other hand, SO_3 is considered an *acidic* oxide because it reacts with water as follows:

$$SO_{3(g)} + H_2O_{(l)} \rightleftarrows 2H^+ + SO_4^{2-} \qquad (2.41)$$

From these reactions it can be seen that K_2O *transferred* one O^{2-} (oxide) ion to H_2O, whereas SO_3 *received* an O^{2-} ion from water. Lux and Flood suggested the general principle that an acid is an oxide ion receptor while a base is an oxide ion donor.

In this way, an oxysalt can be understood as the result of a reaction between an acidic oxide, A, and a basic oxide, B. For example,

$$CaO_{(s)} + CO_{2(g)} \rightleftarrows CaCO_{3(s)} \qquad (2.42)$$

$$Al_2O_{3(s)} + 3I_2O_5 \rightleftarrows 2Al(IO_3)_3 \qquad (2.43)$$

In the presence of a basic oxide, water behaves as an acidic oxide and the resulting hydroxide is its "oxysalt":

$$Na_2O_{(s)} + H_2O_{(l)} \rightleftarrows 2NaOH \qquad (2.44)$$

In general, when an oxide is ionic and water soluble, O^{2-} ions will be produced upon dissolution; these ions are highly unstable in water, as can be seen below,

$$O^{2-}_{(s)} + H_2O_{(l)} \rightleftarrows 2\,OH^- \qquad K > 10^{22} \qquad (2.45)$$

generating OH^- and making the resulting solution basic. On the other hand, if the oxide is highly covalent (as S, N, Cl oxides), the reaction mechanism will be through water breakage; such a breakage can donate an OH^- to the oxide:

$$SO_{2(g)} + H_2O_{(l)} \rightleftarrows H^+ + HSO_3^- \qquad (2.46a)$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-} \qquad (2.46b)$$

and the resulting solution is acidic.

Nevertheless, the following question arises: How covalent does an oxide have to be, in order to be basic? If the criterion to know when an oxide is or is not ionic is the difference in electronegativities, how can it be predicted that Cr (E.N. = 1.66) forms an acid oxide (CrO_3) while Zn (E.N. 1.65) forms an amphoteric oxide (ZnO) and Cd (E.N. = 1.69) forms a basic oxide (CdO)?

To answer this question one must think in terms of fundamental thermodynamic principles. Thus, it can be expected that the reaction between a strong acid and a strong base should be highly exothermic (releasing a lot of heat), while that between a weak acid and a weak base is little exothermic. If a constant a is defined as a measure of the tendency of a binary oxide to accept an O^{2-} ion (i.e., its acidity in terms of Lux and Flood), it would be reasonable to expect that for a reaction between an acidic oxide, A, and a basic oxide, B, the $\Delta H^0_{A,B}$ of the reaction between A and B to produce an oxysalt, C (i.e., A + B = C), is proportional to their difference in acidity.

The empirical relationship

$$-\Delta H^0_{A,B} = [a(A) - a(B)]^2 \qquad (2.47)$$

was proposed and probed with the thermodynamic data ($\Delta H^0_{A,B}$ in kJ mol^{-1}) of a large number of oxysalts (Smith, 1987). This equation applies to a reaction stoichiometry involving the transfer of 1 mole of O^{2-} from B to A. Given that water is a very weak acid, a value of $a_{H_2O} = 0$ was arbitrarily assigned to it. This allows for the calculation of the a values for oxides whose ΔH^0 for reaction with water is known. Table 2.3 shows many of these values.

The a values in Table 2.3 tend to decrease when one moves down in a given group (e.g., Mg, Ca), and increase when one moves to the right in a given period (e.g., Mg, Al, Si, P, S), which agrees well with the expected tendency to accept an O^{2-}. Thus,

TABLE 2.3. Relative acidity values (*a*) for some binary oxides of environmental importance

Oxide	*a* value
SO_3	10.5
Mn_2O_7	9.6
$P_2O_5(P_4O_{10})$	7.5
SO_2	7.1
CrO_3	6.6
CO_2	5.5
SnO_2	2.2
SiO_2	0.9
TiO_2	0.7
H_2O	0.0
Fe_2O_3	−1.7
Al_2O_3	−2.0
ZnO	−3.2
FeO	−3.4
MgO	−4.5
PbO	−4.5
MnO	−4.8
CaO	−7.5

a close estimate is that oxides with $a \leq -5$ are basic; if $-5 \leq a \leq 0$ they are generally amphoteric; and if $a > 0$, they are acidic.

In order to estimate the relative acidity of an oxide from the relative acidity of another oxide and from the oxysalt formed by both, a simple calculation is done according to the Example 2.9.

2.3 Redox Processes

Natural processes involving redox reactions are very frequent. Examples include the oxidation of aqueous ions [like Fe(II) to Fe(III)], oxidation of solids (like pyrite, FeS_2 to SO_4^{2-}), corrosion of metals, production of H_2S by sulfate-reducing bacteria, photoredox processes in the atmosphere, water, and soil, etc. Therefore, it is important to understand the principles underlying redox chemistry and to organize them in the form of tables and diagrams such as those discussed below.

A redox reaction implies a change in the oxidation state of atoms in one or more of the reactant(s). The most common case is when—at least in a formal sense—a chemical species (atom, ion, radical, or molecule) loses one or more electrons while another gains them. The first species increases its oxidation number (or oxidation state) and is said to be *oxidized,* whereas the oxidation state of the second decreases and is said to be *reduced.*

For example, in the formation of calcium oxide from its elements

$$Ca_{(s)} + {}^1/_2O_{2(g)} \rightarrow CaO_{(s)} \qquad (2.48)$$

both reactants are in their zero oxidation state; in the product, Ca has an oxidation state of +2 as a result

Example 2.9 Calculate the relative acidity (*a*) of $CaO_{(s)}$ from the ΔH^0 value in the reaction

$$CaO_{(s)} + CO_{2(g)} \rightleftarrows CaCO_{3(s)} \qquad \Delta H^0_{A,B} = ?$$

Note: You can use the value of $a(CO_2)$ given in Table 2.3.

Answer

To obtain $\Delta H^0_{A,B}$ we look up the values of the separate formation enthalpies of reactants and products in tables of thermodynamic data. Then

$$\Delta H_f^0(CaO) = -151.9 \text{ kcal mol}^{-1}$$
$$\Delta H_f^0(CO_2) = -94.05 \text{ kcal mol}^{-1}$$
$$\Delta H_f^0(CaCO_3) = -288.45 \text{ kcal mol}^{-1}$$

Thus,

$$\begin{aligned}\Delta H^0_{A,B} &= \Delta H_f^0(CaCO_3) \\ &\quad - [\Delta H_f^0(CaO) + \Delta H_f^0(CO_2)] \\ &= -288.45 - (-151.9 - 94.5) \\ &= -42.5 \text{ kcal mol}^{-1}(4.18 \text{ kJ/1 kcal}) \\ &= -177.65 \text{ kJ mol}^{-1}\end{aligned}$$

Applying equation 2.33 and taking $a(CO_2)$ from Table 2.3, one obtains

$$\begin{aligned}\Delta H^0_{A,B} &= [a(CO_2) - a(CaO)]^2 \\ &= [5.5 - a(CaO)]^2 \\ &= +177.65 \text{ kJ mol}^{-1}\end{aligned}$$

and then

$$a(CaO) = -7.8$$

Note: The reported value is −7.5 ± 0.4 (Smith, 1987).

of a $2e^-$ transfer to oxygen, which then acquires its most common oxidation state of -2. In some compounds, O has other oxidation states (e.g., in the peroxides it is -1, and in the superoxides it is $-1/2$).

Conceptually, a redox process can be understood from the perspective of what happens to each of the substances involved. To this end, the oxidation process can be separated from that of reduction, and the overall reaction can likewise be separated into its components as follows:

$$Ca^0 \rightarrow Ca^{2+} + 2e^- \qquad (2.49)$$

and

$$^1/_2O_2^0 + 2e^- \rightarrow O^{2-} \qquad (2.50)$$

When these two reactions are added, the result is CaO (i.e., the sum of Ca^{2+} and O^{2-}), because O_2 takes the electrons given up by Ca.

To illustrate these concepts with examples involving reactions in aqueous media, let us recall that when a small piece of sodium metal is dropped in water, a vigorous, highly exothermic reaction occurs (which turns out to be quite dangerous!). Sodium reduces water to produce hydrogen gas (and OH^- ions), whereas sodium itself gets oxidized to Na^+ ions:

$$2Na_{(s)} + 2H_2O_{(l)} \rightleftarrows 2Na^+ + H_{2(g)} + 2OH^- \qquad (2.51)$$

On the other hand, strong oxidizers like Co^{3+} ions can oxidize water to produce oxygen gas (and H^+ ions), while Co^{3+} becomes reduced into Co^{2+} ions:

$$4Co^{3+} + 2H_2O_{(l)} \rightleftarrows 4Co^{2+} + O_{2(g)} + 4H^+ \qquad (2.52)$$

As already mentioned, each of the above reactions can be broken down into a reduction and an oxidation reaction (called *half-reactions*), making the electron exchange explicit as follows:

Reaction (2.51):

$$2Na_{(s)} \rightleftarrows 2Na^+ + 2e^- \qquad (2.53)$$

$$2H_2O_{(l)} + 2e^- \rightleftarrows H_{2(g)} + 2OH^- \qquad (2.54)$$

Reaction (2.52):

$$4Co^{3+} + 4e^- \rightleftarrows 4Co^{2+} \qquad (2.55)$$

$$2H_2O_{(l)} \rightleftarrows O_{2(g)} + 4H^+ + 4e^- \qquad (2.56)$$

An experimental comparison of the relative strengths of many substances for giving and receiving electrons should yield a relative scale of their oxidative or reductive strengths. In aqueous phase, such a scale exists and is called the *electromotive series*.

An electrochemical cell is formed if each of the half-reactions occurs on an electrode surface in two solutions in separate compartments of a cell, so as to allow electrons to flow between the compartments through a wire (i.e., electronic conductor) and ions to flow through an electrolyte (i.e., ionic conductor). Each solution in equilibrium with its corresponding electrode is called a *half-cell*. Here, the direction of electron flow will depend on the relative tendency of each half-cell to donate electrons to the other. This tendency can be quantified by comparing it to that of a reference half-cell to which an arbitrary value is assigned. The most commonly used reference is the hydrogen half-cell (hydrogen electrode), which includes a 1 M H^+ solution in equilibrium with H_2 gas at a platinum electrode, where the following equilibrium is established:

$$2H^+ + 2e^- \rightleftarrows H_{2(g)} \qquad (2.57)$$

This system is known as the *standard hydrogen electrode* (SHE). The electric potential established by this equilibrium is assigned the value of 0 V. Therefore, when the SHE is compared with a half-cell comprised of a dissolved chemical species in equilibrium with its solid, elemental form or with an inert electrode (i.e., an electrode made of a material like platinum that facilitates electron exchange but does not react with the medium), the electric potential can be measured with a voltmeter and a table of potentials can thus be generated.

If such measurements are performed with a high impedance voltmeter that does not allow current flow through it, at 25°C and 1 atm of pressure with 1 M concentration of the involved species at pH $= 0$, the measured potential difference will be equal to the *electrode potential* of the half-cell. This potential is called its *reduction* or *standard reduction potential*, E^0. The higher the tendency (or electromotive force) of a species to transfer its electrons, the more negative the generated potential will be. Table 2.4 shows the standard potentials of some environmentally important (non-biochemical) redox half-cells, arranged in decreasing order of ability for the species on the right-hand side of the equation to donate electrons. In other words, ozone is the best oxidizer in this table, whereas $Fe(OH)_2$ is the best reducing agent. Redox biochemical reactions are

TABLE 2.4. Electrochemical series involving some environmentally relevant species

Half-Cell Reaction	E^0 (V)
$O_3 + 2H^+ + 2e^- = O_2 + H_2O$	+2.08
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	+1.78
$N_2O + 2H^+ + 2e^- = N_2 + H_2O$	+1.77
$HClO + H^+ + e^- = {}^1/_2Cl_2 + H_2O$	+1.63
$2NO + 2H^+ + 2e^- = N_2O + H_2O$	+1.59
$HBrO + H^+ + e^- = {}^1/_2Br_{2(aq)} + H_2O$	+1.57
$Mn^{3+} + e^- = Mn^{2+}$	+1.51
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	+1.49
$BrO_3^- + 6H^+ + 6e^- = Br^- + 3H_2O$	+1.42
$Cl_{2(g)} + 2e^- = 2Cl^-$	+1.36
$HCrO_4^- + 7H^+ + 3e^- = Cr^{3+} + 4H_2O$	+1.35
${}^1/_2O_2 + 2H^+ + 2e^- = H_2O$	+1.23
$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	+1.23
$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O$	+0.96
$ClO_{2(aq)} + e^- = ClO_2^-$	+0.95
$NO_3^- + 3H^+ + 2e^- = HNO_2 + H_2O$	+0.93
$Fe^{3+} + e^- = Fe^{2+}$	+0.77
$O_2 + 2H^+ + 2e^- = H_2O_2$	+0.68
$I_2 + 2e^- = 2I^-$	+0.54
$H_2SO_3 + 4H^+ + 4e^- = S + 3H_2O$	+0.44
$O_2 + 2H_2O + 4e^- = 4OH^-$	+0.40
$Fe_2O_3 + 4H^+ + 2e^- = 2FeOH^+ + H_2O$	+0.16
$S + 2H^+ + 2e^- = H_2S_{(aq)}$	+0.14
$2H^+ + 2e^- = H_2$	0.00
$CO_2 + 2H^+ + 2e^- = HCOOH$	−0.20
$Fe^{2+} + 2e^- = Fe$	−0.44
$S + 2e^- = S^{2-}$	−0.48
$S + H_2O + 2e^- = HS^- + OH^-$	−0.48
$Fe(OH)_3 + e^- = Fe(OH)_2 + OH^-$	−0.56

Note: Physical states are omitted for simplicity (unless they are required for clarity).

also of paramount importance; they are discussed in Chapter 7.

The potential difference between two of these half-cells (or of their half-reactions) is ΔE^0 (or simply, E^0), and it represents the driving force that exists for the electron transfer to happen. This difference is related to the free energy change of the system and to its equilibrium constant by the well-known expression

$$\Delta G^0 = -nFE^0 = -RT \ln K \qquad (2.58)$$

where ΔG^0 is the free energy change, n is the number of exchanged electrons, F is Faraday's constant (96,496 coulombs/mole of electrons), R is the ideal gas constant, and K is the equilibrium constant. The superscript (^{0}) indicates that the system is at the *standard conditions* defined above. Then the standard potential, E^0 is an indirect measure of ΔG^0 (and of K); if E^0 is positive for an electron exchange reaction, ΔG^0 will be negative and thus the process will be thermodynamically spontaneous. On the other hand, if E^0 is negative, the process will not be spontaneous. If E^0 is zero, the system will be at equilibrium and no net change will be observed. See Examples 2.10 and 2.11.

In some cases, a chemical species may simultaneously undergo reduction and oxidation. For example, when chlorine gas is bubbled through a basic solution, the resulting products contain chlorine in the −1 and +1 oxidation states (i.e., Cl^-

Example 2.10 Is the reaction between metallic Fe and a 1 M solution of a strong (non-oxidizing) acid to produce Fe^{2+} ions thermodynamically spontaneous?

Answer

The half-reactions in this process are

$$Fe_{(s)} \rightleftarrows Fe^{2+} + 2e^-$$

$$2H^+ + 2e^- \rightleftarrows H_{2(g)}$$

and the net reaction is

$$Fe_{(s)} + 2H^+ \rightleftarrows Fe^{2+} + H_{2(g)}$$

Because the half-cell reactions are equilibrium reactions, the standard potential of each is the same, yet opposite in sign, as that of the corresponding oxidation; i.e., from Table 2.4, the potential for the first reaction is −(−0.44) V, whereas for the second reaction, E^0 is 0 V.

To obtain the total free energy change, we calculate the ΔG^0 values for both reactions and then add them. In this reaction, two electrons are transferred, and so $n = 2$. For the first half-reaction, $\Delta G^0 = -nFE^0 = -2F$ (0.44V) and for the second one, $\Delta G^0 = -2F(0) = 0$; then ΔG^0 for the global reaction is given by the sum of both ΔG^0 values $= -2F(0.44\text{V}) + 0$.

After substituting for F, the result is -84916.48 mol e^- (coul/mol e^-) (V)(J·coul^{-1}/V) $\cong -84.92$ kJ. A negative value for ΔG^0 means that the reaction is thermodynamically feasible to occur on its own, i.e., it is spontaneous. (Note that this finding does not predict the rate at which the reaction will occur. This is a matter of *kinetics*, not of *thermodynamics*!)

Example 2.11 Hydrogen peroxide is a common constituent of natural and atmospheric waters, where it participates in many redox processes. It is known to be unstable, as it slowly decomposes (disproportionates) even at room temperature, into oxygen and water:

$$2H_2O_2 \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

Explain this instability (in terms of ΔG^0) with the aid of the following (unbalanced) reactions in acidic media:

$$\begin{array}{ll} O_2 \rightarrow H_2O_2 & E_1^0 = +0.68 \\ H_2O_2 \rightarrow H_2O & E_2^0 = +1.78 \end{array}$$

Answer

The first step is to balance the equations.

$$\begin{array}{lll} 1) & O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O_2 & E_1^0 = 0.68 \\ 2) & H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O & E_2^0 = 1.78 \end{array}$$

Because we want to obtain ΔG^0 and analyze its sign, we invert the first equation and add it to the second one (water is in the liquid state, as usual):

$$2H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O + O_{2(g)} + 2H^+ + 2e^-$$

We now eliminate the common terms on both sides and get

$$2H_2O_2 \rightleftarrows 2H_2O + O_{2(g)}$$

Because the number of electrons is the same in both equations, the resulting ΔG^0 can be analyzed by subtracting

$$E_2^0 - E_1^0 = 1.78\text{ V} - 0.68\text{ V} = 1.10\text{ V}$$

The positive sign of ΔE^0 implies a negative sign for ΔG^0. (Knowing this, we do not need to perform the calculation.) This means that H_2O_2 is thermodynamically unstable, because its disproportionation reaction is spontaneous. In fact, hydrogen peroxide is known to decompose quite easily with light, with temperature, or in the presence of many transition metal ions.

and ClO^-, respectively). This phenomenon is called *disproportionation.* The reaction can be written as follows:

$$Cl_{2(g)} + 2OH^- \rightleftarrows Cl^- + ClO^- + H_2O_{(l)} \quad (2.59)$$

2.3.1 Latimer Diagrams

Because many elements can have more than one oxidation state, Latimer devised a simplified way of summarizing the potentials involved in the chemical interrelations among them. These so-called *Latimer diagrams* (or linear potential diagrams) are drawn by sequentially writing each chemical species in its different oxidation states in the form of a reduction progression. The standard potential for each reaction is written on the uniting line. The potentials for any equilibria among non-sequential oxidation states are represented with a uniting segment on which the corresponding potential is shown.

The steps involved in the hydrogen peroxide decomposition (Example 2.11) can thus be drawn as follows:

$$\overset{0}{O_2}\;\overset{+0.68}{\rule{3em}{0.4pt}}\;\overset{1-}{H_2O_2}\;\overset{+1.78}{\rule{3em}{0.4pt}}\;\overset{2-}{H_2O}$$

The equilibrium between the non-sequential oxidation states (i.e., 0 and −2 in O_2 and H_2O, respectively) cannot be written on the same line as those already drawn, and another line is needed to depict it. In order to calculate the potential involved in this reaction, its stoichiometry must be found first. This can be done by combining the $O_2 \rightarrow H_2O_2$ and $H_2O_2 \rightarrow H_2O$ equations discussed in the Example 2.11 in such a way that the peroxide is eliminated from the overall reaction; the oxygen appears as a reactant, and water as the product:

$$O_{2(g)} \rightarrow H_2O_{(l)} \quad (2.60)$$

The balanced equation is

$$O_{2(g)} + 4H^+ + 4e^- \rightleftarrows 2H_2O_{(l)} \qquad (2.61)$$

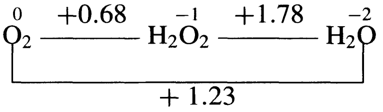
Using the same rationale as in the previous example for calculating the ΔG^0 value for this reaction, and adding the $O_2 \rightarrow H_2O_2$ and $H_2O_2 \rightarrow H_2O$ equations, one obtains

$$\begin{aligned} \Delta G_3^0 &= \Delta G_1^0 + \Delta G_2^0 \\ &= -2F(0.68) + (-2F \times 1.78) \qquad (2.62a) \\ &= -2F(2.46) = -4FE_3^0 \end{aligned}$$

From here, the E^0 value is calculated:

$$E_3^0 = \frac{2.46}{2} = 1.23\ \text{V} \qquad (2.62b)$$

This value is written on the line that unites these two non-sequential oxidation states, and the Latimer diagram for oxygen is completed:



2.3.2 Frost Diagrams

From the above calculation it is clear that the potentials are not additive, and that a "weighted average" has to be used when successive processes involve unequal numbers of electrons. This makes the drawing and the use of these diagrams somewhat confusing.

In order to avoid this difficulty and give a more graphical description of a given system, Frost devised a free energy vs oxidation state diagram as shown below. From eq. 2.58 one has:

$$\Delta G^0 = -nFE^0 \qquad (2.63)$$

Then

$$\Delta G^0/F = -nE^0 \qquad (2.64)$$

When a substance undergoes a change in oxidation state, there is a concomitant change in free energy that is proportional to $-nE^0$, as shown in this equation. For oxygen, the example given above serves as the basis for the calculation of these free energies as follows (units are omitted for simplicity):

$$\boxed{O_2 \rightarrow H_2O_2}$$

$$\Delta G_1^0 = -2\,FE_1^0 = -2\,F(0.68) \qquad (2.65)$$

(where $F = 96{,}496$ C/mol e^-)

$$\Delta G_1^0/F = -2F(0.68)/F = -1.36$$

$$\boxed{H_2O_2 \rightarrow H_2O}$$

$$\Delta G_2^0 = -2\,FE_2^0 = -2\,F(1.78) \qquad (2.66)$$

$$\Delta G_2^0/F = -2F(1.78)/F = -3.56$$

(and $-3.56 - 1.36 = -4.92$)

$$\boxed{O_2 \rightarrow H_2O}$$

$$\Delta G_3^0 = -4FE_3^0 = -4F(1.23) \qquad (2.67)$$

$$\Delta G_3^0/F = -4F(1.23)/F = -4.92$$

Noting that the free energy change for the formation of an element in its standard state is zero, and assuming that this is the case for oxygen (in spite of being *dissolved* in water), one can plot $\Delta G^0/F$ vs oxidation state to get the Frost diagram for oxygen. (These diagrams are also called *oxidation state diagrams*, or *volt-equivalent vs oxidation number diagrams*), as shown in Figure 2.2.

Several features are useful here for analysis. First, if one draws a straight line (see the plot) from the point at zero oxidation state (0, 0) to the point at −2 oxidation state (−2, −4.92), one can observe that the point at the −1 oxidation state (−1, −1.36) lies above this line. This means that the free energy change in the line at the oxidation state of −1 is less negative than it would be if the change from 0 to −2 were to occur directly. Thus, the intermediate (in this case H_2O_2) is *thermodynamically unstable* and decomposes into $H_2O + O_2$. Secondly, the most stable oxidation state for oxygen in aqueous solution under standard conditions is that with the most negative free energy change, i.e., −2. Thirdly, the transition from the oxidation state of zero to −1 has a less positive slope than that of 0 to −2. This means that oxygen converting into water is a more powerful oxidizer than oxygen converting into hydrogen peroxide.

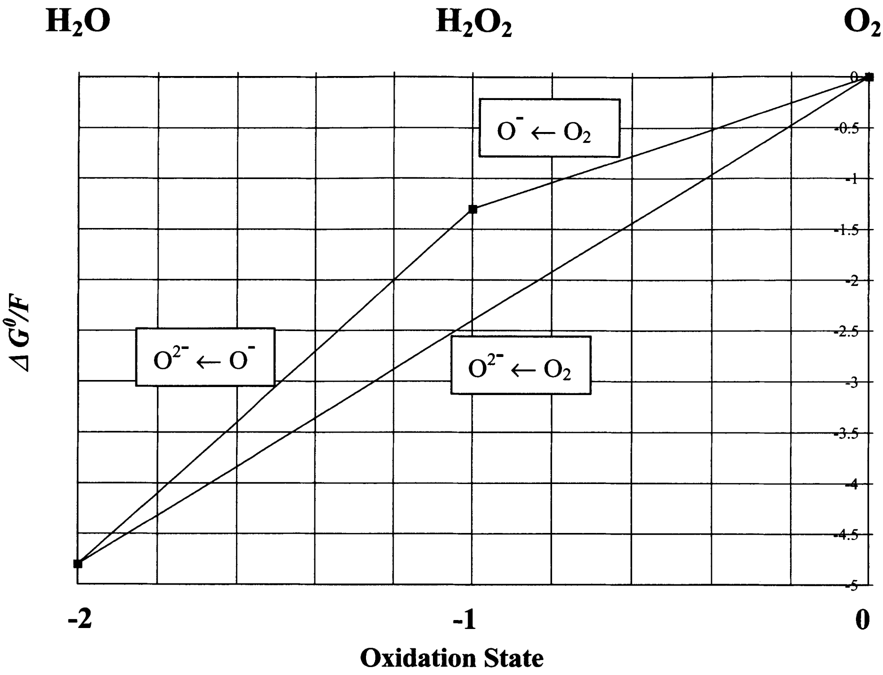


FIGURE 2.2. Frost diagram (i.e., $\Delta G^0/F$ vs oxidation state) for the oxygen system in water.

Example 2.12 involves the Latimer and Frost diagrams of Mn. Key data are summarized in Table 2.5.

2.3.3 Nernst Equation

Let us keep in mind that our target equilibrium is

$$\mathrm{Ox} + ne^- \rightleftarrows \mathrm{Red} \tag{2.68}$$

The entire previous discussion assumed that the system was under standard conditions. What happens if the concentrations, the pH, or T vary?

Then there would be an alteration of ΔG^0 that we will call $-\Delta G'$. The new ΔG will then be

$$\Delta G = \Delta G^0 - \Delta G' \tag{2.69}$$

TABLE 2.5. Standard potentials for manganese equilibria

Reaction	E^0
$Mn^{2+} + 2e^- \rightleftarrows Mn$	−1.03
$Mn^{3+} + e^- \rightleftarrows Mn^{2+}$	1.51
$MnO_2 + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$	1.21
$MnO_4{}^- + 4H^+ + 3e^- \rightleftarrows MnO_2 + 2H_2O$	1.68
$MnO_4^- + e^- \rightleftarrows MnO_4^{2-}$	0.56
$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O$	1.49

Now, if we define $\Delta G'$ in a similar way as ΔG^0, using the reaction quotient (instead of the equilibrium constant), given by

$$Q = \{\Pi[\mathrm{Red}]^{\mathrm{red}}\}/\{\Pi[\mathrm{Ox}]^{\mathrm{ox}}\} \tag{2.70}$$

where $\pi[\mathrm{Red}]^{\mathrm{red}}$ is the product of the concentrations of the species on the *reduced* side of the reaction, and $\pi[\mathrm{Ox}]^{\mathrm{ox}}$ is the product of the concentrations of the species on the *oxidized* side of the reaction (all of these at any point away from equilibrium), one gets

$$\Delta G' = -RT \ln Q \tag{2.71}$$

Substituting ΔG^0 for $-nFE^0$, the result is

$$\Delta G = -nFE^0 + RT \ln\{\Pi[\mathrm{Red}]^{\mathrm{red}}\}/\{\Pi[\mathrm{Ox}]^{\mathrm{ox}}\} \tag{2.72}$$

Dividing both sides by $-nF$, one gets

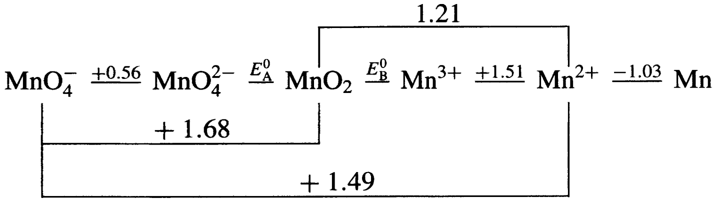
$$-\Delta G/nF = E = E^0 - (RT/nF) \times \ln\{\Pi[\mathrm{Red}]^{\mathrm{red}}\}/\{\Pi[\mathrm{Ox}]^{\mathrm{ox}}\} \tag{2.73}$$

This is the well-known *Nernst equation.* For an accurate thermodynamic definition, activities instead of concentrations must be used. However, as indicated earlier, in order to simplify we assume

Example 2.12 In the Latimer diagram for manganese in acidic medium, (a) find the values of E_A^0 and E_B^0 (see the table below), (b) draw the Frost diagram, and (c) find which is the most stable species of this system in acidic aqueous solution. The standard potential data are summarized in the table given above.

Answer

The corresponding Latimer diagram can be drawn:



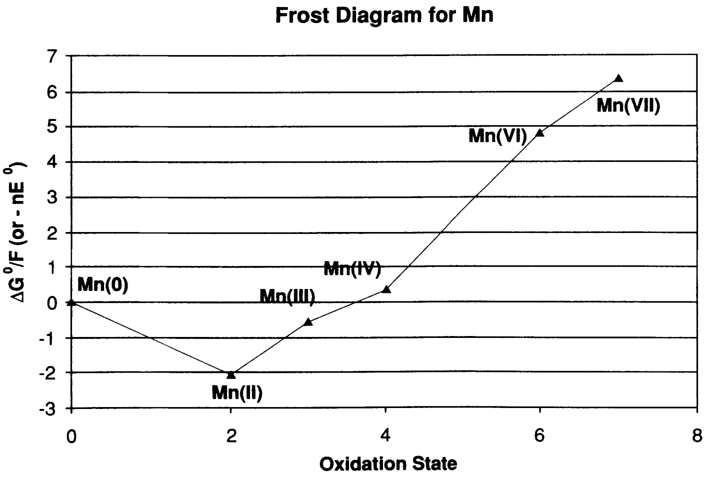
$$\mathrm{MnO_4^-} \xrightarrow{+0.56} \mathrm{MnO_4^{2-}} \xrightarrow{E_A^0} \mathrm{MnO_2} \xrightarrow{E_B^0} \mathrm{Mn^{3+}} \xrightarrow{+1.51} \mathrm{Mn^{2+}} \xrightarrow{-1.03} \mathrm{Mn}$$

$$\mathrm{MnO_2} \xrightarrow{1.21} \mathrm{Mn^{2+}} \qquad \mathrm{MnO_4^-} \xrightarrow{+1.68} \mathrm{MnO_2} \qquad \mathrm{MnO_4^-} \xrightarrow{+1.49} \mathrm{Mn^{2+}}$$

(a) To find the values of E_A^0 and E_B^0 we now calculate the free energy changes for each transition between oxidation states. To do this, one can combine different equations to obtain the desired transition as follows:

Reaction	E^0	ΔG^0
$MnO_4^- + 4H^+ + 3e^- \rightleftarrows MnO_2 + 2H_2O$	1.68	$-3F(1.68)$
$MnO_4^{2-} \rightleftarrows MnO_4^- + e^-$	−0.56	$-F(-0.56)$
$MnO_4^{2-} + 4H^+ + 2e^- \rightleftarrows MnO_2 + 2H_2O$	E_A^0	$-F(5.04 - 0.56)$
	$E_A^0 = 2.24\ \mathrm{V}$ ⇦	$-F(4.48) = -2F(E_A^0)$
$MnO_2 + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$	1.21	$-2F(1.21)$
$Mn^{2+} \rightleftarrows Mn^{3+} + e^-$	−1.51	$-F(-1.51)$
$MnO_2 + 4H^+ + e^- \rightleftarrows Mn^{3+} + 2H_20$	E_B^0	$-(1)FE_B^0 = -F(2.42 - 1.51)$
	$E_B^0 = 0.91$ ⇦	$-F(2.42 - 1.51)$

(b) The Frost diagram can be drawn by performing the same calculations as in the example worked above. One gets the following values for $\Delta G°/F = -nE°$: (0; −2.06; −0.55; 0.36; 4.84; 6.33).



(c) The species with the lowest free energy is Mn^{2+}, and it is the most stable Mn species in acidic media.

these to be reasonably similar if dilute solutions are used.

Applying this equation to our redox system, assuming $T = 25°\mathrm{C}$, using the value of F given earlier and that of the gas law constant ($R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$), and converting from natural log to log base 10, one gets a simplified form of the Nernst equation:

$$E = E^0 - (2.303\ RT/nF)\log([\mathrm{Red}]/[\mathrm{Ox}]) \tag{2.74}$$

or approximately,

$$E = E^0 - (0.059/n)\log([\mathrm{Red}]/[\mathrm{Ox}]) \tag{2.75}$$

2.3.4 Pourbaix Diagrams

For a given system, the equation derived above can be plotted for the different equilibria involving changes in pH and/or changes in oxidation state. This results in the so-called *Pourbaix diagrams* (or E vs pH diagrams). These diagrams are crucial for the understanding of many environmentally important redox processes occurring in aqueous media. We will proceed first to analyze the Pourbaix diagram of water.

The main equilibria in the water redox system are the following:

(a) Water reduction. Water can be reduced to yield hydrogen gas:

$$2H_2O_{(l)} + 2e^- \rightleftarrows H_{2(g)} + 2OH^- \tag{2.76}$$

(b) Water oxidation. Water can be oxidized to yield oxygen gas:

$$2H_2O_{(l)} \rightleftarrows O_{2(g)} + 4H^+ + 4e^- \tag{2.77}$$

From equation 2.76, it is clear that the reduction of water is actually the reduction of its protons, because the oxygen is in an oxidation state of −2 and cannot be reduced any further. Then this equilibrium can be analyzed simply as

$$2H^+ + 2e^- \rightleftarrows H_{2(g)} \tag{2.78}$$

Applying the form of the Nernst equation given in eq. 2.75, one gets

$$E = E^0 - (0.059/n)\log([\mathrm{Red}]/[\mathrm{Ox}]) \tag{2.79}$$

where $[\mathrm{Ox}] = [H^+]$, [Red] is the concentration of H_2 gas, and $n = 2$. Because the concentration of a gas in aqueous solution is best described by its partial pressure, one gets

$$E = E^0 - (0.059/2)\log\{p_{H_2}/[H^+]^2\} \tag{2.80}$$

E^0 for this equilibrium is 0 V (see the introduction to this section). In order to escape from the solution, the partial pressure of hydrogen gas has to be such that it compensates for the pressure of the atmosphere; thus, one can approximate it to one atmosphere ($p_{H_2} = 1$).

Then

$$\begin{aligned} E &= E^0 - (0.059/2)\log\{1/[H^+]^2\} \\ &= 0 - (0.059/2)\log[H^+]^{-2} \end{aligned} \tag{2.81}$$

(units are omitted for simplicity).
Because

$$\log a^b = b\log a \tag{2.82}$$

and

$$\mathrm{pH} = -\log\,[H^+] \tag{2.9b}$$

one gets

$$E = 0.059\log[H^+] = -0.059\ \mathrm{pH} \tag{2.83}$$

Now, for the oxidation of water one has

$$2H_2O_{(l)} \rightleftarrows O_{2(g)} + 4H^+ + 4e^- \tag{2.84}$$

Noting that water is the solvent (and thus its concentration is best described in terms of a unit activity), and using for oxygen the same rationale described above for the partial pressure of hydrogen, the Nernst equation becomes

$$E = E^0 - (0.059/4)\log\{a^2_{H_2O}/[H^+]^4 p_{O_2}\} \tag{2.85}$$

Because $a^2_{H_2O} = 1$, $p_{O_2} = 1$, and $E^0 = 1.23$ V,

$$E = 1.23 - 0.059\ \mathrm{pH} \tag{2.86}$$

(Strictly speaking, one should use the atmospheric partial pressures of hydrogen and oxygen, respectively).

With these two equilibria (eqs. 2.83 and 2.86), the Pourbaix diagram for water can be calculated and drawn (see Table 2.6 and Figure 2.3). The lines are actually *equilibrium* lines. If water is subject to a potential higher than that on the O_2/H_2O line (either by an external applied potential or by the action of a strong oxidizer), the most stable species is $O_{2(g)}$, whereas for a potential below the H_2O/H_2 line (furnished by either an external applied potential or by the action of a strong reducer), the most stable species is $H_{2(g)}$.

The equations in example 2.13 are calculated assuming that the total concentration of *dissolved* Mg

TABLE 2.6. Data for the E vs pH (Pourbaix) diagram for water

pH	Water oxidation $E = 1.23 - 0.059$ pH	Water reduction $E = -0.059$ pH
0	1.23	0
1	1.171	−0.059
2	1.112	−0.118
3	1.053	−0.177
4	0.994	−0.236
5	0.935	−0.295
6	0.876	−0.354
7	0.817	−0.413
8	0.758	−0.472
9	0.699	−0.531
10	0.64	−0.59
11	0.581	−0.649
12	0.522	−0.708
13	0.463	−0.767
14	0.404	−0.826

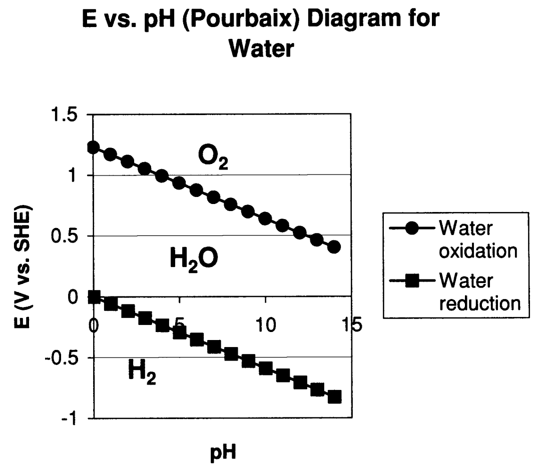


FIGURE 2.3. E–pH diagram for water. (Note that since the potentials are referred to the hydrogen electrode, the E in many diagrams is written as *Eh or* E_h).

Example 2.13 Calculate and draw the Pourbaix diagram for magnesium in aqueous solution at 25°C, assuming that the only three species of Mg present are $Mg_{(s)}$, Mg^{2+}, and $Mg(OH)_{2(s)}$ and that the total concentration of dissolved magnisium species, $[Mg]_{tot} = 1$ M.

Answer

The three equilibria involved can be depicted as follows. The lines and numbers underlying each species indicate the possible equilibria among them:

$$\mathrm{Mg},\ \mathrm{Mg}^{2+},\ \mathrm{Mg(OH)_2}$$

1 3

2

The first step is to write the two redox equilibria (given below by reactions 1 and 3) including H^+, H_2O, e^-, and the acid–base equilibrium (reaction 2), with their corresponding thermodynamic parameters, as shown below. The standard potentials and the K_{sp} are taken from standard tables (e.g., the *CRC Handbook of Chemistry and Physics*).

1. $Mg^{2+} + 2e^- \rightleftarrows Mg_{(s)} \qquad E_1{}^0 = -2.37$ V
2. $Mg^{2+} + 2OH^- \rightleftarrows Mg(OH)_{2(s)}$ *or*

$$Mg(OH)_{2(s)} \rightleftarrows Mg^{2+} + 2OH^-$$
$$K_{sp} = [Mg^{2+}][OH^-]^2 = 8.9 \times 10^{-12}$$

3. $Mg(OH)_{2(s)} + 2e^- + 2H^+ \rightleftarrows Mg_{(s)} + 2H_2O_{(l)}$
$E_2^0 = -1.85$ V

Then, one calculates these three different equilibria:

1. $E = E_1^0 - (0.059/2)\log[Mg^{2+}]^{-1} = -2.37 + (0.059/2)(0) = -2.37$ V
2. $[Mg^{2+}][OH^-]^2 \rightleftarrows 8.9 \times 10^{-12}$

$$[OH^-]^2 = (8.9 \times 10^{-12})/1 = 8.9 \times 10^{-12}$$
$$[OH^-] = \sqrt{8.9} \times \sqrt{10^{-12}} = 2.98 \times 10^{-6}$$

From the water equilibrium,

$$10^{-14} = [H^+][OH^-] = [H^+](2.98 \times 10^{-6})$$

Thus,

$$[H^+] = (10^{-14})/(2.98 \times 10^{-6}) = 3.35 \times 10^{-9}$$
$$\log[H^+] = -8.47$$

and pH = 8.47

3. $E = E_2^0 - (0.059/2)\log[H^+]^{-2}$
$= -1.85 - 0.059$ pH

Lastly, one plots these three equilibria as shown in Figs. A, B, and C, respectively.

In Fig. A one can note that the more oxidized species, i.e., Mg^{2+}, is written above the equilibrium line because the higher the potential, the higher the tendency for electron removal. In Fig. B the $Mg(OH)_2$ is written on the right side of the equilibrium line, because the higher the pH, the higher the concentration of OH^- that favors the hydroxide formation. In Fig. C both rationales just described combine into one.

However, one can note that the Mg^{2+} is not stable in the whole pH interval, because it precipitates at a certain pH (8.47 in this case). Then, Fig. A actually becomes Fig. D. By applying the same idea of establishing limits, Figs. B and C become Figs. E and F, respectively. By combining Figs. D, E, and F one gets the overall Pourbaix diagram for Mg, Fig. G.

Note that standard potential tables may list some reactions involving OH^- instead of H^+ ions. The conversion is relatively simple. For example, for the second equilibrium written above, one can also find in tables:

$$Mg(OH)_{2(s)} + 2e^- \rightleftarrows Mg_{(s)} + 2OH^-$$
$$E^0 = -2.69$$

Here, the Nernst equation becomes

$$\begin{aligned} E &= -2.69 - (0.059/2)\log([OH^-]^2) \\ &= -2.69 - 0.059\log[OH^-] \end{aligned}$$

Because at 25°C

$$-\log[H^+] - \log[OH^-] = 14 = pH + pOH,$$

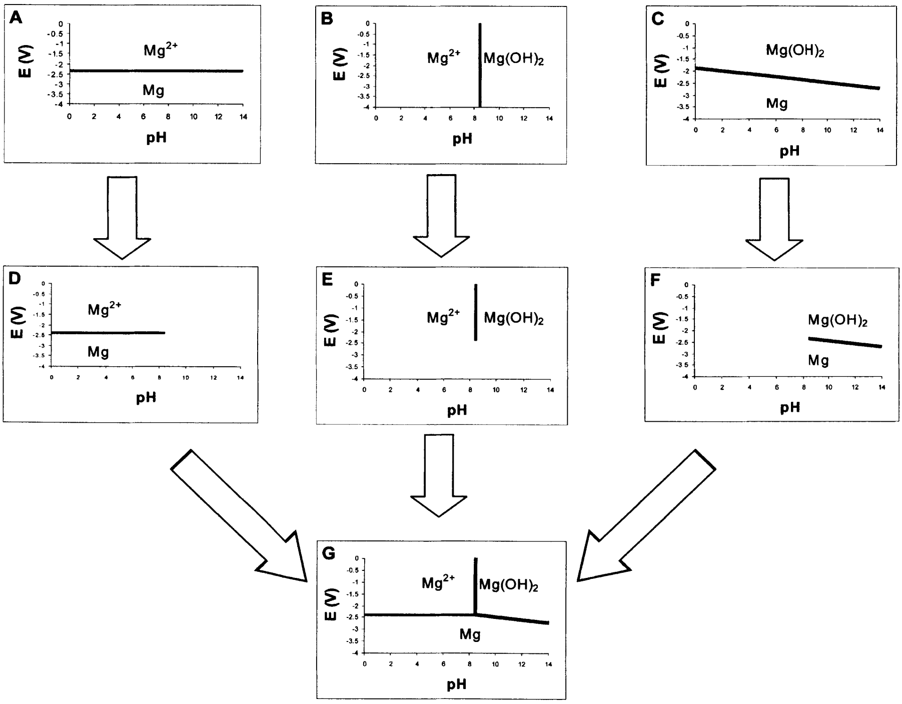
one gets

$$\begin{aligned} E &= -2.69 + 0.059\,pOH \\ &= -2.69 + 0.059[14 - pH] \\ &= -2.69 + 0.84 - 0.059\,pH \\ E &= -1.85 - 0.059\,pH \end{aligned}$$

From this,

$$E_2^0 = -1.85\ V$$

as found in the standard tables.



E vs pH diagram for Mg ($[Mg]_{tot}$ = 1 M). All the potentials used here are referred to the standard hydrogen electrode (SHE). See text.

species at any point is $[Mg]_{tot} = 1$ M. However, this is seldom the case in environmental settings. Thus, one has to use other concentrations for real situations. For example, if one assumes $[Mg]_{tot} = 10^{-6}$ M, the calculations for each one of the reactions then become

1. $E = E_1^0 - (0.059/2)\log[Mg^{2+}]^{-1} = -2.37 + 0.059/2(-6) = -2.37 - 0.177 = -2.547$ V
2. $E = E_2^0 - (0.059/2)\log[H^+]^{-2}$ $= -1.85 - 0.059$ pH
3. $[Mg^{2+}][OH^-]^2 = 8.9 \times 10^{-12}$

$$[OH^-]^2 = (8.9 \times 10^{-12})/10^{-6} = 8.9 \times 10^{-6}$$

$$[OH^-] = \sqrt{8.9} \times \sqrt{10^{-6}} = 2.98 \times 10^{-3}$$

From the water equilibrium,

$$10^{-14} = [H^+][OH^-] = [H^+](2.98 \times 10^{-3})$$

Thus,

$$[H^+] = (10^{-14})/(2.98 \times 10^{-3}) = 3.35 \times 10^{-12}$$

$$\log[H^+] = -11.47$$

$$\text{and pH} = 11.47$$

One can note that the values for the $Mg^{2+}/Mg_{(s)}$ and the $Mg(OH)_{2(s)}/Mg^{2+}$ equilibria at this concentration of 10^{-6} (i.e., $E = -2.547$ V and pH = 11.47) are different from those using a 1 M concentration (i.e., $E = -2.37$ V, and pH = 8.47). This means that the more dilute the Mg^{2+} concentration, the more difficult its reduction to Mg^0. Also, the more dilute the Mg^{2+} concentration, the more difficult its precipitation as $Mg(OH)_{2(s)}$.

In contrast, the value for the $Mg(OH)_{2(s)}/Mg_{(s)}$ equilibrium ($E = -1.85 - 0.059$ pH) is the same in both cases because the concentration of dissolved magnesium does not appear in this equilibrium expression (see also Examples 2.14 and 2.15).

Standard reduction potentials for reactions in biochemical systems are normally determined at pH = 7. From the discussion above, it can be seen that the corresponding potentials for the hydrogen and oxygen reduction reactions at this pH value are

$$2H^+ + 2e^- \rightleftarrows H_{2(g)} \quad E = -0.413 \text{ V} \quad (2.87)$$

$$1/2O_{2(g)} + 2H^+ + 2e^- \rightleftarrows H_2O_{(l)} \quad E = +0.817 \text{ V} \quad (2.88)$$

Example 2.14 Calculate and draw the equilibrium lines in the aluminum Pourbaix diagram (in aqueous media) for a total dissolved aluminum concentration of 10^{-6} M. Assume that the main species existing in equilibrium and their corresponding values of ΔG_f^0 are those shown in the table.

Species	ΔG_f^0, kJ/mol
$Al_{(s)}$	0
$Al^{3+}_{(aq)}$	−485.1
$Al(OH)_{3(s)}$	−1147.1
$Al(OH)^-_{4(aq)}$	−1305.2
$OH^-_{(aq)}$	−157.3

Also assume that the only equilibria present are

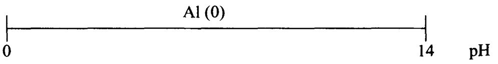
1. $Al_{(s)}/Al^{3+}_{(aq)}$
2. $Al^{3+}_{(aq)}/Al(OH)_{3(s)}$
3. $Al(OH)_{3(s)}/Al(OH)^-_{4(aq)}$
4. $Al_{(s)}/Al(OH)_{3(s)}$
5. $Al_{(s)}/Al(OH)^-_{4(aq)}$

Answer

A. Acid–Base Equilibria

From example 2.13, we know that we must first establish the predominance zones. We do this for each oxidation state as follows:

(a) Al (0): It is the only Al (0) species in the whole pH interval, and so its predominance-zone diagram is



(b) Al (III): This can exist as $Al^{3+}_{(aq)}$, $Al(OH)_{3(s)}$, and $Al(OH)^-_{4(aq)}$. We need to analyze at what pH values does each equilibrium occur (i.e., equilibria 2 and 3) at the concentration given in the example.

i. Equilibrium 2:

The desired equilibrium is

$$Al^{3+} \rightleftarrows Al(OH)_{3(s)}$$

We balance the equation by adding $3OH^-$ to the left side:

$$Al^{3+} + 3OH^- \rightleftarrows Al(OH)_{3(s)}$$

(Recall that for convenience, the phase of the aqueous species is not written in this book).

Perhaps we are most accustomed to seeing this type of equation written backwards:

$$Al(OH)_{3(s)} \rightleftarrows Al^{3+} + 3OH^-$$

This is a dissolution equilibrium that is governed by the thermodynamic constant called K_{sp} (solubility product, see Example 2.1). To calculate the K_{sp} value, we now use the $\Delta G_f{}^0$ values from the table. First we use them to calculate the ΔG^0 for this reaction and we then use this value to calculate the numerical value for K_{sp}. Because $[Al^{3+}]$ is given, we are able to calculate $[OH^-]$ and thus the pH. Mathematically speaking:

$$\begin{aligned}\Delta G_i^0 &= \left(\Delta G^0_{f,Al^{3+}} + 3\Delta G^0_{f,OH^-}\right) - \Delta G^0_{f,Al(OH)_3}\\ \Delta G_i^0 &= [-485.1 + 3(-157.3)] - (-1147.1)\\ &= 190.1\ \text{kJ/mol}\end{aligned}$$

From equation 2.58:

$$\Delta G_i^0 = -RT \ln K_{sp}$$

and:

$$\ln K_{sp} = -\frac{\Delta G_i^0}{RT} = 2.303 \log K_{sp}$$

Then, at 25°C we get:

$$\begin{aligned}\log K_{sp} &= -\frac{\Delta G_i^0}{2.303\,RT}\\ &= -\frac{190.1\,\frac{\text{kJ}}{\text{mol}}}{2.303\left(8.31434\,\frac{\text{J}}{\text{K mol}}\right)(298\ K)\left(\frac{1\ \text{kJ}}{10^3\ \text{J}}\right)}\\ &= -\frac{190.1}{5.706} = -33.3\end{aligned}$$

Then,

$$K_{sp} = 10^{-33.3}$$

and since

$$K_{sp} = [Al^{3+}][OH^-]^3,$$

$$\text{and } [OH^-]^3 = \frac{K_{sp}}{[Al^{3+}]}$$

Then,

$$\begin{aligned}[OH^-] &= \sqrt[3]{\frac{K_{sp}}{[Al^{3+}]}} = \left(\frac{10^{-33.3}}{10^{-6}}\right)^{1/3}\\ &= 7.94 \times 10^{-10}\end{aligned}$$

and from Example 2.1, at 25°C

$$K_W = 10^{-14} = [H^+][OH^-]$$

$$[H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{7.94 \times 10^{-10}} = 1.26 \times 10^{-5}$$

and

$$pH = -\log[H^+] = 4.90$$

ii. Equilibrium 3:

We balance the equation by adding one OH^- to the left side:

$$Al(OH)_{3(s)} + OH^- \rightleftarrows Al(OH)_4^-$$

We now name the parameter governing this equilibrium as K_C (complexation constant).

Using the same strategy as above we get:

$$\begin{aligned}\Delta G_{ii}^0 &= \Delta G^0_{f,Al(OH)_4^-} - \left(\Delta G^0_{f,Al(OH)_3} + \Delta G^0_{f,OH^-}\right)\\ &= (-1305.2) - [(-1147.1) + (-157.3)]\\ &= -0.8\ \text{kJ/mol}\\ &= -RT \ln K_C\end{aligned}$$

Then,

$$\log K_C = \frac{0.8}{2.303RT} = \frac{0.8}{5.706} = 0.14$$

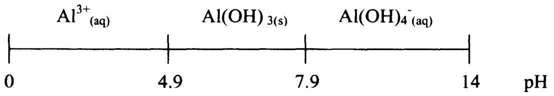
$$K_C = 10^{0.14} = \frac{[\mathrm{Al(OH)_4^-}]}{[\mathrm{OH^-}]} = \frac{10^{-6}}{[\mathrm{OH^-}]}$$

Lastly,

$$[\mathrm{OH^-}] = \frac{10^{-6}}{10^{0.14}} = 10^{-6.14}, \text{ and}$$

$$\mathrm{pH} = 7.86$$

With the results from (i) and (ii) we now draw the predominance-zone diagram for the Al(III) species:



B. Redox Equilibria

By superimposing this diagram with that generated earlier, we can see that the redox equilibria given in the question statement have the following boundaries (in the $0 < \mathrm{pH} < 14$ region):

iii. $\mathrm{Al_{(s)}/Al^{3+}_{(aq)}}$ $0 < \mathrm{pH} < 4.9$
iv. $\mathrm{Al_{(s)}/Al(OH)_{3(s)}}$ $4.9 < \mathrm{pH} < 7.9$
v. $\mathrm{Al_{(s)}/Al(OH)^-_{4(aq)}}$ $7.9 < \mathrm{pH} < 14$

We now analyze the equation for the potential that governs each one.

iii. Here, the desired equilibrium (written in the standard format as a reduction) is

$$\mathrm{Al^{3+}} \rightleftarrows \mathrm{Al_{(s)}}$$

We balance this equation by adding $3e^-$ to the left side:

$$\mathrm{Al^{3+}} + 3e^- \rightleftarrows \mathrm{Al_{(s)}}$$

To calculate E^0, we use equation 2.58 again:

$$\Delta G^0_{iii} = -nFE^0_{iii} = \Delta G_{f,\mathrm{Al}} - \Delta G_{f,\mathrm{Al^{3+}}}$$
$$= 0 - (-485.1\ \mathrm{kJ/mol})$$

$$E^0_{iii} = -\frac{485.1\ \mathrm{kJ/mol\ Al}}{\frac{3\ \mathrm{mol\ e^-}}{\mathrm{mol\ Al}}\left(96496\frac{\mathrm{Coul}}{\mathrm{mol\ e^-}}\right)\left(\frac{1\frac{\mathrm{J}}{\mathrm{V}}}{1\ \mathrm{Coul}}\right)\left(\frac{1\ \mathrm{kJ}}{10^3\ \mathrm{J}}\right)}$$
$$= -1.68\ \mathrm{V}$$

$$E_{iii} = -1.68 - \frac{0.059}{3}\log\frac{1}{[\mathrm{Al^{3+}}]}$$
$$= -1.68 - \frac{0.059}{3}\log 10^6 = -1.80\ \mathrm{V}$$

iv. The equilibrium that we need to balance is:

$$\mathrm{Al(OH)_{3(s)}} \rightleftarrows \mathrm{Al_{(s)}}$$

We proceed as above and obtain

$$\mathrm{Al(OH)_{3(s)}} + 3e^- \rightleftarrows \mathrm{Al_{(s)}} + 3\mathrm{OH^-}$$

We now obtain E^0:

$$\Delta G^0_{\mathrm{iv}} = [\Delta G^0_{f,\mathrm{Al}} + 3\Delta G^0_{f,\mathrm{OH^-}}] - \Delta G^0_{f,\mathrm{Al(OH)_3}}$$
$$= [0 + 3(-157.3)] - (-1147.1)$$
$$= 675.2\ \mathrm{kJ/mol}$$

$$E^0_{iv} = -\frac{675.2\ \frac{\mathrm{kJ}}{\mathrm{mol\ Al}}}{\frac{3\ \mathrm{mol}\ e^-}{\mathrm{mol\ Al}}\left(96496\frac{\mathrm{Coul}}{\mathrm{mol\ e^-}}\right)\left(\frac{1\ \mathrm{J/V}}{1\ \mathrm{Coul}}\right)\left(\frac{1\ \mathrm{kJ}}{10^3\mathrm{J}}\right)}$$
$$= -2.33\ \mathrm{V}$$

By simple inspection, we note that this reaction depends on E as well as on pH, because both $\mathrm{OH^-}$ and e^- are involved in it. Then, we must use Nernst equation (eq. 2.73) to find the corresponding equilibrium expression:

$$E_{iv} = E^0_{iv} - \frac{0.059}{n}\log[\mathrm{OH^-}]^3$$
$$= -2.33 - \frac{0.059}{3}\log[\mathrm{OH^-}]^3$$
$$= -2.33 - 0.059\log[\mathrm{OH^-}]$$
$$= -2.33 - 0.059\log\left(\frac{K_w}{[\mathrm{H^+}]}\right)$$
$$= -2.33 - 0.059\log(10^{-14}) - 0.059\log[\mathrm{H^+}]^{-1}$$
$$= -2.33 + 0.83 + 0.059\log[\mathrm{H^+}]$$
$$E_{iv} = -1.50 - 0.059\mathrm{pH}$$

v. The equilibrium here is:

$$\mathrm{Al(OH)_4^-} \rightleftarrows \mathrm{Al_{(s)}}$$

We balance it by adding e^- and $\mathrm{OH^-}$ as required:

$$\mathrm{Al(OH)_4^-} + 3e^- \rightleftarrows \mathrm{Al_{(s)}} + 4\mathrm{OH^-}$$

Then we get E^0 from ΔG^0:

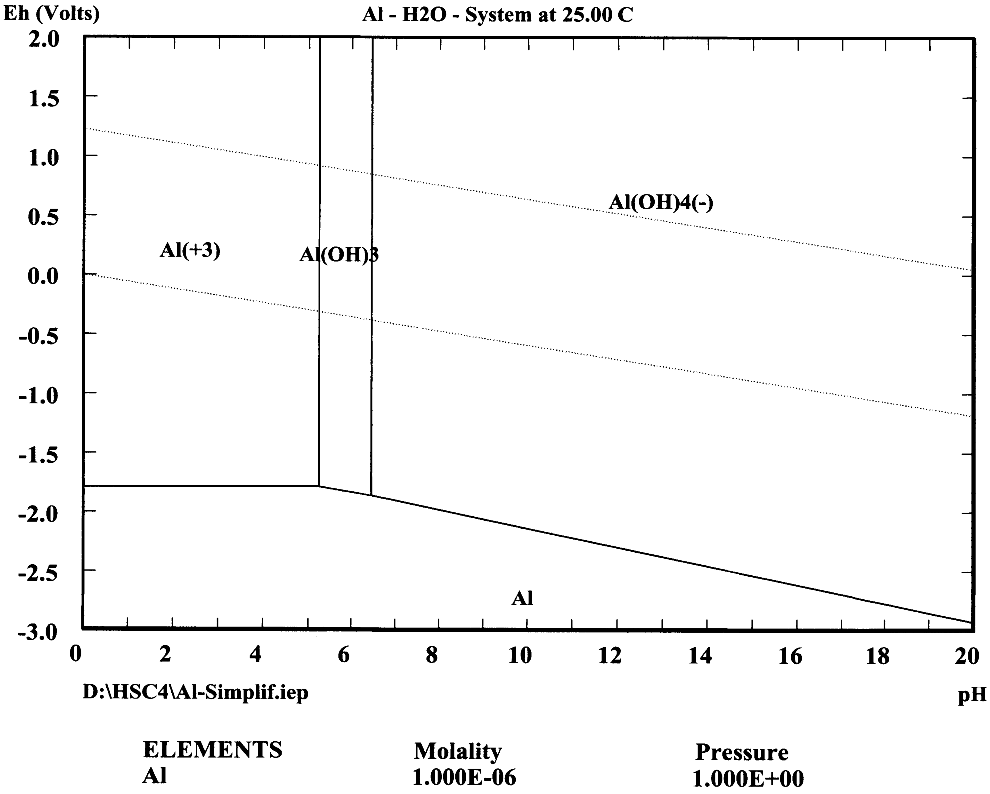
$$\Delta G^0_{\mathrm{v}} = [\Delta G^0_{f,\mathrm{Al}} + 4\Delta G^0_{f,\mathrm{(OH)^-}}] - \Delta G^0_{f,\mathrm{Al(OH)_4^-}}$$
$$= [0 + 4(-157.3)] - (-1305.2)$$
$$= 676.0\ \mathrm{kJ/mol}$$

We proceed as above to find E and get:

$$E_v^0 = -\frac{676}{3(96496)(10^{-3})} = -2.33\ \mathrm{V}$$

$$\begin{aligned}
E_v &= E_v^0 - \frac{0.059}{3}\log\left(\frac{[\mathrm{OH}^-]^4}{[\mathrm{Al(OH)}_4^-]}\right)\\
&= -2.33 - \frac{(0.059)}{3}\log[\mathrm{Al(OH)}_4^-]^{-1}\\
&\quad -\frac{(0.059)4}{3}\log[\mathrm{OH}^-]\\
&= -2.33 - \frac{0.059}{3}\log(10^{-6})^{-1}\\
&\quad -0.079\log[\mathrm{OH}^-]\\
&= -2.33 - 0.118 - 0.079\log\left(\frac{K_w}{[\mathrm{H}^+]}\right)\\
&= -2.33 - 0.118 - 0.079\log 10^{-14}\\
&\quad -0.079\log[\mathrm{H}^+]^{-1}\\
E_v &= -1.34 - 0.079\,\mathrm{pH}
\end{aligned}$$

By comparing the values calculated in this problem with those plotted with the commercial program used to generate the following figure (HSC Chemistry© 4.0, by Outkumpu), which uses molal concentrations, we note that they match quite well and that the differences in using molar or molal units are practically negligible in such dilute solutions. (The dotted lines represent the water equilibria). Note: The difference in the calculated pH for equilibrium # 3 and that in the plot is possibly due to the fundamental thermodynamic data used.



From this diagram it can be seen that $Al(OH)_3$ is amphoteric because it can dissolve when an acid or a base are added to it (yielding Al^{3+} and $Al(OH)_4^-$, respectively). In addition, Al metal can also reactively dissolve in these cases, producing $H_{2(g)}$ plus Al^{3+} and $Al(OH)_4^-$, respectively.

Example 2.15 Repeat the problem in Example 2.14, but this time use a total dissolved aluminum concentration of 10^{-3} M. Compare both diagrams and comment on any possible differences. (See the note at the end of Example 2.14).

Answer

By performing the corresponding calculations one obtains:

(a) *Acid–Base equilibria:*

$$Al(OH)_{3(s)} \rightleftarrows Al^{3+} + 3OH^- \quad pH = 3.90$$

$$Al(OH)_{3(s)} + OH^- \rightleftarrows Al(OH)_4^- \quad pH = 10.86$$

(b) *Redox Equilibria*

$$Al^{3+} + 3e^- \rightleftarrows Al_{(s)} \quad E = -1.74\,V$$

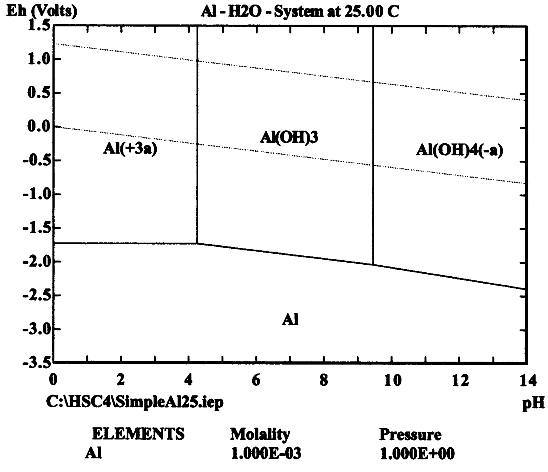
$$Al(OH)_{3(s)} + 3e^- \rightleftarrows Al_{(s)} + 3OH^-$$

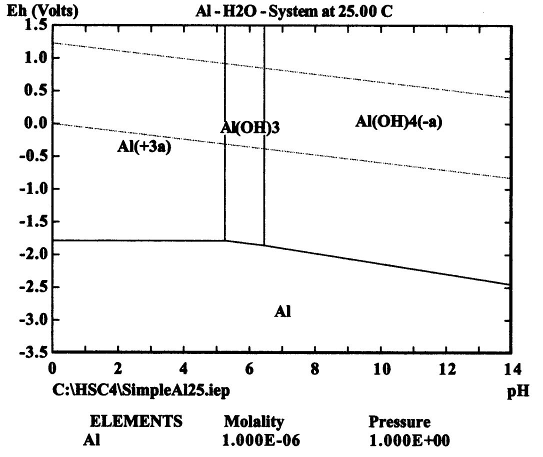
$$E = -1.50 - 0.059\,pH$$

$$Al(OH)_4^- + 3e^- \rightleftarrows Al_{(s)} + 4OH^-$$

$$E = -1.28 - 0.079\,pH$$

By comparison, we note that the pH required for Al^{3+} precipitation is smaller at 10^{-3} M than at 10^{-6} M (also compare both plots). (Note that molalities were used here instead of molarities, but the difference is very small). On the other hand, the pH required for the formation of $Al(OH)_4^-$ at 10^{-3} M is higher than that at 10^{-6} M. This means that precipitation is easier at higher concentrations, and that more OH^- are required for complex formation (and thus a higher pH) at higher concentrations of the metal ion. With regard to the redox processes, we note that a less negative potential is required for the reduction of a higher concentration of the metal ion to the elemental form (i.e., −1.74 V is required for 10^{-3} M, whereas −1.80 V is needed for 10^{-6} M). Interestingly the E equation for the reduction of the metal hydroxide to the elemental form is exactly the same in both cases. This is because the concentration of the metal ion in any of its forms does not appear in the equation for this equilibrium. Lastly, it is easier to reduce the metal complex at high concentrations; this result as well as that of the metal ion reduction, imply that lower concentrations of a metal ion entail a greater difficulty for this reduction.





2.3.5 The p*E* Scale

The value of pH in the expression 2.9b,

$$\mathrm{pH} = -\log[\mathrm{H}^+]$$

measures the relative tendency of a solution to *accept* protons (i.e., low pH values mean a low tendency to accept protons, whereas high pH values mean the opposite). In a similar way one can visualize a new variable:

$$\mathrm{p}E = -\log[e^-] \qquad (2.89)$$

as a measure of the tendency of a solution to *accept* electrons (i.e., a low p*E* value means a low tendency to accept electrons, and vice versa).

One must note that in this expression there is a necessary deviation from the common usage of a p*X* in Chemistry. For a species *X*, p*X* is defined in general as $-\log a_x$ (or as $-\log[X]$, when the activity coefficient is near unity). However, there *cannot* be physical reality in saying that p*E* = − log [concentration of the potential, *E*] because such a concept is meaningless here.

In addition, there is a certain degree of discrepancy in the literature as to the interpretation of p*E*, either as a measure of the *true* concentration of electrons (see Howard, 1998), or of their *effective* concentration or activity (see Baird, 1995), or else of their *hypothetical* activity (see Stumm and Morgan, 1996). Such discrepancies seem to stem from the fact that neither free nor hydrated electrons exist in solution in appreciable concentrations, but they can exist in the neighborhood of an electrode; also, hydrated e^- can be generated in photolyzed solutions (see Stumm and Morgan, 1996).

In spite of the previous discussion, one can relate pE to the potential in the Ox $+\mathrm{ne}^- \rightleftarrows$ Red system discussed above by the simple equation:

$$\mathrm{p}E = E/[2.303\ RT/F] \qquad (2.90)$$

that at 25°C becomes

$$\mathrm{p}E = E/0.059 \qquad (2.91)$$

For standard conditions one can write

$$\mathrm{p}E^0 = E^0/0.059 \qquad (2.92)$$

Because equation 2.58 gives

$$\Delta G^0 = -nFE^0 = -RT\ln K$$

then

$$E^0 = (2.303\ RT/F)(1/n)\log K \qquad (2.93)$$

As discussed above, at 25°C the first term is 0.059 and then

$$\mathrm{p}E^0 = E^0/0.059 = [0.059\ (1/n)\log K]/0.059 \qquad (2.94)$$

or simply

$$\mathrm{p}E^0 = (1/n)\log K \qquad (2.95)$$

Because for the reaction Ox $+\mathrm{ne}^- \rightleftarrows$ Red at 25°C one has

$$E = E^0 - (0.059/n)\log Q \qquad (2.96)$$

$$\text{where } Q = \{\Pi[\mathrm{Prod}]^p]\}/\{\Pi[\mathrm{React}]^r\} = ([\mathrm{Red}]/[\mathrm{Ox}])$$

then

$$\mathrm{p}E = E/0.059 = (1/0.059)\{E^0 - (0.059/n)\log([\mathrm{Red}]/[\mathrm{Ox}])\} \qquad (2.97)$$

or

$$\mathrm{p}E = E^0/0.059 - (1/n)\log([\mathrm{Red}]/[\mathrm{Ox}])\} = \mathrm{p}E^0 - (1/n)\log([\mathrm{Red}]/[\mathrm{Ox}]) \qquad (2.98)$$

(Note that $[e^-]$ does not appear in *Q*, because it is already accounted for in the definition of p*E*). We are ready now to use this helpful set of relationships to do calculations involving redox equilibria. See Examples 2.16, 2.17 and 2.18.

Furthermore, when the equilibrium constants for a redox system are known, one can also take the following route to a p*E* expression. Let us use the oxidation of water again as an example.

$$2\mathrm{H_2O_{(l)}} \rightleftarrows \mathrm{O_{2(g)}} + 4\mathrm{H}^+ + 4e^- \quad \log K = -83.1 \qquad (2.99)$$

The complete equilibrium expression (i.e., taking electrons into account), is

$$K = \mathrm{p_{O_2}}[\mathrm{H}^+]^4\,[e^-]^4 = 10^{-83.1} \qquad (2.100)$$

Taking negative logs on both sides,

$$-\log K = -\log \mathrm{p_{O_2}} - 4\log[\mathrm{H}^+] - 4\log[e^-] \qquad (2.101)$$

Because $\mathrm{p_{O_2}} = 0.21$ atm, pH $= -\log[\mathrm{H}^+]$, and p*E* $= -\log[e^-]$, then

$$83.1 = 0.17 + 4\mathrm{pH} + 4\mathrm{p}E \qquad (2.102)$$

Example 2.16 Write the equations that relate pE as a function of pH for (a) the oxidation and (b) the reduction of water.

Answer

(a) We look at the oxidation first:

$$2H_2O_{(l)} \rightleftarrows O_{2(g)} + 4H^+ + 4e^-$$

Writing it as a reduction,

$$O_{2(g)} + 4H^+ + 4e^- \rightleftarrows 2H_2O_{(l)}$$

At 25°C,

$$E = E^0 - (0.059/n)\log\{1/(p_{O_2}[H^+]^4\}$$

Then,

$$\begin{aligned} pE &= E/0.059 = (1/0.059) \\ &\quad \times \{1.23 - (0.059/4)\log(1/(p_{O_2}[H^+]^4)\} \\ &= (1.23/0.059) - (1/4)\log(1/(p_{O_2}[H^+]^4) \\ &= 20.85 + 0.25\log p_{O_2} + 0.25\log[H^+]^4 \end{aligned}$$

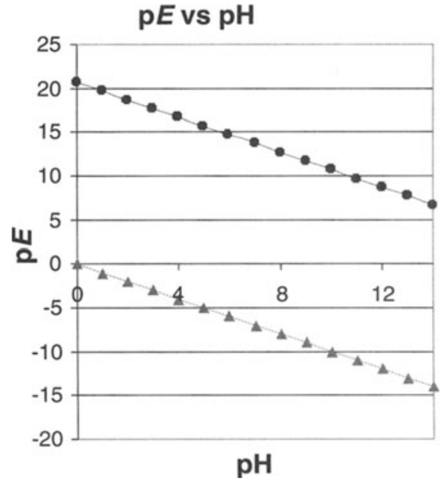
Using $p_{O_2} = 0.21$ atm (although using 1 atm as we did in the calculation of the Pourbaix diagram form water does not change things much), one gets

$$pE = 20.85 - 0.17 + \log[H^+] = 20.68 - pH$$

(b) In the same fashion, one can apply the pE equation to the reduction of water as discussed in Section 2.3.4 (the exercise is left to the reader) and get:

$$pE = -pH$$

By plotting these two equations, the complete pE vs pH diagram for water is obtained, which is equivalent (with a y-axis displacement) to the Pourbaix diagram for water drawn above.



Example 2.17 Manganese is ubiquitous in natural waters. Its main representative equilibrium is between dissolved Mn(II) and precipitated Mn(IV) in the form of γ-MnO_2, hereby simply written as MnO_2 (see Baird, 1995). Such an equilibrium can be written as:

$$MnO_{2(s)} + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O_{(l)} \qquad E^0 = 1.21\ V$$

With this information,

(a) Calculate the value of K for this reaction, and interpret it qualitatively in the light of the Frost diagram for manganese (as drawn in the Example 2.12).
(b) Calculate the pE at the surface of a certain lake, where water has a pH = 7.5, and $[Mn^{2+}] = 10^{-5.5}$ M. For this step, assume that dioxygen is absent.
(c) Write the *balanced* equation for the oxidation of Mn^{2+} by dioxygen that produces MnO_2, and find its equilibrium constant.

(d) With the same set of conditions described above (pH = 7.5 and 25°C), but now assuming $p_{O_2} = 0.21$ atm, calculate the concentration of Mn^{2+} at equilibrium in the system by *using* p*E*. Interpret your result.

(e) Do the same calculation as in (d), but *without* using pE.

Answer

(a) From eqs. 2.92 and 2.95,

$$pE^0 = (1/n)\log K = E^0/0.059$$

Then, $E^0 = (0.059/2)\log K$

$$\log K = 2(1.21)/0.059 = 41.0$$

and $K = 10^{41}$

This means that the equilibrium in the $MnO_{2(s)}/Mn^{2+}$ system is strongly driven toward Mn^{2+}. This agrees well with the Frost diagram in Example 2.12, that shows the high stability of Mn^{2+} in aqueous media.

(b) From eq. 2.97,

$$\begin{aligned} pE &= E/0.059 = (1/0.059)\{E^0 - (0.059/n) \\ &\quad \times \log\{\Pi[\text{Prod}]^p\}/\{\Pi[\text{React}]^r\} \\ &= (1/0.059)\{1.21 - (0.059/2) \\ &\quad \log\{[Mn^{2+}]/[H^+]^4\} \\ &= 20.51 - \tfrac{1}{2}\log[Mn^{2+}] + (4/2) \\ &\quad \log[H^+] \\ &= 20.51 - \tfrac{1}{2}\log[Mn^{2+}] - 2\,pH \\ &= 20.51 + 2.75 - 2\,(7.5) \end{aligned}$$

Lastly,

$$pE = 8.26$$

(c) We write the two half-reactions involved (i.e., the inverse of the target equilibrium and of the water–dioxygen equilibrium, eq. 2.84) and add them:

$$Mn^{2+} + 2H_2O_{(l)} \rightleftarrows MnO_{2(s)} + 4H^+ + 2e^- \qquad E^0 = -1.21$$

$$O_{2(g)} + 4H^+ + 4e^- \rightleftarrows 2H_2O_{(l)} \qquad E^0 = 1.23$$

$$Mn^{2+} + H_2O_{(l)} + {}^1/_2\,O_{2(g)} \rightleftarrows MnO_{2(s)} + 2H^+ \qquad E^0 = 0.02\text{ V}$$

and

$$\log K = nE^0/0.059 = 0.68$$

$$K = 10^{0.68}$$

This small value means that the oxidation of Mn^{2+} by dioxygen under these conditions is not thermodynamically favored.

(d) First we find the p*E* of water under these conditions.

$$pE = 20.68 - pH = 13.18$$

This must be equal to the p*E* of the Mn^{2+} equilibrium found in part (b):

$$pE = 20.51 - {}^1/_2\log[Mn^{2+}] - 2pH = 13.18$$

Because pH = 7.5, one gets

$$\begin{aligned} -\tfrac{1}{2}\log[Mn^{2+}] &= -20.51 + 13.18 + 2pH \\ &= 7.67 \end{aligned}$$

$$[Mn^{2+}] = 10^{-15.3} = 4.6 \times 10^{-16}\text{ M}$$

Such a small amount is due to the oxidizing conditions that favor the more oxidized Mn(IV) species.

(e) Do the same calculation as in (d), but *without* using p*E*.
One can approach the problem by using the definition of *K*:

$$K = [H^+]^2/([Mn^{2+}]\,p_{O_2}^{1/2})$$

$$\begin{aligned} [Mn^{2+}] &= [H^+]^2/(p_{O_2}^{1/2}K) \\ &= (10^{-7.5})^2/(0.21^{1/2} \times 10^{0.68}) \\ &= 4.6 \times 10^{-16}\text{ M} \end{aligned}$$

which is the same result as in (d).

Example 2.18 Nitrates can be reduced in acidic media to produce ammonium ions (see Baird, 1995). E^0 for this reaction is +0.836 V.

(a) Write a balanced equation for the reduction of one mole of NO_3^- ions to NH_3.
(b) Without performing any calculations, would you expect the equilibrium ratio of NH_4^+ to NO_3^- ions to be large or small at the pH of pure water in contact with air (i.e., pH ca. 5.7, see Example 6.4) under oxic conditions?
(c) Find the $[NH_4^+]/[NO_3^-]$ ratio at pH = 6 for water at $pE = 11$ (i.e., oxic conditions).
(d) Find the $[NH_4^+]/[NO_3^-]$ ratio at pH = 6 for water at $pE = -3$ (i.e., anoxic conditions).

Answer

(a) $NO_3^- + 10H^+ + 8e^- \rightleftarrows NH_4^+ + 3H_2O_{(l)}$
(b) At pH = 5.7 there are not enough H^+ to drive the reaction toward products. In addition, oxic conditions favor the more oxidized species. Because the nitrogen in NO_3^- is in an oxidation state of +5, whereas that in NH_4^+ is −3, the former is favored and the equilibrium is displaced toward the reactants. Thus, a small $[NH_4^+]/[NO_3^-]$ would be expected.
(c) Find the ratio $r = [NH_4^+]/[NO_3^-]$ at a pH = 6 for water at $pE = 11$ (i.e., oxic conditions).

$$pE = E/0.059 = (1/0.059)$$
$$\{E^0 - (0.059/8)\log [NH_4^+]/[NO_3^-]\,[H^+]^{10}\}$$
$$= (E^0/0.059) - (1/8)\log [NH_4^+]/[NO_3^-]$$
$$-(1/8)\log[H^+]^{-10}$$
$$= 14.17 - 1/8 \log r + 1.25 \log [H^+]$$
$$= 14.17 - (1/8)\log r - 1.25\,\text{pH}$$

At pH = 6 we get

$$pE = 6.67 - (1/8)\log r$$

If $pE = 11$, then

$$\log r = 8(6.67 - 11) = -34.6$$
$$r = [NH_4^+]/[NO_3^-] = 10^{-34.6}$$

this confirms our prediction in (b).
(d) If $pE = -3$, then

$$\log r = 8[6.67 - (-3)] = 77.4$$
$$r = [NH_4^+]/[NO_3^-] = 10^{77.4}$$

which means that under anoxic conditions, $[NH_4^+]$ is by far the predominant species.

and

$$pE = (1/4)(83.1 - 0.17 - 4\,\text{pH}) = 20.73 - \text{pH} \qquad (2.103)$$

which is the same result as that obtained above. The small discrepancy is due to the different sources used for the thermodynamic data (i.e., K and E^0 values), and for errors derived from rounding-off.

As an additional note, it is important to keep in mind that the diagrams discussed above are *thermodynamic* diagrams and that they were constructed for *specific conditions*. The principles outlined in this section should suffice as a guide for the construction of diagrams under other different conditions.

References and Further Reading

Baird, C. *Environmental Chemistry*; W. H. Freeman: New York, 1995. Chapters 3, 8.

Bratsch, S. G. "Electronegativity and the Acid-Base Character of Binary Oxides," *J. Chem. Educ.* **1988,** *65,* 877–878.

Bunce, N. J. *Introduction to Environmental Chemistry*; Wuerz Publishing: Winnipeg, 1993. Chapter 11.

Chiriac, V.; Balea, G. "Buffer Index and Buffer Capacity for a Simple Buffer Solution," *J. Chem. Educ.* **1997,** *74,* 937–939.

Eilbeck, W. J.; Mattock, G. *Chemical Processes in Waste Water Treatment*; Ellis Horwood: Chichister, 1987.

Freiser, H. "Enhanced Latimer Potential Diagrams Via Spreadsheets," *J. Chem. Educ.* **1994,** *71,* 786–788.

Friedel, A.; Murray, R. "Using Oxidation State Diagrams to Teach Thermodynamics and Inorganic Chemistry," *J. Chem. Educ.* **1977,** *54,* 485–487.

Frost, A. A. "Oxidation Potentials-Free Energy Diagrams," *J. Am. Chem. Soc.* **1951,** *73*, 2680–2683.

Howard, A. G. *Aquatic Environmental Chemistry*; Oxford Science Publications, Oxford University Press: Oxford, 1998.

HSC Chemistry© 4.0. Outokumpu Research Oy. P.O. Box 60, FIN-28101 Pori, Finland. Fax +358 (2) 626 5310.

Ibanez, J. G.; Silva, A.; Bravo, M. A. "The Effect of Oxide Acidity upon the Heats of Decomposition of Metal Oxysalts," *Ind. Eng. Chem. Res.* **1999,** *38*, 1065–1068.

Kim, C. "Introduction of Aquatic Chemistry in General Chemistry Curriculum: Spreadsheet Calculation Approaches," *J. Chem. Educ.* **2003,** *80*, 1351–1352. JCE Web Ware 2003, http://www.jce.divched.org/JCEDLib/WebWare/collection/reviewed/WW020/index.html

Lewis, A.; Bumpus, J. A.; Truhlar, D. G.; Cramer, C. J. "Molecular Modeling of Environmentally Important Processes: Reduction Potentials," *J. Chem. Educ.* **2004,** *81*, 596–604.

Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 75th ed.; CRC Press: Boca Raton, FL, 1994.

Lin, S. S.; Gurol, M. D. "Catalytic Decomposition of Hydrogen Peroxide on Iron Oxide: Kinetics, Mechanism, and Implications," *Environ. Sci. Technol.* **1998,** *32*, 1417–1423.

Martinez de Ilarduya, J. M.; Villafañe, F. "A Warning for Frost Diagrams Users," *J. Chem. Educ.* **1994,** *71*, 480–482.

Ramette, R. W. *Chemical Equilibrium and Analysis*; Addison-Wesley: Reading, MA, 1981.

Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*, 2nd ed.; W. Freeman: New York, 1994. Chapter 7.

Smith, D. W. "An Acidity Scale for Binary Oxides," *J. Chem. Educ.* **1987**, *64*, 480–481.

Smith, D. W. "Stability Index Diagrams: Pictorial Representations of the Relative Stabilities of Oxidation States for Metallic Elements," *J. Chem. Educ.* **1996,** *73*, 1099–1102.

Stumm, W.; Morgan, J. J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd ed.; Wiley: New York, 1996. Chapter 12.

Summers, D. B. *Chemistry Handbook*, 2nd ed.; Willard Grant Press: Boston, MA, 1975.

Vitz, Ed. "Redox Redux: Recommendations for Improving Textbook and IUPAC Definitions," *J. Chem. Educ.* **2002,** *79*, 397–400.

Wentworth, W. E.; Becker, R. S. *General Chemistry,* 2nd ed.; Houghton-Mifflin: Boston, MA, 1980.

Zumdahl, S. S.; Zumdahl, S. A. *Chemistry*, 5th ed.; Houghton Mifflin: Boston, MA; 2000. Chapter 14.

3

Chemistry Fundamentals, Part B

In this chapter we deal with complexes and complex formation, chemical kinetics, photochemical processes, and radioactivity. Understanding of these subjects is important in many areas of Environmental Chemistry.

3.1 Complexes and Complex Formation

3.1.1 Definition and Generalities

Metal cations in solution are surrounded by *ligands* (i.e., solvent molecules, anions, or non-solvent neutral molecules). The bonding that develops is normally a result of the sharing of one or more pairs of electrons of the ligand with the metal ion, which makes a covalent coordinate bond; thus, the resulting species is called *coordination compound* or *complex.*

3.1.2 Modification of Properties of Metal Ions

Ligands can participate in a complex by sharing one or more pairs of electrons; they can thus be classified as monodentate, bidentate, or polydentate. Examples of monodentate ligands include F^-, Cl^-, Br^-, CN^-, NH_3, H_2O, and OH^-. All of these have atoms that possess a lone pair of electrons. Typical examples of bidentate ligands include ethylenediamine, $NH_2CH_2CH_2NH_2$ that can bind the metal cation through its two nitrogen atoms, and oxalate, $-OOC-COO-$ that uses its two available electron pairs from the charged oxygens for binding. An example of a polydentate ligand is ethylenediaminetetraacetate, $EDTA^{4-}$ $[(-OOC-CH_2)_2N-CH_2-CH_2-N(CH_2-COO-)_2]$ that has six possible coordinating points resulting from its two nitrogens and four of its oxygens.

Complexes can have any kind of charge: positive, negative, or zero as a result of the addition of the individual charges. They are normally written in square brackets. For example,

$$Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ \tag{3.1}$$

$$Fe^{2+} + EDTA^{4-} \rightarrow [Fe\ EDTA]^{2-} \tag{3.2}$$

$$Pt^{2+} + 2NH_3 + 2Cl^- \rightarrow [Pt(NH_3)_2Cl_2] \tag{3.3}$$

Note that the aqueous cations are commonly written without the solvent molecules that accompany them.

Besides the possibility of charge modification, there can be some other consequences of the formation of metal ion complexes including dramatic changes in solubility, color, standard potential, coordination number, geometry, stereochemistry, magnetic susceptibility, and reactivity.

For example, the participation of metal ions in redox reactions usually depends on their standard potentials, which are altered upon complexation. Such a standard potential modification (from E^0_{aq} to $E^0_{complex}$) is due to changes in free energy. The following sequence of equations shows this effect for a solvated metal ion in different oxidation states (M^{m+} and $M^{(m-n)+}$) that reacts with a ligand (L). Here, we assume that the ligand is non-charged and that the different oxidation states form complexes with the same number of ligands. (The sequence for a charged ligand and for different numbers of ligands is essentially the same).

$$M^{m+} + ne^- \rightleftarrows M^{(m-n)+} \qquad \Delta G_1^0 = -nFE_{aq}^0 \tag{3.4}$$

$$M^{m+} + pL \rightleftarrows ML_p^{m+} \qquad \Delta G_2^0 = -RT \ln K_m \tag{3.5}$$

$$M^{(m-n)+} + pL \rightleftarrows ML_p^{(m-n)+} \qquad \Delta G_3^0 = -RT \ln K_{m-n} \tag{3.6}$$

where

$$K_m = [ML_p^{m+}]/([M^{m+}][L]^p) \tag{3.7}$$

and

$$K_{m-n} = [ML_p^{(m-n)+}]/([M^{(m-n)+}][L]^p) \tag{3.8}$$

are the formation constants of ML_p^{m+} and $ML_p^{(m-n)+}$, respectively.

If we add eq. 3.6 to eq. 3.4 and subtract eq. 3.5, we obtain

$$ML_p^{m+} + ne^- \rightleftarrows ML_p^{(m-n)+} \tag{3.9a}$$

$$\Delta G_4^0 = -nFE_{aq}^0 + RT \ln [K_m/K_{m-n}] \tag{3.9b}$$

Now, if we divide ΔG_4^0 by $-nF$, we get

$$(\Delta G_4^0/-nF) = E_{complex}^0 = E_{aq}^0 - (RT/nF) \ln [K_m/K_{m-n}] \tag{3.10}$$

which shows that the standard potential of the metal ion is modified by a term that involves the natural log of the ratio of the equilibrium constants. If the equilibrium constant of the complex that contains the metal ion in the higher oxidation state is larger than that of the lower oxidation state, the standard potential will shift toward a more negative value, whereas the opposite is true if the lower oxidation state is more stable (i.e., has a larger complex formation constant). The former case is more common, because a highly positively charged metal ion in aqueous solution will become more stable upon complexation with an electron-donating ligand. See Example 3.1. Some exceptions are those cases in which a back donation of electron density from the metal to the ligand occurs.

From the example just discussed, it is clear that complexation can have a dramatic effect upon some of the redox and non-redox properties of a given metal ion system. Changing solution conditions and concentrations may shift the different equilibria from spontaneity to non-spontaneity, and vice versa. See Example 3.2.

Another consequence of complex formation is the possibility of having alternate reaction mechanisms. For example, Cu^+ is normally unstable in aqueous solutions. (In fact, it does not even

Example 3.1 Estimate the $E_{complex}^0$ for the system with $Fe^{2+/3+}$ as the metal ions and $EDTA^{4-}$ as the ligand. Take the approximate log values of the complex formation constants as 14 and 25 for the $EDTA^{4-}$ complexes of Fe^{2+} and Fe^{3+}, respectively. The E_{aq}^0 can be found in any table of standard potentials.

Answer

The reactions involved are

$$Fe^{3+} + e^- \rightleftarrows Fe^{2+} \qquad \Delta G_1^0 = -nFE_{aq}^0$$

$$Fe^{3+} + EDTA^{4-} \rightleftarrows [FeEDTA]^- \qquad \Delta G_2^0 = -RT \ln K_m$$

$$Fe^{2+} + EDTA^{4-} \rightleftarrows [FeEDTA]^{2-} \qquad \Delta G_3^0 = -RT \ln K_{m-n}$$

$$[FeEDTA]^- + e^- \rightleftarrows [FeEDTA]^{2-} \qquad \Delta G_4^0 = -nFE_{complex}^0$$

Applying eq. 3.9b,

$$\begin{aligned}\Delta G_4^0 &= -nFE_{aq}^0 + RT \ln [K_m/K_{m-n}]\\ &= -nFE_{aq}^0 + RT \ln [10^{25}/10^{14}]\\ &= -nFE_{complex}^0\end{aligned}$$

If both sides are now divided by $-nF$, and we assume room temperature, with $E_{aq}^0 = 0.77\ V$ we obtain

$$\begin{aligned}&\Delta G_4^0/(-nF)\\ &= E_{complex}^0 = E_{aq}^0 + (RT/-nF) \ln [10^{25}/10^{14}]\\ &= 0.77 - (0.06/1) \log 10^{11} = 0.11\ \text{V}\end{aligned}$$

Example 3.2 In oxic waters, Mn^{2+} is normally oxidized to $MnO_{2(s)}$. Under certain circumstances, Mn^{3+} is also produced. In order to better understand manganese cycling at the oxic/anoxic interface, thermodynamics offers its predictive power. From this point of view, and assuming standard conditions and concentrations,

(a) Estimate the value of the equilibrium constant (under standard conditions) for the disproportionation of Mn^{3+} into $Mn^{2+} + MnO_{2(s)}$. Is this reaction spontaneous?

(b) EDTA is known to form Mn(III) and Mn(II) complexes. The following data have been reported:

$$Mn^{3+} + EDTA^{4-} \rightleftarrows [Mn(III)EDTA]^{-} \qquad K_1 = 7.1 \times 10^{24}$$

$$Mn^{2+} + EDTA^{4-} \rightleftarrows [Mn(II)EDTA]^{2-} \qquad K_2 = 1.1 \times 10^{14}$$

Estimate E^0 for the reaction

$$[Mn(III)EDTA]^{-} + e^{-} \rightleftarrows [Mn(II)EDTA]^{2-}$$

(c) Calculate the value of K for the disproportionation of $[Mn(III)EDTA]^{-}$ into $[Mn(II)EDTA]^{2-} + MnO_2$. Is this reaction spontaneous?

Note: to solve this problem, you may use additional E^0 data from the Mn Frost diagram (see Example 2.12).

Answer

(a) The equation

$$Mn^{3+} \rightleftarrows Mn^{2+} + MnO_2$$

must first be balanced. To do this, we adjust the number of manganese species on both sides; then we add water to the left side to balance the oxygens from MnO_2. After that, we add H^+ on the right side to balance the hydrogens from water as well as the excess positive charges of the left side, and we get the balanced equation

$$2Mn^{3+} + 2H_2O_{(l)} \rightleftarrows Mn^{2+} + MnO_{2(s)} + 4H^{+}$$

Next, we must find ΔG to know whether this disproportionation is spontaneous or not. To this end, we need to write both half reactions and their ΔG^0 values (equal to $-nFE^0$) separately:

Half reaction	ΔG^0
$Mn^{3+} + e^{-} \rightleftarrows Mn^{2+}$	$-nF(1.51)$
$MnO_{2(s)} + 4H^{+} + e^{-} \rightleftarrows Mn^{3+} + 2H_2O_{(l)}$	$-nF(0.91)$

We then invert the second reaction, add it to the first one, and get the desired equation and its ΔG^0:

$$2Mn^{3+} + 2H_2O_{(l)} \rightleftarrows Mn^{2+} + MnO_{2(s)} + 4H^{+}$$

$$\Delta G^0 = -F(1.51) + F(0.91) = -F(0.60)$$

This value is equal to $-RT \ln K$, and thus

$$-RT \ln K = -F(0.60)$$

$$(RT \ln K)/F = 0.60$$

As discussed earlier, at room temperature this becomes:

$0.06 \log K = 0.60$, and thus $K = 10^{10}$. (Note: the exact value depends on the MnO_2 phase). In any case, such a K value means that the Mn^{3+} disproportionation into $Mn^{2+} + MnO_2$ *is spontaneous*, as can also be predicted from its Frost diagram and from the ΔG^0. (The fact that Mn^{3+} can be produced in oxic waters is probably due to kinetic rather than thermodynamic stability).

(b) To estimate E^0_{complex} for the reaction: $[Mn(III)EDTA]^{-} + e^{-} \rightleftarrows [Mn(II)EDTA]^{2-}$, we use equation 3.9b:

$$E^0_{\text{complex}} = E^0_{\text{aq}} - (RT/nF) \ln [K_m/K_{m-n}]$$

At room temperature,

$$E^0_{\text{complex}} = 1.51 - [(0.06/1) \log [7.1 \times 10^{24}/1.1 \times 10^{14}] = +0.86\,\text{V}$$

(This is a good estimate. The literature value is +0.824 V).

Example 3.2 (*Cont.*)

(c) The equation must first be balanced. Because $[\mathrm{Mn(III)EDTA}]^- \rightleftarrows [\mathrm{Mn(II)EDTA}]^{2-} + \mathrm{MnO}_{2(s)}$ is unbalanced, we first adjust the number of manganese species on both sides, i.e., $2\,[\mathrm{Mn(III)EDTA}]^- \rightleftarrows [\mathrm{Mn(II)EDTA}]^{2-} + \mathrm{MnO}_{2(s)}$.
Then we add another EDTA to the right side and water to the left side to balance the oxygens from MnO_2. After that, we add enough H^+ on the right side to balance the hydrogens from water as well as the excess positive charges of the left side, and we get the balanced equation

$$2[\mathrm{Mn(III)EDTA}]^- + 2H_2O_{(l)} \rightleftarrows [\mathrm{Mn(II)EDTA}]^{2-} + \mathrm{MnO}_{2(s)} + \mathrm{EDTA}^{4-} + 4H^+$$

Next, we must find ΔG^0 to know whether this disproportionation is spontaneous or not. To this end, we note that one can obtain this reaction by subtracting twice the $[\mathrm{Mn(III)EDTA}]^-$ formation equation from the Mn^{3+} disproportionation reaction:

$$\begin{array}{l} 2\mathrm{Mn}^{3+} + 2H_2O_{(l)} \rightleftarrows \mathrm{Mn}^{2+} + \mathrm{MnO}_{2(s)} + 4H^+ \\ -2(\mathrm{Mn}^{3+} + \mathrm{EDTA}^{4-} \rightleftarrows [\mathrm{Mn(III)EDTA}]^-) \\ \hline 2[\mathrm{Mn(III)EDTA}]^- + 2H_2O_{(l)} \rightleftarrows \mathrm{Mn}^{2+} + \mathrm{MnO}_{2(s)} + 2\mathrm{EDTA}^{4-} + 4H^+ \end{array}$$

After that, the $[\mathrm{Mn(II)EDTA}]^{2-}$ formation reaction is added to this, and one gets the desired complex disproportionation:

$$2[\mathrm{Mn(III)EDTA}]^- + 2H_2O_{(l)} \rightleftarrows [\mathrm{Mn(II)EDTA}]^{2-} + \mathrm{MnO}_{2(s)} + \mathrm{EDTA}^{4-} + 4H^+$$

Then, $\Delta G^0_{\mathrm{cd}} = \Delta G^0_{\mathrm{d}} - 2\Delta G^0_{\mathrm{cf,h}} + \Delta G^0_{\mathrm{cf,l}}$

where ΔG^0_{cd} is the free energy change for the Mn (III) complex disproportionation, ΔG^0_{d} is for the Mn(III) disproportionation, $\Delta G^0_{\mathrm{cf,h}}$ is for the Mn(III) complex formation, and $\Delta G^0_{\mathrm{cf,l}}$ is for the Mn(II) complex formation. (The subscripts *h* and *l* are for the *higher* and *lower* oxidation state, respectively).
Substituting, one gets

$$\Delta G_{\mathrm{cd}} = -RT \ln 10^{10} - 2(-RT \ln 7.1 \times 10^{24}) - RT \ln (1.1 \times 10^{14})$$

$$\Delta G_{\mathrm{cd}} = -RT \ln[10^{10} \times 1.1 \times 10^{14}/(7.1 \times 10^{24})^2] = -RT \ln(2.18 \times 10^{-26})$$

From here, *K* for the complex disproportionation is 2.18×10^{-26}. Because this is smaller than unity, it is clear that the disproportionation of the Mn(III) complex is not thermodynamically feasible under standard conditions, contrary to the disproportionation of the aqueous Mn(III) species that was exemplified in (a).

appear in the Cu Pourbaix diagram!). However, the electrochemical reduction of Cu^{2+} ions in the presence of Cl^- involves a Cu^+ intermediate due to the stabilization of this Cu^+ in the presence of this ligand. With respect to complex formula writing, the following order is normally used:

external cation [internal cation/neutral ligands/ anionic ligands] anion

For example, $[\mathrm{Ag(NH_3)_2}]\mathrm{NO_3}$, $\mathrm{Na_2[Fe(II)\ EDTA]}$, $[\mathrm{Pt(NH_3)_2Cl_2}]$, and $[\mathrm{Co(III)}en_2\mathrm{Cl_2}]\mathrm{ClO_4}$ (here, *en* = ethylenediamine). To write the names, the order is: external cation, neutral ligands, anionic ligands, internal cation (with its oxidation state in parenthesis–unless obvious), and anion. General Chemistry and Inorganic Chemistry books can be consulted for a more thorough discussion and examples.

3.1.3 Geometry of Metal Complexes

The number of ligands that surround the metal cation is called its *coordination number*. This number can normally be correlated with the geometry of the complex. The most common number is 6, but this is by no means an absolute rule. Some examples are given in Table 3.1 and in Examples 3.3 and 3.4.

TABLE 3.1. Geometries of common metal complexes.

Coordination no.	Geometry of the complex	Examples
2	Linear	$[Ag(NH_3)_2]^+$
3	Planar	$[HgI_3]^-$
	Pyramidal	$[SnCl_3]^-$
4	Tetrahedral	$[AlCl_4]^-$
	Square planar	$[PtCl_4]^{2-}$
5	Trigonal bipyramid*	$[Ni(CN)_5]^{3-}$
	Square pyramid*	$[Ni(CN)_5]^{3-}$
6	Octahedral	$[Fe(H_2O)_6]^{2+}$
7,8,9	Geometries vary, although such complexes are less common.	Various

*Note: this complex can alternate between both geometries depending on its energy content.

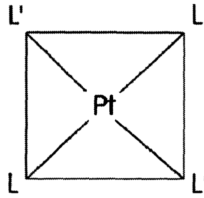
3.1.4 Inner and Outer Sphere Complexes

When metal cations are placed in aqueous solutions two kinds of *spheres* normally appear: (a) a sphere of water molecules that binds directly to the metal, called *inner coordination sphere* (or simply, *inner sphere*), and (b) a more loosely bound group of water molecules (not directly bound to the metal), called *outer coordination sphere* (or simply, *outer sphere*). In this way, a cationic complex can have an outer sphere interaction with an ionic ligand or a solvent molecule without displacing the inner ligands directly bonded to the metal. At higher anion concentrations, the outer sphere complex $[M(H_2O)_6]^{n+}A^{n-}$ is more prevalent than its corresponding inner sphere complex, $[M(H_2O)_5A]$. Interestingly, the number of inner-sphere water molecules surrounding a metal cation is normally the same as the number of donor atoms in its complexes in the solid state. The most common number of waters in the inner coordination sphere is six, whereas the number of waters in

Example 3.3 A given complex, $ML_2L'_2$ (where L and L′ are different ligands) has two possible geometrical isomers, *cis* and *trans*. What is its geometry?

Answer

It must be square planar. In tetrahedral complexes there cannot exist geometrical isomers, because all four positions are equivalent. See the figure:

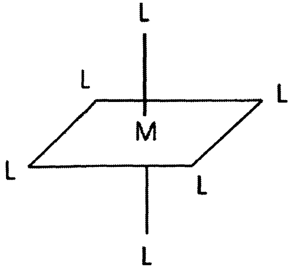


Example 3.4 Draw or build a model for a complex in the octahedral geometry.

(a) Are all six positions equivalent?

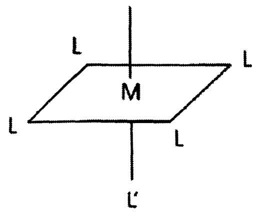
(b) Can the complex $[ML_4L'_2]$ have geometrical (*cis–trans*) isomers?

Answer

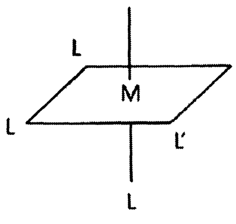


(a) Yes, all six positions are equivalent.

(b) Yes, it can have geometrical isomers because the following two structures are not equivalent:



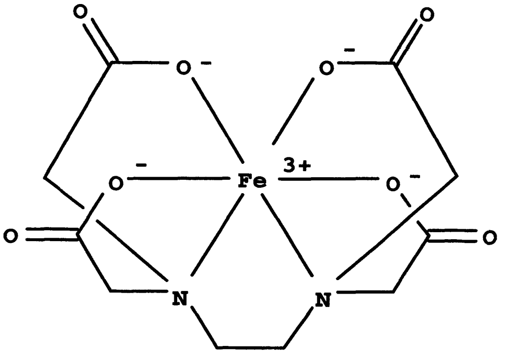
***trans*-isomer**



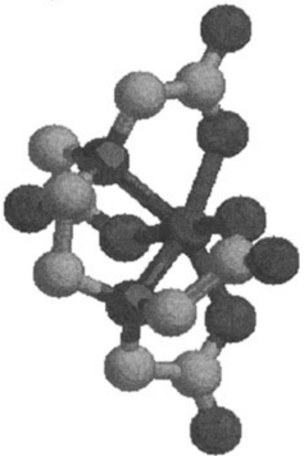
***cis*-isomer**

Example 3.5 Find the structure of $EDTA^{4-}$ and draw a satisfactory representation of its octahedral complex with Fe^{3+}.

Answer



Or in a 3-D view,



the outer coordination sphere ranges from three to twenty-two.

Water is an excellent binding molecule because it can act as a Lewis base by coordinating to a metal cation, and as a Lewis acid by coordinating to a given anion through its hydrogen atoms.

3.1.5 Mono and Polydentate ligands. The HSAB Approach

Small metal ions (acids, from the Lewis perspective) with a high positive charge are said to be *hard* in the sense that they can easily polarize anions to form covalent bonds; large metal ions with a small charge are said to be *soft*. Some metal ions are intermediate between these two extremes. In the same manner, donor atoms in ligands (bases, from the Lewis perspective) can be classified as hard or soft, depending on whether they have a large or small charge density, respectively.

A very important finding is that hard cations (e.g., Be^{2+}, Al^{3+}, Ti^{4+}) prefer ligands with hard donor atoms (e.g., F, O, Cl), and soft cations (e.g., Ag^{+}, Cd^{2+}, Tl^{+}) prefer ligands with soft donor atoms (e.g., I, Te, As). This fact has a myriad of applications, because it can be advantageously used for analysis, selective reactions, metal ion separation, removal, recovery, etc. It is an application of the Hard Soft Acid Base (HSAB) principle enunciated by Pearson at the end of the 1960s.

3.1.6 The Chelate Effect

Ligands that use more than one pair of electrons to form a complex are called *chelating agents*, and the resulting complexes are called *chelates*. This is due to the observation that they form closed rings with the central metal ions, resembling the trapping of an object by a crab's claws (crab in Greek is χελη). Interestingly, chelates are usually much more stable than their corresponding monodentate complexes. This is called the *chelate effect*. For example, when nickel forms the ammonia monodentate complex in aqueous solution, its stability constant is relatively large:

$$Ni^{2+}_{(aq)} + 6NH_{3(aq)} \rightleftarrows [Ni(NH_3)_6]^{2+}_{(aq)} \quad \beta_6^{NH_3} = 10^{8.6} \tag{3.11}$$

(Note that all the physical states are specified here for the sake of clarity of the demonstration that follows). However, when it forms the ethylenediamine complex, its stability increases considerably, as shown by the corresponding constant:

$$Ni^{2+}_{(aq)} + 3C_2H_8N_{2(aq)} \rightleftarrows [Ni(en)_3]^{2+}_{(aq)} \quad \beta_3^{en} = 10^{18.3} \tag{3.12}$$

Even though the origin of this effect and the comparison of constants with different units (i.e., $\beta_6^{NH_3}$ and β_3^{en}) has caused controversy, the chelate effect can be an entropic effect due to the increase in the number of dissolved species produced upon

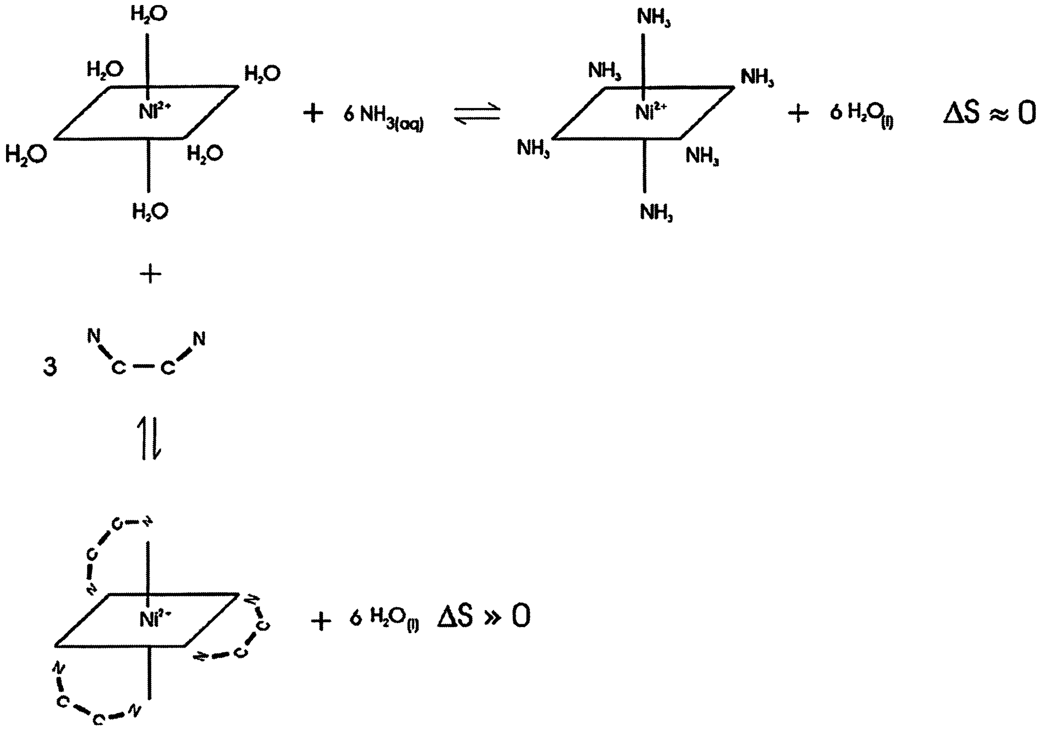


FIGURE 3.1. The chelate effect.

chelation. A simplified explanation is given in Figure 3.1 by noting the changes in values of the thermodynamic parameters ΔG^0, ΔH^0, and ΔS^0 for reactions 3.11 and 3.12.

Because the values of ΔH^0 for both reactions are the result of the breaking and forming of the same number and type of bonds (i.e., six Ni–O bonds are broken, and six Ni–N bonds are formed in both reactions), they are essentially equal. One can then visualize from $\Delta G^0 = \Delta H^0 - T\Delta S^0$ that for the same temperature, the value of ΔS^0 determines the value of ΔG^0.

Because $\Delta G^0 = -RT \ln K$, then one can predict that $\beta_3^{en} > \beta_6^{NH_3}$, which is actually the case as demonstrated by the values of the equilibrium constants given above. In essence, the chelate effect is then an entropic effect. A simplified equation has been proposed for obtaining a first approximation to the formation constant of a chelate, by using the formation constant of the complex with the corresponding monodentate ligand as follows:

$$\log \beta_m(\text{chelate}) = \log \beta_n(\text{monodentate}) + (n-1)\log 55.5 \quad (3.13)$$

where m and n represent the number of incoming ligands in the chelate and the monodentate cases, respectively (see Example 3.6).

Example 3.6 In the example just discussed, β_m is the formation constant of the ethylenediamine complex (to be estimated), β_n is the global formation constant for the ammonia complex (as discussed in Section 2.1.2), and n = number of ammonia ligands = 6. Obtain β_m.

Answer

$$\begin{aligned}\log \beta_m &= \log 10^{8.6} + (6-1)\log 55.5\\ &= 17.3, \text{ and } \beta_m = 10^{17.3}\end{aligned}$$

This is a reasonable approximation to the experimental value of $10^{18.3}$.

3.1.7 Reactions of Complexes

These can be classified as *ligand-exchange* and *electron-exchange* reactions.

3.1.7.1 Ligand-Exchange or Ligand Substitution Reactions

When an arriving ligand replaces an existing ligand in the inner sphere of a complex, three mechanisms can occur:

a. *Associative mechanism* (also called A). The arriving ligand reacts directly with the central metal ion, forming an intermediate with a higher coordination number than the original complex. In a second step, one of the original ligands leaves the complex:

$$[ML_6] + A \rightleftarrows [ML_6A] \qquad (3.14)$$

$$[ML_6A] \rightarrow [ML_5A] + L \qquad (3.15)$$

(Although the A-type mechanism is akin to the bimolecular nucleophilic substitutions (S_N2) encountered in organic chemistry, this terminology is not used in inorganic mechanisms).

b. *Dissociative mechanism* (also called D). The complex loses one of the original ligands, producing an intermediate with a lower coordination number, and another ligand arrives and takes its place. This D-type mechanism can be exemplified by the sequence:

$$[ML_6] \rightleftarrows [ML_5] + L \qquad (3.16a)$$

$$[ML_5] + A \rightarrow [ML_5A] \qquad (3.16b)$$

c. *Interchange mechanism* (also called I). In most inorganic substitution reactions, the bond cleavage between the metal atom and the leaving group (L), and bond formation involving an incoming ligand (A) are thought to take place concurrently. In other words, the leaving and entering ligands exchange in one step by forming a "transition state" or "activated complex" (but not an intermediate with different coordination numbers). The following reaction illustrates the I-type mechanism:

$$[ML_6] + A \rightarrow [L\text{- - -}ML_5\text{- - -}A] \rightarrow [ML_5A] + L \qquad (3.17)$$

Two kinds of interchange mechanisms are suggested: a) *dissociative interchange*, I_d where bond cleavage dominates over bond formation, and b) *associative interchange*, I_a in which bond formation plays a dominant role.

It is noteworthy that the rates for these reactions are typical for a given metal ion, more or less independently of the ligands exchanged. In general, those metal ions that favor the formation of strongly covalent bonds (frequently the small ions) undergo exchange reactions more slowly than those that form more ionic bonds (large ions). Martell and Hancock have enunciated three very useful rules to determine whether a metal ion will undergo fast or slow ligand exchange reactions:

1. For constant metal ion charge and for the same ligand, rates increase with metal ion size.
2. For constant metal ion size, rates increase with decreasing cation charge. For example, Co^{2+} undergoes ligand-exchange reactions much faster than Co^{3+}.
3. The more stable the electron arrangement (i.e., higher *Ligand Field Stabilization Energy*, LFSE), the slower the rates. For example, Co^{3+} exhibits much lower ligand-exchange rates than Mn^{3+} due to its high LFSE.

At high pH values some *anionic ligands* like $EDTA^{4-}$ and NTA^{3-} compete with hydroxyl and carbonate ions (usually present in water due to the dissolution of CO_2 from the air) for the metal ions existing in solution. On the other hand, at low pH it is *the metals and the protons* that compete for the ligand.

Stability constants are not always the best predictive tool for measuring the ease and the extent of chemical reactions involving complexes nor their stability with time, because their *kinetic* behavior can often be even more crucial. For example, when ligand exchange reactions of ML (e.g., [FeEDTA]) with other metal ions (e.g., Zn^{2+} or Ca^{2+}) are kinetically slow, they do not significantly influence ligand speciation. Another typical example of the *thermodynamics vs kinetics* competition is the fact that the degradability of some metal complexes (e.g., metal–NTA) is related to their kinetic lability, rather than to their thermodynamic stability constants. Kinetic rather than thermodynamic data are then used to classify metal complexes as *labile*, *quasi-labile*, *slowly labile*, and *inert* (or *stable*). See Section 3.2.6.

There are catalysts for specific metal complex reactions. For example, the formation of

[Cr(III)EDTA] is known to be catalyzed by the carbonate/bicarbonate system.

Ligand–ligand competition involving two ligands contending for the same metal ion is used to determine the stability constants of the complexes involved. Another example of the application of ligand–ligand competition phenomena is the technique of *ligand-exchange chromatography*, where metal ion competition for the same ligand is used for the quantitation of the ligand. For example, in the reaction

$$[\mathrm{M(III)EDTA}] + \mathrm{Fe(III)} \rightleftarrows [\mathrm{Fe(III)EDTA}] + \mathrm{M} \qquad (3.18)$$

where M is a metal ion different from iron, the [Fe(III)EDTA] is analyzed after the exchange (for example, with a UV detector). A similar concept is used to examine a variety of metal–EDTA chelates, whereby they are transformed into another complex (e.g., [CuEDTA] or [LuEDTA]) that can be more easily monitored.

3.1.7.2 Electron-Exchange Reactions

Many metal complexes can undergo electron transfer reactions with other complexes, with oxidation–reduction agents, or with electrified surfaces (electrodes). If such a transfer does not produce net chemical change, it is called *electron exchange.* Again, the criterion for thermodynamic spontaneity is the change in the Gibbs free energy (ΔG).

Electron transfer reactions with other metal complexes can occur by two mechanisms:

a. *Outer-sphere* mechanism. Both complexes retain their coordination spheres, and the transferred electron (or electrons) passes through both. An example is

$$[\mathrm{Fe(H_2O)_6}]^{2+} + [\mathrm{Mn(H_2O)_6}]^{3+} \rightleftarrows [\mathrm{Fe(H_2O)_6}]^{3+} + [\mathrm{Mn(H_2O)_6}]^{2+} \qquad (3.19)$$

b. *Inner-sphere* mechanism (also called *ligand-bridged* mechanism). The complexes involved form at least one "bridge" with a ligand between them, and an electron passes through it. A typical example is $[\mathrm{Co(II)EDTA}]^{2-}$, which is rapidly oxidized by $[\mathrm{Fe(CN)_6}]^{3-}$ (as well as by naturally occurring manganese oxides):

$$[\mathrm{Co(EDTA)}]^{2-} + [\mathrm{Fe(CN)_6}]^{3-} \rightleftarrows [\mathrm{Co(EDTA)}]^{-} + [\mathrm{Fe(CN)_6}]^{4-} \qquad (3.20)$$

Metal complexes can be oxidized or reduced at the inner metal cation and/or at the ligand by other compounds or by electron transfer at an electrode. Conditions can be set as to selectively perform the redox reaction affecting either or both parts of the complex. In the above reaction, $[\mathrm{Fe(CN)_6}]^{3-}$ oxidizes Co(II) to Co(III); on the other hand, $\mathrm{PbO_2}$ is known to selectively oxidize EDTA in this [Co(II)EDTA] complex. Another example is the remediation of effluents containing $\mathrm{Cu(CN)_2}$, which has been accomplished electrochemically by removing $\mathrm{Cu^{2+}}$ and $\mathrm{CN^-}$ simultaneously, with reduction of the former to its elemental form and oxidation of the latter to cyanate (see Section 10.1.4).

3.2 Chemical Kinetics

The study of *how* and *how fast* chemical reactions occur is the purpose of chemical kinetics.

The *rate* of a reaction can be defined as the variation of the concentration of a reactant or product in a constant-volume (i.e., batch or intermittent) system. This rate is directly proportional to the number of collisions (*collision frequency*) among reacting atoms or molecules per unit time, according to the *collision theory*:

$$\text{Rate} \propto \frac{\text{Collision frequency}}{\text{time}} \qquad (3.21)$$

For example, in the simple mono-directional reaction

$$\text{A (Reactant)} \rightarrow \text{B (Product)} \qquad (3.22)$$

the rate of disappearance of A to form B is normally directly proportional to the concentration of A, as follows:

$$\text{Rate} \propto [\mathrm{A}] \qquad (3.23)$$

and

$$\text{Rate} = k[\mathrm{A}] \qquad (3.24)$$

where the square brackets indicate the molar concentration of A, in mol $\mathrm{L^{-1}}$, and k is the *rate constant* (defined below). The average rate of disappearance of A is then defined as the change in concentration of A, $\Delta[\mathrm{A}]$ (where $\Delta[\mathrm{A}]$ is the final concentration of A, $[\mathrm{A}]_f$ minus the initial concentration of A, $[\mathrm{A}]_0$) with a change in time, Δt (Δt = final time, t_f minus the initial time, t_0).

This means that

$$\text{Rate} = -\frac{[\mathrm{A}]_f - [\mathrm{A}]_0}{t_f - t_0} = -\frac{\Delta[\mathrm{A}]}{\Delta t} \qquad (3.25)$$

If infinitesimal increments are taken, then

$$\text{Rate} = -\frac{d[\text{A}]}{dt} \tag{3.26}$$

For practical purposes, the initial time, t_0, is taken as the zero time (i.e., the reaction start time). Therefore, $\Delta t = t_f - t_0 = t_f - 0 = t_f$, or simply t. Thus, we can rewrite eq. 3.25 as

$$\text{Rate} = -\frac{[\text{A}]_f - [\text{A}]_0}{t} \tag{3.27}$$

In this expression, the rate has a negative sign because [A] decreases as the reaction proceeds and the overall result is positive, which avoids having to deal with negative rates.

We can expand this approach by using the general stoichiometric equation

$$a\text{A} + b\text{B} + \cdots \rightarrow g\text{G} + h\text{H} + \cdots \tag{3.28}$$

where the rate of this reaction can be expressed as:

$$\frac{1}{a}\left(-\frac{d[\text{A}]}{dt}\right) = \frac{1}{b}\left(-\frac{d[\text{B}]}{dt}\right) = \frac{1}{g}\left(\frac{d[G]}{dt}\right) = \frac{1}{h}\left(\frac{d[\text{H}]}{dt}\right) \tag{3.29}$$

For example, if we are studying the decomposition reaction:

$$2\text{HI}_{(g)} = \text{H}_{2(g)} + \text{I}_{2(g)} \tag{3.30}$$

at constant volume and measure the rate of change of the I_2 concentration to be $1.5 \times 10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}$, then that *is* the rate of the reaction. From the stoichiometry we can see that also

$$\frac{d[\text{H}_2]}{dt} = 1.5 \times 10^{-2}\ \text{mol L}^{-1}\ \text{s}^{-1} \tag{3.31}$$

and that

$$\frac{d[\text{HI}]}{dt} = -3 \times 10^{-5}\ \text{mol L}^{-1}\ \text{s}^{-1} \tag{3.32}$$

We can avoid these conversion factors that relate the different rate expressions, by defining the rate in terms of an *equivalent concentration* instead of the *molar concentration*. If X is the number of equivalents per liter that reacted in a time t, then dX/dt is a convenient expression of the reaction rate. However, the definition of equivalent must be made explicit.

Besides concentration, other variables can be used to define/measure a reaction rate such as pressure (as in a gas-phase reaction), or absorbance (as in a colored reaction), or pH change (as in an acid–base reaction), etc. Many variables are related to concentration in a linear way.

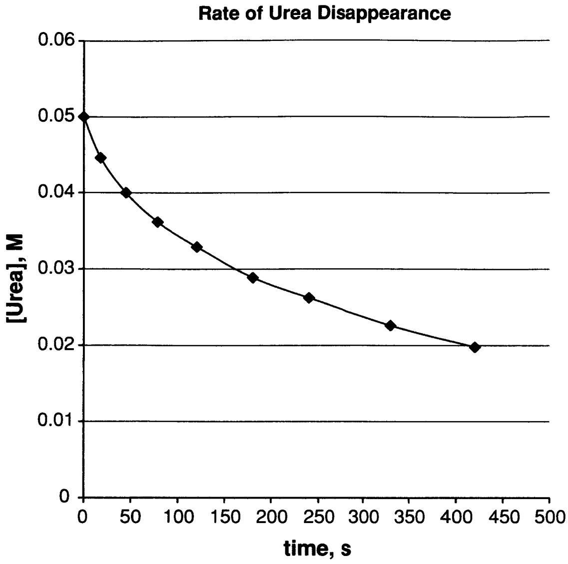


FIGURE 3.2. Concentration of urea as a function of time.

If the concentration of a reactant or a product is graphically represented as a function of the reaction time, then the reaction rate at any given time is numerically equal to the slope of the curve at that instant of time. For example, for the reaction of urea with 1-pentanol:

$$\text{NH}_2\text{CONH}_2 + \text{C}_5\text{H}_{11}\text{OH} \rightarrow \text{NH}_2\text{COOC}_5\text{H}_{11} + \text{NH}_3 \tag{3.33}$$

the rate of urea *disappearance* is shown in Figure 3.2.

Here, the slope of the exponential curve is given by

$$\text{slope} = d[\text{NH}_2\text{CONH}_2]/dt \tag{3.34}$$

and its value at different times can be calculated from Figure 3.2 as follows:

(a) At $t = 0$ s,

$$[(4.46 - 5) \times 10^{-2}]/(18 - 0) = -3.00 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

(b) At $t = 420$ s,

$$[(1.98 - 2.26) \times 10^{-2}]/(420 - 330) = -0.311 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

and the reaction rates under these conditions are 3.00×10^{-4} (at $t = 0$) and 0.311×10^{-4} (at $t = 420$ s), in mol L^{-1} s^{-1}.

3.2.1 Factors That Influence the Rate of a Mono Directional Reaction

The rate of a reaction depends in the first place on the properties of the reactant species (molecules, ions, radicals). Typically, it also depends on:

1. The concentration of the reactants.
2. The reaction temperature.

Therefore, in order to understand why molecules react at an observed rate, it is necessary to express the rate as a function of magnitudes that are independent of temperature and concentration.

The rate of a reaction can also be influenced by other factors such as

3. Presence of catalysts or inhibitors.
4. Concentration of products.
5. Visible or UV light irradiation.
6. Ionizing radiation such as α, β, or γ rays.

3.2.1.1 Dependence of the Rate of Reaction on Concentrations: The Rate Law

The *rate law* of a reaction is generally dependent on the concentration of the reactants. At a given temperature, the rate law for a chemical reaction can be expressed as:

$$\text{rate} = k[A]^{\alpha}[B]^{\beta} \tag{3.35}$$

where A and B are the reactants, α and β are numerical constants, and k is a constant known as the rate constant (see below). The α and β constants are obtained from experimental data and are not necessarily related to the stoichiometric coefficients (except in elementary reactions). The sum of $\alpha + \beta$ is known as the *global* or *total reaction order*. Thus, if $\alpha + \beta = 2$ this reaction is called a *second-order* reaction. If $\alpha = 1$ and $\beta = 1$, the reaction is said to be first order with respect to A and first order with respect to B. The coefficients α and β are not necessarily integers.

If we consider the following reaction that occurs very fast at room temperature and atmospheric pressure

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)} \tag{3.36}$$

the corresponding experimental rate law is given by

$$-\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = k[NO]^2[O_2] \tag{3.37}$$

and the reaction is of *third order* (as could be expected if it were based on the values of the stoichiometric coefficients).

However, the decomposition reaction of potassium hypochlorite in aqueous solution is

$$3KClO \rightarrow KClO_3 + 2KCl \tag{3.38}$$

and has the following rate law

$$\frac{d[KClO_3]}{dt} = k[KClO]^2 \tag{3.39}$$

which shows that this is a *second-order* reaction, while stoichiometrically, *third order* could be expected.

It is important to realize that for some reactions it is not possible to speak of a reaction order. In many cases, the relationship between the rate of a reaction and the concentrations involved is much more complex than that of eq. 3.37 or 3.39. Frequently, the concentrations appear on the denominator of the rate law. A complex rate law equation results from the fact that the reaction occurs by means of a complicated reaction mechanism. For example, the reaction:

$$H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)} \tag{3.40}$$

has the rate law

$$\frac{1}{2}\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + k'\dfrac{[HBr]}{[Br_2]}} \tag{3.41}$$

which indicates that this reaction does not occur by a simple collision of a hydrogen molecule with a bromine molecule. Instead, it takes place through five different reactions:

$$Br_2 + M \text{ (any other molecule)} \rightarrow 2Br + M \tag{3.42}$$

$$Br + H_2 \rightarrow HBr + H \tag{3.43}$$

$$H + Br_2 \rightarrow HBr + Br \tag{3.44}$$

$$H + HBr \rightarrow H_2 + Br \tag{3.45}$$

$$2Br + M \rightarrow Br_2 + M \tag{3.46}$$

Altogether, the reactions 3.42 through 3.46 are known as the *reaction mechanism*, whereas each one is called an *elementary* reaction. The reaction between hydrogen and bromine is then a complex reaction because more than one elemental reaction is involved.

An elementary reaction is then a reaction that occurs exactly as written. For example, if we state that the reaction:

$$OH^- + CH_3Br \rightarrow CH_3OH + Br^- \tag{3.47}$$

is an elementary reaction, then it means that an OH^- ion collides with a molecule of methyl bromide, producing a *short-lived intermediate* called an *activated complex* (or *transition state*). This transition species is formed as a result of the collision of reactant molecules before they are converted into the product(s) (in this case, a methanol molecule and a bromide ion).

Many gas-phase reactions involving atoms and free radicals are elementary. Two examples are

$$H_{(g)} + C_2H_{6(g)} \rightarrow C_2H_{5(g)} + H_{2(g)} \tag{3.48}$$

and

$$NO_{2(g)} + NO_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)} + NO_{(g)} \tag{3.49}$$

Elementary reactions are sometimes classified according to their *molecularity*, that is, the number of reactant molecules participating in the chemical change. For instance, the rearrangement of CH_3NC to CH_3CN is *unimolecular*, whereas the reaction between H and C_2H_6 is *bimolecular*. Thus, the *molecularity* of a reaction and its *reaction order* are two different things, although in some cases they may have the same numerical value. (The rate law of a non-elementary reaction can only be obtained experimentally).

3.2.1.2 The Rate Constant

We know from experience that the rate of a chemical reaction also depends on temperature. This dependence is expressed by what is called the *Arrhenius equation*:

$$k = Ze^{-E_a/RT} \tag{3.50}$$

were k is the rate constant, E_a is the activation energy (measured in kJ/mol), R is the gas constant (0.0821 L atm/mol K), T is the temperature in the Kelvin scale (absolute temperature), and Z is the *frequency factor* that represents the collision frequency. The Arrhenius equation can be expressed in a simpler form by taking the natural logarithm of both sides:

$$\begin{aligned}\ln k = \ln Ze^{-E_a/RT} &= \ln Z + \ln (e^{-E_a/RT}) \\ &= \ln Z - \frac{E_a}{RT} \end{aligned} \tag{3.51}$$

The activation energy is defined as the minimum energy required to initiate a chemical reaction. The higher the activation energy, the higher the barrier that prevents less energetic molecules from colliding and forming the activated complex mentioned above, resulting in a slow conversion to products.

3.2.2 Integrated rate equations

In chemical kinetics, typical experimental data consist of the concentration of the species present at different times. Such data can then be fitted to the appropriate rate law that is usually expressed in differential form. Very often it is more convenient to use rate laws in the integrated form, as illustrated below for different reaction orders.

3.2.2.1 Zeroth-Order Reactions

Consider the reaction:

$$A \rightarrow \text{Products} \tag{3.52}$$

If one measures the rates at different times and finds them to be independent of the concentration of A, then the differential equation is

$$r = -\frac{d[A]}{dt} = k[A]^0 \tag{3.53}$$

Because the exponent is zero, then

$$-\frac{d[A]}{dt} = k \tag{3.54}$$

or

$$d[A] = -kdt \tag{3.55}$$

Integrating this expression, and considering that at time = 0 the concentration of A is $[A]_0$ (i.e., the initial concentration of A), then

$$\int_{A_0}^{A} d[A] = -k \int_0^t dt \tag{3.56}$$

$$[A] - [A]_0 = -kt \tag{3.57}$$

$$[A] = [A]_0 - kt \tag{3.58}$$

For a zeroth-order reaction, a plot of concentration vs time gives a straight line with slope $= -k$. (The units of k here are mol L^{-1} s^{-1}).

3.2.2.2 First-Order Reactions

For the overall reaction:

$$A \rightarrow \text{Products} \tag{3.59}$$

If the differential equation is

$$r = -\frac{d[A]}{dt} = k[A] \tag{3.60}$$

then

$$-\frac{d[\mathrm{A}]}{[\mathrm{A}]} = kdt \tag{3.61}$$

$$\int_{\mathrm{A}_0}^{\mathrm{A}} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = -k\int_0^t dt \tag{3.62}$$

Integrating and substituting the limits:

$$\ln[\mathrm{A}] - \ln[\mathrm{A}]_0 = -kt \tag{3.63}$$

$$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt \tag{3.64}$$

A plot of the natural logarithm of concentration vs time gives a straight line with a slope $= -k$. (The units of k are s^{-1}).

This last equation may be rearranged to give

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-kt} \tag{3.65}$$

which emphasizes that the concentration of A decays exponentially.

3.2.2.3 Second-Order Reactions

(a) Type I

This involves reactions where the rate law is dependent of the concentration of one species to the second power.

For the overall reaction:

$$2\mathrm{A} \rightarrow \text{Products} \tag{3.66}$$

If the differential equation is

$$r = -\frac{1}{2}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2 \tag{3.67}$$

then

$$\int_{\mathrm{A}_0}^{\mathrm{A}} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -2k\int_0^t dt \tag{3.68}$$

Integrating and substituting the limits:

$$\frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_0} = 2kt \tag{3.69}$$

$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + 2kt \tag{3.70}$$

Thus, for this type of second-order kinetics, a plot of the reciprocal of the concentration vs time gives a straight line of slope $= 2k$. (The units of the second-order rate constant are $\mathrm{mol}^{-1}\ \mathrm{L\ s}^{-1}$).

(b) Type II

This is first order in each of two reactants. Then, for the overall reaction:

$$\mathrm{A} + \mathrm{B} \rightarrow \text{Products} \tag{3.71}$$

the differential equation is

$$r = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}][\mathrm{B}] \tag{3.72}$$

If the initial concentrations of A and B are the same, the treatment is as in Type I. When the initial concentrations are different, the differential equation is integrated by parts and then limits are substituted:

$$\frac{1}{[\mathrm{A}]_0 - [\mathrm{B}]_0}\ln\frac{[\mathrm{A}][\mathrm{B}]_0}{[\mathrm{A}]_0[\mathrm{B}]} = kt \tag{3.73}$$

Thus a plot of the logarithmic term vs time gives a straight line with a slope equal to $k([\mathrm{A}]_0 - [\mathrm{B}]_0)$.

3.2.2.4 Higher-Order Reactions

The mathematics involved for higher-order reactions become more difficult and such a treatment is beyond the scope of this book. For example, the integrated rate equations for the three types of third-order reactions are given in Table 3.2.

3.2.3 Complex Reactions

Chemical reactions that do not follow simple reaction order kinetics are called *complex reactions.* The experimental rate equations provide crucial evidence for deducing their mechanism. A convenient

TABLE 3.2. Integrated rate equations for the three types of third-order reactions

Type	Rate law	Integrated rate equation
I	$r = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^3$	$-\left(\frac{1}{[\mathrm{A}]^2} - \frac{1}{[\mathrm{A}]_0^2}\right) = 2kt$
II	$r = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2[\mathrm{B}]$	$-\frac{1}{([\mathrm{A}]_0 - [\mathrm{B}]_0)}\left(\frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_0}\right) + \frac{1}{([\mathrm{A}]_0 - [\mathrm{B}]_0)^2}\ln\frac{[\mathrm{A}][\mathrm{B}]_0}{[\mathrm{A}]_0[\mathrm{B}]} = kt$
III	$r = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}][\mathrm{B}][\mathrm{C}]$	$-\frac{1}{([\mathrm{A}]_0 - [\mathrm{B}]_0)([\mathrm{B}]_0 - [\mathrm{C}]_0)([\mathrm{C}]_0 - [\mathrm{A}]_0)}\ln\left\{\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right)^{([\mathrm{B}]_0-[\mathrm{C}]_0)}\left(\frac{[\mathrm{B}]}{[\mathrm{B}]_0}\right)^{([\mathrm{C}]_0-[\mathrm{A}]_0)}\left(\frac{[\mathrm{C}]}{[\mathrm{C}]_0}\right)^{([\mathrm{A}]_0-[\mathrm{B}]_0)}\right\} = kt$

classification of complex reactions is based on the *participation modes* of the elementary reactions that compose them: (i) consecutive, (ii) opposing, (iii) concurrent, and (iv) a combination of two or more of these types.

For the first three types it is possible to write down differential rate equations for reactants, products, and intermediates as follows. (For more complicated cases it becomes increasingly difficult—often even impossible—to obtain exact integrated solutions, and approximate methods have been developed. These methods fall outside of the scope of this book).

3.2.3.1 Consecutive Reactions

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \tag{3.74}$$

Here, reactant A is converted to product C via intermediate B.

The differential equations are

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] \tag{3.75}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] \tag{3.76}$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}] \tag{3.77}$$

If only A is present at the beginning of the reaction in a concentration $[\mathrm{A}]_0$, then eq. 3.75 may be integrated to give the simple first-order equation:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t} \tag{3.78}$$

The differential equation for B becomes:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]_0 e^{-k_1 t} - k_2[\mathrm{B}] \tag{3.79}$$

and its integration results in

$$[\mathrm{B}] = \frac{k_1}{k_2 - k_1}[\mathrm{A}]_0 \left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{3.80}$$

Lastly, for C one gets

$$[\mathrm{C}] = [\mathrm{A}]_0 \left(1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1}\right) \tag{3.81}$$

3.2.3.2 Opposing (Reversible) Reactions

The simplest example for opposing first-order reactions is:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \text{ and } \mathrm{A} \xleftarrow[k_{-1}]{} \mathrm{B} \tag{3.82}$$

If only A is initially present at a concentration $[\mathrm{A}]_0$ and a given amount (x) has reacted at a time t, the differential rate equation is:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] \tag{3.83}$$

which may be re-written using $[\mathrm{A}] = [\mathrm{A}]_0 - x$ and $[\mathrm{B}] = x$ as

$$\frac{dx}{dt} = k_1([\mathrm{A}]_0 - x) - k_{-1}x \tag{3.84}$$

When the system reaches equilibrium, the value of x becomes x_e. At that point the forward and back reactions proceed at equal rates, and so

$$\frac{dx}{dt} = 0 \tag{3.85}$$

Under these conditions

$$k_1([\mathrm{A}]_0 - x_e) = k_{-1}x_e \tag{3.86}$$

The differential equation in then transformed, so it can be easily integrated:

$$\frac{dx}{dt} = \frac{k_1[\mathrm{A}]_0}{x_e}(x - x_e) \tag{3.87}$$

By integration:

$$\ln\left(\frac{x_e}{x_e - x}\right) = k_1\frac{[\mathrm{A}]_0}{x_e}t \tag{3.88}$$

Thus, by measuring the concentration of A or B until equilibrium is reached, a plot of

$$\ln\left(\frac{x_e}{x_e - x}\right) \text{ vs } t$$

results in a straight line of slope

$$\left(k_1\frac{[\mathrm{A}]_0}{x_e}\right)$$

and hence k_1 can be obtained. The value of k_{-1} can then be obtained from eq. 3.86.

The equilibrium constant, K is given by

$$K = \frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{x_e}{[\mathrm{A}]_0 - x_e} \tag{3.89}$$

or

$$K = \frac{k_1}{k_{-1}} \tag{3.90}$$

The equilibrium constant is equal to the ratio of rate constants for the forward and backward reactions. Such a relationship is valid for opposing reactions in an equilibrium system.

3.2.3.3 Parallel Reactions

Considering the following mechanism:

$$A \xrightarrow{k_1} B \tag{3.91}$$

$$A \xrightarrow{k_2} C \tag{3.92}$$

the differential rate equations for reactant and products are

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] - k_2[\mathrm{A}] = -(k_1 + k_2)[\mathrm{A}] \tag{3.93}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] \tag{3.94}$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{A}] \tag{3.95}$$

If at the beginning of the reaction only A is present at a concentration $[\mathrm{A}]_0$, then eq. (3.93) may be integrated to give the first-order equation

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -(k_1 + k_2)t \tag{3.96}$$

or

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{3.97}$$

The differential equation for B becomes:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{3.98}$$

that may be integrated to give:

$$[\mathrm{B}] = \frac{k_1}{k_1 + k_2}[\mathrm{A}]_0\left(1 - e^{-(k_1+k_2)t}\right) \tag{3.99}$$

Similarly, from this equation one gets for [C]:

$$[\mathrm{C}] = \frac{k_2}{k_1 + k_2}[\mathrm{A}]_0\left(1 - e^{-(k_1+k_2)t}\right) \tag{3.100}$$

From these two equations it can be easily shown that at all times:

$$\frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{k_1}{k_2} \tag{3.101}$$

3.2.4 The Steady-State Approximation

Let us consider a consecutive two-step reaction as in the example above:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \tag{3.102}$$

If $k_2 \gg k_1$, as soon as B is formed it rapidly reacts to give C, and its concentration remains constant during almost all the reaction period. We then say that B reaches a *steady-state* concentration, expressed by $[\mathrm{B}]_{ss}$ = constant. The rate is then:

$$\left(\frac{d[\mathrm{B}]}{dt}\right)_{ss} = 0 \tag{3.103}$$

and

$$\left(\frac{d[\mathrm{C}]}{dt}\right)_{ss} = k_2[\mathrm{B}]_{ss} \tag{3.104}$$

From eq. 3.76 and 3.103 we have

$$\left(\frac{d[\mathrm{B}]}{dt}\right)_{ss} = k_1[\mathrm{A}]_{ss} - k_2[\mathrm{B}]_{ss} = 0 \tag{3.105}$$

then,

$$k_1[\mathrm{A}]_{ss} = k_2[\mathrm{B}]_{ss} \tag{3.106}$$

and

$$\left(\frac{d[\mathrm{C}]}{dt}\right)_{ss} = k_1[\mathrm{A}]_{ss} \tag{3.107}$$

Now we will use the condition stated above (i.e., $k_2 \gg k_1$) and apply it to the exact solution for this system (eq. 3.80). Firstly, we multiply eq. 3.80 by k_2:

$$k_2[\mathrm{B}] = \frac{k_2 k_1}{k_2 - k_1}[\mathrm{A}]_0\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{3.108}$$

Because $k_2 \gg k_1$, we then get:

$$k_2[\mathrm{B}] = \frac{k_2 k_1}{k_2}[\mathrm{A}]_0\left(e^{-k_1 t}\right) \tag{3.109}$$

Using eq. 3.78:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t} \tag{3.110}$$

one gets $$k_2[\mathrm{B}] = k_1[\mathrm{A}]_0\left(e^{-k_1 t}\right) = k_1[\mathrm{A}] \tag{3.111}$$

This is the same result as that obtained from the steady-state hypothesis (eq. 3.106). The validity of the steady-state assumption should be proved for each reaction to ensure consistency between the assumption and the experimental data.

3.2.5 Catalysis

A catalyst is a substance that increases the rate of a reaction leading to the product(s), whereby the catalyst does not undergo any chemical change. The phenomenon of catalysis was known to chemists as far back as the 19th century. Only in the 20th century did chemists understand the behavior of a catalyst. Now it is recognized that catalysts are substances that change the rate of a chemical reaction without affecting the equilibrium distribution of reactants or products. A basic example is the common laboratory preparation of oxygen gas by the thermal decomposition of potassium chlorate as shown below:

$$2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)} \qquad (3.112)$$

However, this reaction proceeds very slowly even if it is heated up. The rate of decomposition can be increased if we add a small amount of the solid black compound, manganese(IV) oxide (MnO_2), as a catalyst to $KClO_3$ before heating the reactant. At the end of the reaction, black MnO_2 can be recovered quantitatively.

A catalyst speeds up a reaction by providing *new pathways* (elementary steps) with more favorable reaction kinetics than those that exist in the uncatalyzed reaction. Catalysts do so by interacting with the reactant in a reaction pathway that significantly *lowers* the activation energy, E_a, in comparison to the uncatalyzed reaction.

The Arrhenius equation (eq. 3.50) helps us understand how catalysis works. In catalysis we know by definition that $\text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}}$. This is true because the rate constant k depends upon the frequency factor Z (or the number of collisions per unit time), the activation energy, E_a (i.e., the energy barrier) and the absolute temperature, T. Addition of a catalyst to an otherwise slow reaction, thus, increases the rate by increasing Z while lowering E_a at the same time. As a general rule, the rate increases with temperature. This is shown in Figure 3.3, which represents the graph of reaction coordinate (x axis) vs free energy (y axis). E_a is represented in the graph.

Typically, a catalyst forms an unstable intermediate (designated as A–C, where A is a reactant and C is the catalyst) that undergoes a series of cyclic reactions involving *associative (bond-forming)*, and *dissociative* (*bond-breaking*) steps. As the reaction reaches the end of the cycle (i.e., formation of the desired product), the catalyst is regenerated and then the next cycle starts again. Ultimately, an effective catalyst may perform a large number of cycles (called *turnovers*), each time producing the product before becoming poisoned with impurities or byproducts that reduce the catalyst's effectiveness (or may even decompose it). The higher the number of turnovers, the more effective the catalyst.

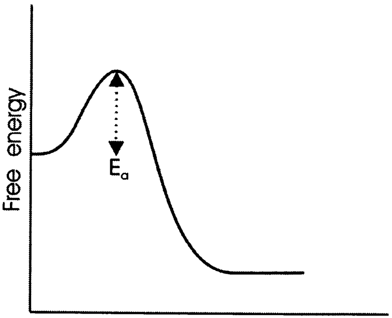


FIGURE 3.3. Reaction coordinate (x axis) vs free energy (y axis).

3.2.6 Kinetics of Metal–Complex Dissociation

As discussed in Section 3.1.2, the speciation of metals is of paramount importance for understanding many aspects of their environmental behavior. Often times the kinetic behavior of a metal complex ML (rather than its thermodynamic behavior) determines its speciation. The dissociation-formation of ML is given by

$$ML \underset{k_f}{\overset{k_d}{\rightleftharpoons}} M + L \qquad (3.113)$$

(charges are omitted for simplicity). Here, M is a metal ion, L is a ligand, and k_d and k_f are the rate constants for dissociation and formation, respectively. Those complexes that dissociate fast (i.e., large k_d) are called *labile*, whereas those that dissociate slowly (or do not dissociate at all, small k_d) are called *inert*. Of course one can encounter dissociation kinetics between those two extremes (i.e., *quasi-labile* and *slowly-labile* complexes).

To study such kinetics, the experimental criterion to classify the different types of complexes is their degree of dissociation with time. This degree of dissociation is given by the fraction of ML dissociated at a given time:

$$\text{fraction of ML dissociated} = \frac{[M]}{[M]_{TOT}} \qquad (3.114)$$

Because $[M]_{TOT}$ is the sum of [M] + [ML], this equation is the same as that defined in Section 2.1.2 (see eq. 2.19) for a single-ligand complex:

$$f_M = \frac{[M]}{[M]_{TOT}} = \frac{[M]}{[M] + [ML]} \qquad (3.115)$$

By knowing the initial concentration of the complex,

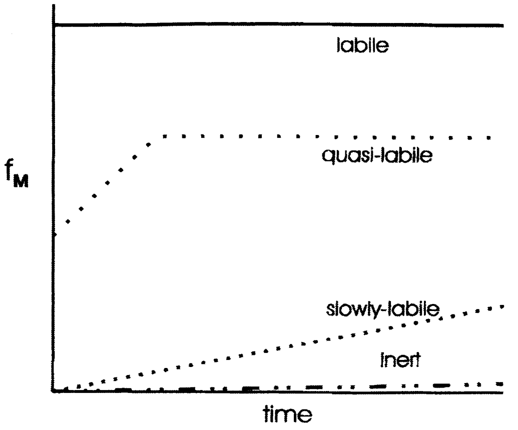


FIGURE 3.4. Kinetic behavior of metal complexes.

$[ML]_0$ and experimentally analyzing the concentration of M as a function of time, one can obtain [ML] at any time by difference. Then, f_M can be calculated and plotted (as schematically shown in the Example 2.5). The different types of complexes are then evidenced by their dissociation kinetics. See Figure 3.4. (Note that the quasi-labile curve in this figure does not represent a single mechanism and further—and more complicated—analysis is required to explain such behavior).

The next task is to obtain the value of k_d for a given reaction. Because reaction 3.113 commonly follows first-order (or pseudo first-order) kinetics, one can relate f_M, k_d and t through the expression.

$$k_d t = \ln\left(\frac{1}{1 - f_M}\right) \tag{3.116}$$

(see Example 3.7 for its derivation). Then, k_d can be directly obtained from a plot of

$$\ln\left(\frac{1}{1 - f_M}\right) \text{ vs } t$$

Metal complexes can thus be classified according to their k_d values (in s^{-1}), as shown in Figure 3.5 (see Rodriguez, 1997).

3.3 Photochemical Processes

Natural light can induce a variety of processes of environmental importance either directly (when

Example 3.7 Derive eq. 3.116 for the reaction 3.113. (Assume this to be a mono-directional reaction).

Answer

$$ML \xrightarrow{k_d} M + L$$

If we make [ML] = A and consider this to be a first-order reaction, then from eq. 3.60:

$$\frac{dA}{dt} = -k_d A$$

Uniting variables, integrating both sides, and applying limits (A_0 at the time t_0 and A at a time t), one gets:

$$\int_{A_0}^{A_t} \frac{dA}{A} = -\int_0^t k_d dt$$

$$\ln A_t - \ln A_0 = -k_d t$$

$$\ln\left(\frac{A_t}{A_0}\right) = -k_d t$$

$$e^{-k_d t} = \frac{A_t}{A_0} = \frac{[ML]_t}{[ML]_0} = \frac{[ML]}{[ML]_0}$$

Because

$$[ML]_0 = [M] + [ML]$$

then

$$[ML] = [ML]_0 - [M]$$

Also, since

$$[M]/([M] + [ML]) = f_M$$

then

$$\begin{aligned} e^{-k_d t} &= \frac{[ML]_0 - [M]}{[ML]_0} \\ &= 1 - \frac{[M]}{[ML]_0} = 1 - \frac{[M]}{[M] + [ML]_0} = 1 - f_M \end{aligned}$$

Taking natural logs on both sides,

$$-k_d t = \ln(1 - f_M)$$

and finally one gets eq. 3.116:

$$\begin{aligned} k_d t &= -\ln(1 - f_M) = \ln(1 - f_M)^{-1} \\ &= \ln\left(\frac{1}{1 - f_M}\right) \end{aligned}$$

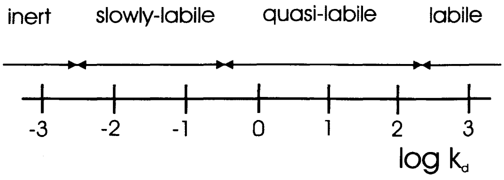


FIGURE 3.5. Classification of metal complexes according to their dissociation kinetics.

light is absorbed by the species of interest) or indirectly (when the species of interest reacts with an intermediate called *mediator*, previously excited or produced by light). Environmentally important phenomena include photosynthesis, photodissociation (e.g., the rupture of organic and inorganic molecules), photoproduction of highly reactive radicals, photodissolution of minerals, photoredox reactions, photochemical smog, etc.

3.3.1 Photochemical Processes After the Absorption of Light

A molecule possesses different energy states: rotational, vibrational, vibrational–rotational, translational, and electronic. Different types of electromagnetic radiation are capable of transforming the normal states in molecules to produce altered states. For example, UV and visible light normally produce electronic transitions from the ground state to excited states. Once the absorbing species (D) is in an excited state (D*), it can undergo a variety of processes:

a. Emit light and return to the ground state (*fluorescence*).

$$\mathrm{D}^* \rightarrow \mathrm{D} + h\nu \qquad (3.117)$$

b. Return to the ground state by loss of the extra energy from the excited state, due to interactions with the surrounding media in such a way that this energy is lost by radiation-less processes (*internal conversion*).

c. Return to the ground state by collision with a receptor molecule, A (*collision deactivation*). The electronic energy may be dissipated as kinetic energy with the surrounding medium, or the colliding molecule may become excited and undergo further reaction (*photosensitization*).

$$\mathrm{D} + h\nu \rightarrow \mathrm{D}^* \qquad (3.118)$$

$$\mathrm{D}^* \rightarrow \mathrm{D} + \text{energy} \qquad (3.119)$$

$$\mathrm{D}^* + \mathrm{A} \rightarrow \mathrm{D} + \mathrm{A}^* \qquad (3.120)$$

$$\mathrm{A}^* \rightarrow \text{products} \qquad (3.121)$$

d. Undergo electronic rearrangement with the formation of a new excited state of different multiplicity (*intersystem crossing*). The multiplicity ($\mathcal{M}$) defines the state of a molecule, and can be calculated by the formula

$$\mathcal{M} = 2\mathcal{S} + 1 \qquad (3.122)$$

where $\mathcal{S}$ = the absolute value of the total electronic spin in the molecule, obtained by adding the spins of all the unpaired electrons (each counts for $\pm {}^1/_2$). For example, N_2 does not have any unpaired electrons, and thus $\mathcal{M} = 2(0) + 1 = 1$. This is called a *singlet*, *S*. On the other hand, O_2 is known to possess two unpaired electrons, and thus $\mathcal{M} = 2|({}^1/_2 + {}^1/_2)| + 1 = 3$. This is called a *triplet*, *T*.

e. Break apart or react to form new products (*photolysis*).

$$D^* \rightarrow \text{products} \qquad (3.123)$$

From the above discussion, it is clear that for a photochemical process to occur, incident photons must be absorbed first. The more effective the absorption of light in a given spectral region (i.e., the higher the *absorption cross-section* for the excitation light), the more *efficient* the photoreaction is. This is measured by the *molar extinction coefficient* or *absorptivity*, ε_λ normally expressed in L mol^{-1} cm^{-1}. The number of molecules photolyzed per photon of incident light in a fixed period of time is called the *quantum yield for photolysis*, Φ.

3.3.2 Beer's Law

Because the absorption of light is essential to photochemical phenomena, a relationship has been established between the amount of incident light (I_λ^0) of a particular wavelength (λ), and the light transmitted (I_λ) by a given sample with a definite concentration (c) and with a characteristic absorptivity (ε_λ) in a cell of pathway b (in cm) as follows:

$$I_\lambda = I_\lambda^0 10^{-\varepsilon_\lambda bc} \qquad (3.124)$$

Dividing the intensity terms and taking logs on both sides, one can rearrange this equation as follows:

$$\log\left(I_\lambda^0/I_\lambda\right) = \varepsilon_\lambda bc \qquad (3.125)$$

The term on the left side is called *optical density* or *absorbance, A*.

3.3.3 Homogeneous and Heterogeneous Processes

Photochemical processes can occur in a single phase (*homogeneous photolysis*) or at the interface between two phases (*heterogeneous photolysis*). An example of the former is the photodissociation of H_2O_2 in aqueous solution to produce the highly reactive $^\bullet OH$ radicals; an example of the latter is the generation of these same $^\bullet OH$ radicals on the surface of colloidal particles of a semiconductor (e.g., TiO_2) upon light absorption (see Section 10.1.1).

3.4 Radiochemistry

Radioactivity is significant in the study of environmental phenomena due to its possible effects on living organisms. One finds it for example in the atmosphere (e.g., radon and its decay products), in water near uranium-production sites, in wastes from warfare and nuclear operations, and dispersed as a result of accidents (e.g., the Chernobyl accident, 1986). We will now review some salient features of radioactivity and key radiation properties.

Radioactivity is a spontaneous process of decay or disintegration of heavy nuclei (nuclides) generating different types of radiation such as alpha particles, beta and gamma rays, neutrons, positrons, etc., and forming a nuclide of a new element(s). These radiations (including X-rays) are called *ionizing radiations*, because they are capable of removing electrons from atoms or molecules, forming ions. The radiations that do not displace electrons from atoms or molecules are called *non-ionizing radiations* (e.g., visible light, infrared light, ultraviolet light, microwaves, and radio frequency waves). All radiations coming out of radioactivity are considered dangerous because they are associated with radiation energy. *Radiation energy* is measured in units of kilo (thousand) electron volts (keV) or in mega (millions) electron volts (MeV). The *electron volt* (eV) is defined as the energy involved in moving one electron through a potential difference of 1 volt. Thus, 1 keV = 10^3 eV, and 1 MeV = 10^6 eV. See examples 3.8 and 3.9.

Low-energy beta (β) particles associated with < 250 keV energy may penetrate the superficial layer of skin. The high-energy (β) radiations with energies greater than 1 MeV will penetrate the skin a centimeter or more. On the other hand, alpha (α) particles with energies in the range 1–10 MeV do not seem to penetrate the skin. However, both α and β particles inside the body can surely damage the cells (i.e., they are internal hazards) and thus they must not be taken into human bodies. Gamma (γ) rays and X-rays are high-energy radiations and can cause severe damage to the cell. A short profile of five different kinds of ionizing radiations is given in Table 3.3.

Almost all naturally occurring elements are made up of isotopes. Isotopes are atoms of the same

TABLE 3.3. Primary types of ionizing radiations

Radiation type	Nature	Effects
Alpha (α) particle	It is a double positive charge carrying helium nucleus ($^4_2He^{2+}$) released spontaneously from a high-atomic mass radioactive element. It has low penetration power and can be stopped by a thin sheet of paper or a layer of air.	Has no external hazards; has internal hazards.
Beta (β) particle	It is a negatively charged particle equivalent to an electron (e^- or β^-). It is emitted by a radioactive material. A beta particle carrying a positive charge is called a *positron* (β^+).	May cause skin burns. It is both an external and internal hazard.
Gamma γ-ray	It is a high-energy, highly penetrating ray; it always occurs with fission. It usually accompanies alpha and beta radiations. It can be shielded by using a dense material such as lead sheets. It is emitted from the nucleus.	Because it is highly penetrating, it is both an external and internal hazard.
X-ray	It is a high-energy, highly penetrating radiation. Its origin is the inner orbital electrons in an atom. X-rays are produced by the sudden acceleration of charge particles.	It poses high external hazards.

Example 3.8 Name additional nuclear or extra-nuclear particles.

Answer

Protons (^1_1p *or* $^1_1\mathrm{H}$), positrons ($^{\ 0}_{+1}e$), neutrinos, antineutrinos, and so on.

Example 3.9 What is the energy in eV and MeV associated with beta particles, corresponding to 230 keV?

Answer

$$230\ \mathrm{keV}\frac{10^3\ \mathrm{eV}}{1\ \mathrm{keV}} = 230 \times 10^3\ \mathrm{eV} \qquad 230\ \mathrm{keV}\frac{1\ \mathrm{MeV}}{10^6\ \mathrm{keV}} = 2.30 \times 10^{-4}\ \mathrm{MeV}$$

element that contain the same number of protons but a different number of neutrons. An isotope of a particular element is indicated with the symbol ^A_ZX. Here X stands for the symbol of the element, A represents the mass number (defined as the sum of the number of protons and neutrons), and Z indicates the number of protons in the isotope or its atomic number. All isotopes of the same element, therefore, have the same atomic number. Each isotope of an element represents a nuclide of that element. As a result of radioactivity, an unstable nuclide decays to form a new nuclide with lower energy. The emitted radiation produced carries the extra energy. The decaying nuclide is called the *parent nuclide* and the newly formed nuclide is called the *daughter nuclide.*

It is important to understand that *radioactivity* is the *outcome of a nuclear reaction.* Nuclear reactions are different from chemical reactions. In chemical reactions, one or more substances change to one or more new substances containing the same number and kind of atoms of elements (i.e., no new atoms or nuclei are formed). In nuclear reactions, atoms of one element are transformed into atoms of another element. Moreover, a chemical reaction is the outcome of bond breaking (in reactants) and bond forming (in products), and involves orbital electrons; in nuclear reactions, nucleons such as protons, neutrons, etc., are involved. Nuclear reactions take place with a measurable mass change that accounts for the large energy change.

3.4.1 Decay kinetics

Note that the rate of radioactive decay depends only upon the number of nuclei present in an element constituting the compound. All radioactive nuclei decay at a characteristic rate. The activity or the radioactivity decay rate (referred to as A) is defined as the change in the number of radioactive isotopes, ΔN divided by the change in time, Δt. Thus,

$$A = -\frac{N_t - N_0}{t - 0} = -\frac{\Delta N}{t} \tag{3.126}$$

where N_0 and N_t are the number of radioactive nuclei present at $t = 0$ and $t = t$, respectively. Here the negative sign appears because the number of radioactive nuclei undergoing decay decreases with time. The activity A is also proportional to the number of radioactive nuclei N present at a given time t:

$$A = \lambda N_t \tag{3.127}$$

where λ is the decay constant. Combining these two equations we find

$$A = -\frac{\Delta N}{\Delta t} = \lambda N_t \tag{3.128}$$

As deduced from the section on kinetics, the radioactive decay follows first-order kinetics because the activity A depends upon N raised to the power one. Solving this equation as discussed there, the following expression can be obtained:

$$\ln\frac{N_0}{N_t} = \lambda t \tag{3.129}$$

and the corresponding decay half-life, $t_{1/2}$ is given by

$$t_{1/2} = \frac{0.693}{\lambda} \tag{3.130}$$

The half-life of radioactive isotopes is defined as the time it takes for half of the radioactive nuclei to decay. Thus, after one half-life, half of the original radioactive isotopes have been disintegrated and half are left for decay; after the second half-life, one-quarter of the original nuclei remains and so on. A simple way of finding how much of the radioactive sample remains after each half-life, is determined as follows:

- After *one* half-life, $\frac{1}{2}$ of the original amount left
- After *two* half-lives, $(\frac{1}{2} \times \frac{1}{2}) = \frac{1}{4}$ or $\frac{1}{2^2}$ of the original amount is left
- After *three* half-lives, $(\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}) = \frac{1}{8}$ or $\frac{1}{2^3}$ of the original amount is left

Thus, after n half-lives, $1/2^n$ of the original amount is left. See Example 3.10.

The following equation shows the decreasing activity A of a radioactive material as a function of time:

$$A = A_0 e^{-(0.693t/t_{1/2})} \tag{3.131}$$

where t is the time during which the activity A_0 has decreased (as indicated by the negative sign) to A and $t_{1/2}$ is the half-life of the material.

3.4.2 Units of Radiation

In order to understand the effects of radiation on any material, let us define how one measures radiation. Radiation is measured in several units. The SI unit for radioactivity is the *becquerel* (Bq), which is defined as one disintegration (d) per second (s) (Bq = d/s). However, the most common unit is the *curie* (Ci) and its definition is based on the number of radium-226 isotopes present in 1 gram of the element that disintegrate in one second. One Ci is thus exactly equal to 3.70×10^{10} disintegrations per second

$$1\ \text{Ci} = 3.70 \times 10^{10}\ \text{d/s} \tag{3.132}$$

Because this number is very large, smaller units of Ci such as the millicurie (mCi), microcurie (μCi), etc. are commonly used:

$$\begin{aligned} 1\ \text{mCi} &= 3.70 \times 10^{10} \times 1.0 \times 10^{-3}\ \text{d/s} \\ &= 3.7 \times 10^{7}\ \text{d/s} \end{aligned} \tag{3.133}$$

$$\begin{aligned} 1\ \mu\text{Ci} &= 3.70 \times 10^{10} \times 1.0 \times 10^{-6}\ \text{d/s} \\ &= 3.7 \times 10^{4}\ \text{d/s} \end{aligned} \tag{3.134}$$

Still another unit is the *roentgen* (R). One roentgen is defined as the quantity of X-rays or gamma radiation that produces ions carrying 2.10×10^9 units of electrical charge in 1 cubic centimeter (cm^3) of dry air at 273 K and 1 atm pressure. The roentgen measures the quantity of radiation produced from a source and thus expresses the exposed dose of radiation. Thus, if a person was exposed to 1 R/min in front of an X-ray machine for 1 min, that person is said to have received a dose of 1 R. Ionization of this kind kills both normal and abnormal cells. That is why great care is taken when a person is exposed to X-ray beams in diagnostic medicine.

The SI unit for *absorbed doses* (i.e., the amount of all radiations absorbed in any material) is the *gray* (Gy), defined as the absorption of 1 joule of energy per kilogram of material (J/kg). In the U.S. another unit for dose is used. It is called *rad*, which stands for *r*adiation *a*bsorbed *d*ose. One rad is equal to the absorption of 0.01 joule of energy per kilogram of material. Thus, 1 Gy = 100 rads.

The units for *dose equivalent*, which represents the biological effect of all radiations, are of two kinds:

1. *Rem:* This older term is the short abbreviation for *r*oentgen *e*quivalent *m*an. It is defined as the dose of radiation absorbed, multiplied by a modifying factor called *quality factor* Q, or relative biological effectiveness, RBE that takes into account the type of radiation (of any kind) and how the radiation is absorbed. Thus, for beta, gamma and X-rays, the quality factor is 1; for alpha radiation it may be as high as 20, and for neutrons it varies from 3 to 10.

Example 3.10 How much of 1.00 g of the I-131 isotope will be left after 32 days? Its half-life, $t_{1/2}$ is 8.0 days.

Answer

Number of half-lives $= \frac{32.0\ \text{days}}{8.0\ \text{days}} = 4$. After 4 half-lives, the amount of I-131 left is:

Original amount (g) $\times \frac{1}{2^4} = 1.0\ \text{g} \times \frac{1}{2^4} = 0.063\ \text{g}$ (after rounding-off).

2. *Sievert* (Sv): It is a more modern unit that substitutes the rem, as it reflects the biological effect of radiation. It is defined as the absorbed dose in Gy multiplied by a somewhat complicated factor that takes into account for example the quality factor defined above, the part of the body irradiated and the time and volume of exposure. 1 Sv = 100 rems.

3.4.3 Detection Devices for Ionizing Radiations and Protection From Radiation

For detecting and measuring ionization radiation, five different kinds of devices are mainly used.

3.4.3.1 Geiger Counter or Ionization in Gas-Filled Tubes

A Geiger counter is used frequently to detect and measure ionization radiation. It is used not only to detect radiation, but also to measure or count the number of radiations happening per unit in time. Although the Geiger counter is the most widely used equipment, it is not very sensitive to alpha and low-energy beta radiations.

3.4.3.2 Scintillation Devices

A scintillation device is a material that, upon interaction with any radiation, produces light that is proportional to the energy of the radiation. Sodium iodide crystals or germanium serve as scintillation materials.

3.4.3.3 Photographic Films

Photographic plates are used to detect the intensity of radiation; the darker the plate becomes, the stronger is the radiation. Photographic films are also used in dosimeters that measure the radiation dose to the area on the body exposed to the radiation. The pocket dosimeter is an ionizing chamber serving as a capacitor. It consists of two electrodes: the positively charged electrode serves as the central electrode and the negatively charged electrode serves as the outer electrode. When the electrodes are exposed to any radiation, the air surrounding the central electrode becomes ionized in direct proportion to the intensity of the radiation dose.

3.4.3.4 Semiconductors

Because of their high sensitivity, semiconductors are slowly becoming more popular as devices for detecting and measuring radiation doses.

3.4.3.5 Thermoluminescence

Thermoluminescent materials absorb and store radiation that is subsequently released as light when the material is heated. The amount of light released is directly proportional to the amount of radiation absorbed.

References and Further Reading

Agger, R. M.; Hedrick, C. E. "The Effect of Carbonate on the Chromium (III)-EDTA Reaction," *J. Chem. Educ.* **1966**, *43*, 541–544.

American Chemical Society. SciFinder Scholar 2006. (One can give a chemical formula and get the structure from the searched information). http://www.cas.org/SCIFINDER/SCHOLAR/index.html

Baird, C. *Environmental Chemistry*; W. H. Freeman: New York, 1995.

Bolton, H. Jr.; Girvin, D. C.; Plymale, A. E.; Harvey, S. D.; Workman, D. J. "Degradation of Metal-Nitrilotriacetate Complexes by Chelatobacter Heintzi," *Environ. Sci. Technol.* **1996**, *30*, 931–938.

Borrell, P. *Photochemistry: A Primer*, Edward Arnold: London, 1973. Chapter 5.

Cotton, F. A.; Wilkinson, G. *Basic Inorganic Chemistry*; Wiley: New York, 1976. Chapters 6, 7.

Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988. Chapter 29.

Eilbeck, W. J.; Mattock, G. *Chemical Processes in Waste Water Treatment*; Ellis Horwood: Chichister, 1987.

Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981. Chapters 1–3.

Ibanez, J. G.; Choi, C. S.; Becker, R. S. "Aqueous Redox Transition Metal Complexes for Electrochemical Applications as a Function of pH," *J. Electrochem. Soc.* **1987**, *134*, 3083–3089.

Ibanez, J. G.; Gonzalez, I.; Cardenas, M. A. "The Effect of Complex Formation upon the Redox Potentials of Metallic Ions," *J. Chem. Educ.* **1988**, *65*, 173–175.

Jensen, D. L.; Boddum, J. K.; Redemann, S.; Christensen, T. H. "Speciation of Dissolved Iron (II) and Manganese (II) in a Groundwater Pollution Plume," *Environ. Sci. Technol.* **1998**, *32*, 2657–2664.

Johnson, A. R.; McQueen, T. M.; Rolfa, K. T. "Species Distribution Diagrams in the Copper–Ammonia System: An Updated and Expanded Demonstration Illustrating Complex Equilibria," *J. Chem. Educ.* **2005**, *82*, 408–414.

Klewicki, J. K.; Morgan, J. J. "Kinetic Behavior of Mn(III) Complexes of Pyrophosphate, EDTA and Citrate," *Environ. Sci. Technol.* **1998**, *32*, 2916–2922.

Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 75th ed.; CRC Press: Boca Raton, FL, 1994.

Manahan, S. E. *Environmental Chemistry*, 6th ed.; Lewis Publishers: Boca Raton, FL, 1994. Chapter 13.

Manku, G. S. *Theoretical Principles of Inorganic Chemistry*; McGraw-Hill: New Delhi, 1980. Chapters 8, 10.

Martell, A. E.; Hancock, R. D. *Metal Complexes in Aqueous Solutions*; Plenum Press: New York, 1996. Chapters 1, 2, 3, 7.

McArdell, C. S.; Stone, A. T.; Tian, J. "Reaction of EDTA and Related Aminocarboxylate Chelating Agents with $Co^{III}OOH$ (Heterogenite) and $Mn^{III}OOH$ (Manganite)," *Environ. Sci. Technol.* **1998**, *32*, 2923–2930.

Nowack, B.; Lutzenkirchen, J.; Behra, P.; Sigg, L. "Modeling the Adsorption of Metal-EDTA Complexes onto Oxides", *Environ. Sci. Technol.* **1996**, *30*, 2397–2405.

Pettit, L. D.; Powell, K. J.; Ramette, R. W.; Koether, M. *SolEq: Solution Equilibria, Principles and Applications* (CD Rom); Academic Software: Otley, U. K., 1999.

Porter, G. B. "Introduction to Inorganic Photochemistry: Principles and Methods," *J. Chem. Educ.* **1983**, *60*, 785–790.

Rajeshwar, K.; Ibanez, J. G. *Environmental Electrochemistry: Fundamentals and Applications in Pollution Abatement*; Academic Press: San Diego, 1997. Chapters 5, 6.

Ramette, R. W. *Chemical Equilibrium and Analysis*; Addison-Wesley: Reading, MA, 1981.

Rodriguez-Procopio, J. Ortiz-Viana, M. del M.; Hernandez-Hernandez, L. "Microcolumn Ion-Exchange Method for Kinetic Speciation of Copper and Lead in Natural Waters," *Environ. Sci. Technol.* **1997**, *31*, 3081–3085.

Rojas-Hernandez, A.; Ramirez, M. T.; Gonzalez, I.; Ibanez, J. G. "Predominance-Zone Diagrams in Solution Chemistry. Dismutation Processes in Two-Component Systems (M-L)," *J. Chem. Educ.* **1995**, *72*, 1099–1105.

Shriver, D. F.; Atkins, P. W.; Overton, T. L.; Rourke, J. P.; Weller, M. T.; Armstrong, F. A. *Inorganic Chemistry*, 4th ed.; W. Freeman: New York, 2006.

Skinner, Gordon B. *Introduction to Chemical Kinetics*; Academic Press: New York, 1974. Chapter 2.

Stumm, W.; Morgan, J. J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd ed.; Wiley, New York, 1996. Chapter 12.

Summers, D. B. *Chemistry Handbook,* 2nd ed.; Willard Grant Press: Boston, MA, 1975.

Torrents, A.; Anderson, B. G.; Bilboulian, S.; Johnson, W. E.; Hapeman, C. J. "Atrazine Photolysis: Mechanistic Investigations of Direct and Nitrate-Mediated Hydroxy Radical Processes and the Influence of Dissolved Organic Carbon from the Chesapeake Bay," *Environ. Sci. Technol.* **1997**, *31*, 1476–1482.

Walton, H. F. "Ligand-Exchange Chromatography: A Brief Review," *Ind. Eng. Chem.* **1995**, *34*, 2553–2554.

Wilkinson, Fk. *Chemical Kinetics and Reaction Mechanisms*; Van Nostrand-Reinhold: New York, 1980. Chapters 2, 3.

Xue, Y.; Traina, S. J. "Oxidation Kinetics of Co (II)-EDTA in Aqueous and Semi-Aqueous Goethite Suspensions," *Environ. Sci. Technol.* **1996**, *30*, 1975–1981.

Ye, L.; Lucy, C. A. "Chromatographic Determination of Metal-EDTA Complexes with Post Column Detection Using Fluorescent Ternary Complexes," *Anal. Chem.* **1995**, *67*, 2534–2538.

Zevos, N. "Radioactivity, Radiation, and the Chemistry of Nuclear Waste," *J. Chem. Educ.* **2002**, *79*, 692–696.

Part 2

The Chemistry of Natural Environmental Processes

4

The Chemistry of Processes in the Atmosphere

Beautiful blue skies and pink-color sunsets are direct consequences of the existence of an atmosphere. Sunlight scattered by *gaseous molecules* around our planet is responsible for the blue color of the sky. When we look at sunless sky, the light we observe is mainly *scattered* light. On the other hand, *particulate matter* also scatters light but toward the red side of the visible spectrum, and therefore small airborne dust particles produce a spectacular pink-reddish color. In this chapter we discuss the location, composition, and some properties of our atmosphere.

4.1 Air

As an initial approach to our topic, air can be defined as a gaseous mixture that gives sustenance to life on Earth because of the presence of dioxygen. Its main composition has remained remarkably steady for ages, and its major constituents are nitrogen (78.1%), dioxygen (20.9%), and argon (0.9%).

From another point of view, air is the term we use to define a more complex structure known as the *atmosphere*, that is, the relatively thin layer of a low-density fluid a few hundred kilometers high surrounding our planet. On a scale of cubic meters, air can be considered as a homogeneous mixture of constant composition, but on a larger scale the atmosphere cannot be considered uniform. Where does the atmosphere end? This is a difficult question, but practically all of its mass (i.e., an estimated annual mean of 5.13×10^{21} g) is within 100 kilometers.

The subdivision of the atmosphere in layers can be better understood if we examine its temperature profile as seen in Figure 4.1.

The main layers of concern in atmospheric chemistry are the *troposphere* and the *stratosphere.* The lowest layer—the troposphere—extends from ground level up to a level of 10–15 km, depending on the latitude and time of the year. The temperature change with altitude (i.e., the *lapse rate*) within the troposphere decreases at a rate of 5–6 K/km. If the slope of the lapse rate changes to positive, then we have a *thermal inversion.* Temperature decreases may be thermodynamically explained by the expansion of gases brought about by the heating of constituents near the surface of the Earth, which capture the IR radiation emitted from its surface. Warm air tends to rise because it is more buoyant than cold air; this makes vertical mixing one of the main pathways for spreading the air constituents within this region. Convective activity plays a very important role in most of the weather we experience. The troposphere is the stratum in which the Earth's weather occurs. It is also within this layer that air pollution takes place.

The *stratosphere* is the layer above the *tropopause* (i.e., the layer of constant temperature between the troposphere and the stratosphere, see Figure 4.1) where the temperature rises with altitude up to a maximum of about 273 K; the temperature reaches this point at about 50 km (at the equator and mid-latitude regions). The increase in temperature with height suppresses vertical motions, leading to vertical stratification of the air masses contained in the stratosphere. The altitude at which the maximum temperature is observed is called the *stratopause.* Further increases in altitude are then accompanied by a progressive fall in temperature through the region known as *mesosphere*, down to a minimum

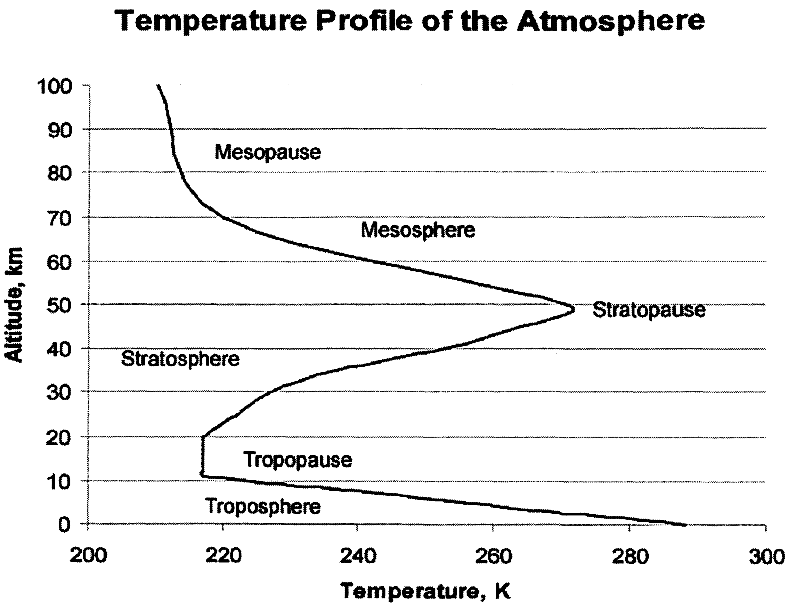


FIGURE 4.1. Distribution of layers in the atmosphere.

which is reached again at 85 km, called *mesopause*. Further increases in altitude cause a rapid increase in temperature (at about 5 K/km) through the region called the *thermosphere*.

The movement of atmospheric constituents within a region and between regions is a key process in atmospheric chemistry. For example, the transport of chemicals from the troposphere to the stratosphere sets off the depletion of ozone. Conversely, the downward transport from the stratosphere increases ozone in the troposphere. The phenomenon that most distinguishes the troposphere from the stratosphere is the rate of vertical mixing. The time scale for the vertical transport of air and other chemical species in the troposphere can be of a few hours, whereas vertical transport in the stratosphere can last months or years.

4.2 How Did the Earth's Atmosphere Form?

About 4.5 billion years ago, the Earth started to condense from the gas and dust of the primordial solar nebula, along with the Sun and its other retinue of planets and their satellites. The Earth-to-be collected the material of the gaseous solar nebula in an accrual process that took many millions of years. Collisions with other celestial bodies such as meteors and comets were intense and frequent. Collisions with very large bodies, called *planetesimals*, blew the proto-Earth apart only to reform again, although with a mass increase. The heavier materials (like nickel and iron) started sinking below the lighter, silicon-containing elements. Many of the gases present on Earth were carried here via collisions with these other celestial bodies. Eventually, the collisions persisted as the growing Earth attracted most of the smaller bodies and remaining gases in its orbit around the Sun. Heavier gases became trapped in the coalescent molten rocks. Lighter gases such as methane, ammonia, and hydrogen captured by the Earth, formed its first atmosphere. Dioxygen was not part of this atmosphere. The intense ultraviolet radiation reaching this primordial atmosphere broke apart the methane and ammonia molecules, freeing hydrogen atoms. Being light in weight and having high velocities due to the high temperature, the hydrogen was able to escape the Earth's atmosphere, leaving it depleted in hydrogen.

Meanwhile, gases originally trapped below the surface were released into the atmosphere through volcanic eruptions and other crust openings. The atmosphere began to fill with carbon dioxide, nitrogen, and water vapor. Oceans developed as water vapor condensed and fell as rain in ceaseless storms. Large amounts of carbon dioxide were removed from the atmosphere and sequestered in carbonate rocks and sea water.

Photolysis of carbon dioxide and water vapor yielded some atmospheric oxygen. Initially, however, every oxygen atom that was produced reacted quickly with rocks on the surface and gases already present in the atmosphere. Life developed early on in the oceans. Initial life forms on the planet were various types of bacteria that thrived in the anoxic environment. Oxygen started to form about 2.5 billion years ago, when simple photosynthetic plants (i.e., certain types of algae) and cyanobacteria (i.e., blue-green algae) appeared, removing carbon dioxide and allowing dioxygen to build up. Ozone (i.e., trioxygen) also started to build up. Around 500,000,000 years ago the atmospheric content of dioxygen and ozone closely resembled present values.

4.3 Amounts of Constituents in the Atmosphere

There are two ways in atmospheric chemistry to represent the amount (or mass) of a substance: the *concentration* and the *mixing ratio.* The concentration is the amount (or mass) of a substance in a given volume divided by that volume. The mixing ratio is the ratio of the amount (or mass) of a substance in a given volume to the amount (or mass) of all the air constituents in that volume. In this definition air denotes only constituents in the gaseous phase, including water vapor, but not condensed-phase water or particulate matter. The mixing ratio remains unchanged by differences in pressure or temperature associated with altitude or meteorological variability, whereas the concentration depends on pressure and temperature, in accordance with the ideal gas equation of state. (Concentration is most commonly used for particles, and mixing ratio for gases). The mixing ratio may be expressed as (a) mole fraction, (b) mass fraction, or (c) hybrid quantities, such as the amount of substance per volume of air "reduced" to a standard temperature and pressure (i.e., 273 K and 1 atm) using the ideal gas law. The presence of water vapor causes the mixing ratio to change with humidity; therefore, it is customary to refer the mixing ratio to a dry or wet basis. The most common units used for gaseous constituents are the *parts per million* (ppm), *parts per billion* (ppb), and *parts per trillion* (ppt), indicating the number of parts of the constituent in 10^6, 10^9, or 10^{12} parts of air, respectively. Because these parts may be referred to in volume or mass, it is convenient to express them as ppmv or ppmm, respectively. In atmospheric chemistry, ppm implicitly means ppmv. See Table 4.1.

TABLE 4.1. Mixing ratios of some important atmospheric gases

Component	Formula	ppmv	mg m^{-3}	Main source of selected components
Nitrogen	N_2	780,840	8.95×10^5	
Dioxygen	O_2	209,460	2.74×10^5	
Argon	Ar	9,340	1.52×10^4	
Water[c]	H_2O	variable (5,000–40,000)	variable	geogenic
Carbon dioxide[a,b]	CO_2	360	648	biogenic and anthropogenic
Neon	Ne	18	14.9	
Helium	He	5.2	0.85	
Methane[a,b]	CH_4	1.7	1.1	biogenic and anthropogenic
Krypton[b]	Kr	1.14	3.91	
Hydrogen	H_2	0.58	0.048	
Nitrous oxide[a]	N_2O	0.5	0.9	biogenic and anthropogenic
Xenon	Xe	0.09	0.5	
Carbon monoxide[a]	CO	0.03–0.12	0.034–0.14	chemical and anthropogenic
Ozone[b]	O_3	0.01–0.15	0.02–0.29	photochemical
Ammonia[a]	NH_3	0.01	0.007	biogenic
Nitrogen dioxide[a,b]	NO_2	0.001	0.002	geogenic and anthropogenic

Notes: Substances considered as atmospheric pollutants are denoted by the superscript *a*.

Substances denoted by the superscript *b* can even occur at higher values than those in the table.

Water concentration is also reported as humidity (absolute or relative); relative humidity is expressed by the fraction of specific humidity to the maximum specific humidity possible for a given pressure and temperature.

The main sources of atmospheric gases are further explained in the text.

Example 4.1 Consider a mixing ratio of 0.1 ppm of ozone. Convert this concentration into (a) moles of ozone per moles of air, (b) molecules of ozone per molecule of air, and (c) cubic centimeters of ozone per cubic centimeter of air.

Answer

(a) 0.1 moles of ozone for 10^6 moles of air

(b) Alternatively, there is one molecule of ozone in every 10^7 molecules of air, or

(c) There is 1 cubic centimeter of ozone in every 10^7 cubic centimeters of air.

A different way to express the mixing ratio of a trace gas in air is its number of molecules per cubic centimeter (i.e., reduced concentration) referred to 298 K of temperature and 1 atm of pressure. Following our example, we have

$$\begin{aligned}0.10\,\text{ppm} &= \frac{0.10\,\text{cm}^3\text{O}_3}{10^6\,\text{cm}^3\,\textbf{air}}\\ &= \frac{0.1\,\text{cm}^3\text{O}_3 \times 1\,\text{atm} \times 6.02\times 10^{23}\,\frac{\text{molecules}}{\text{mol}}}{10^6\,\text{cm}^3\textbf{air}\times 0.082\frac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\times 10^3\,\frac{\text{cm}^3}{\text{L}}\times 298\,\text{K}}\\ &= 2.0\times 10^{12}\,\frac{\text{molecules O}_3}{\text{cm}^3\,\textbf{air}}\end{aligned}$$

A third way to represent the concentration of a chemical species in the atmosphere is as micrograms (10^{-6} g) of the target species per each cubic meter of air, generally at 298 K and 1 atm pressure. Thus

$$\begin{aligned}0.10\,\text{ppm} &= \frac{0.10\,\text{cm}^3\text{O}_3}{10^6\,\text{cm}^3\,\textbf{air}}\\ &= \frac{0.10\,\text{cm}^3\text{O}_3 \times 1\,\text{atm} \times 47.9982\frac{\text{g O}_3}{\text{molO}_3}\times 10^6\,\frac{\mu\text{g}}{\text{g}}}{10^6\,\text{cm}^3\textbf{air}\times \frac{1\text{m}^3}{10^6\,\text{cm}^3\,\textbf{air}}\times 82\frac{\text{cm}^3\cdot\text{atm}}{\text{K}\cdot\text{mol}}\times 298\,\text{K}}\\ &= 2.0\times 10^2\mu\text{g}\cdot\text{m}^{-3}\end{aligned}$$

The latter units are mainly used for chemical species that are in a different phase, such as particulate matter and aerosols (e.g., Pb, PM_{10}, and $PM_{2.5}$, see section 8.4.1).

One last way to express concentration is the *column abundance*, which is the total amount or mass of a gas within a vertical column of air above a specific location. Column abundances have units of amount per area (i.e., mol m^{-2}, kg m^{-2}). In the particular case of stratospheric ozone, data are reported in Dobson units (DU). The number of DU is numerically equal to the thickness (in units of 10^{-5} m) that an ozone column of an area of 10 deg x 5 deg would occupy if compressed into a layer at 273 K and 1 atmosphere. In other words, under these conditions 1 DU is equivalent to a thickness of 0.01 mm. For the purpose of conversion, one DU is approximately equivalent to a column density of ozone molecules of 2.69×10^{20} m^{-2}, or 446.2 µmol m^{-2} or 21.4 mg m^{-2}. A typical column abundance of ozone of 300 DU corresponds to an ozone column that would be 3 mm thick or 134 mmol m^{-2}.

The atmosphere is a dynamic system where its constituents are continuously in exchange with the oceans, lakes, forests, and biological organisms. We understand this dynamism through what we call *cycles* that involve a number of physical, chemical, as well as biological processes (see Chapter 7). To completely determine a cycle, all *sources* and *sinks* as well as their contributions have to be established.

Even though the composition of the atmosphere can be considered constant, it is not at equilibrium. In fact, the atmosphere exchanges matter and momentum with the Earth's surface through the cycles mentioned above. A better description would be that some components in the atmosphere are in a *steady-state* condition. The term steady state describes the balance between the input and output of an atmospheric constituent. If F_{in} and F_{out} are the fluxes inward and outward of the atmosphere, respectively, a steady-state condition requires that

$$F_{\text{in}} = F_{\text{out}} = A/\tau \qquad (4.1)$$

where A is the total amount of the gas in the atmosphere and τ is the *residence time* (Table 4.2) of that gas. (The IUPAC definition of residence time is the

TABLE 4.2. Approximate residence times of some air components

Component	Residence time
Hydrogen sulfide	1 day
Methyl sulfide	1 day
Ammonia	2 days
Sulfur dioxide	3–7 days
Nitric oxide	4 days
Nitrogen dioxide	4 days
Hydrogen chloride	4 days
Methyl iodide	5 days
Formic acid	10 days
Methyl chloride	30 days
Carbon monoxide	35 days
Carbon disulphide	40 days
Carbonyl sulfide	1 year
Methane	3.6 years
Carbon dioxide	4 years
Nitrous oxide	20–30 years

following: "The average time a molecule or aerosol spends in the atmosphere after it is released or generated there. For compounds with well defined sources and emission rates, this is estimated by the ratio of the average global concentration of a substance to its production rate on a global scale. It is a function of not only the emission rates but the loss rates by chemical and physical removal processes").

If $F_{\text{in}} > F_{\text{out}}$ we have an *accumulation* of the gas, whereas if $F_{\text{in}} < F_{\text{out}}$ we have a *depletion.* A dramatic example of accumulation is that of carbon dioxide, which has increased its concentration since the beginning of the 20th century and therefore it is one of the probable causes of *global warming.* On the other hand, we have stratospheric ozone which is being depleted, jeopardizing some life forms by the decreased absorption of UV radiation. The *average residence time* (i.e., lifetime) of a gaseous constituent introduced into the atmosphere can vary from minutes up to hundreds of years, depending on its chemical and physical properties. Very reactive or very water-soluble gases will tend to have short residence times; for instance, sulfur dioxide has a residence time of 3–7 days, and that of ammonia is of 2 days. Low reactive or non-soluble gases will tend to stay very long times in the atmosphere: for instance, methane has a residence time of 3.6 years, and chlorofluorocarbons (CFCs) have residence times of 50 to 200 years!

In order to understand where constituents of the atmosphere come from, we will classify them according to their origin. In some cases there is not a sharp division (e.g., a burning forest), while in others there is more than one origin. Thus,

- *Geogenic* refers to activities of the Earth's crust without the participation of living organisms; some examples include volcanic activity, wind-blown dust, sea sprays, and incoming meteors.
- *Biogenic* refers to any biological activity that produces or consumes chemicals; for example, oxygen is involved in photosynthesis and respiration.
- *Anthropogenic* refers to the production of chemicals resulting from human activities; lead pollution and acid rain are some examples.

4.4 Tropospheric Chemistry

In spite of the high concentration of dioxygen in the atmosphere, reaction with this molecular species is not the main route toward the oxidation of trace components. The principal oxidative chemical species (in daytime chemistry) is the hydroxyl free radical, $^\bullet$OH. Reactions with dioxygen require higher activation energies than reactions with free radicals like $^\bullet$OH. How fast a trace gas reacts with hydroxyl radicals can be a measure of its residence time in the atmosphere. If a trace gas is inert toward these radicals, then its residence time will be high and it will be transported to the stratosphere; such is the case of CFCs, N_2O, CH_4, and CH_3Cl. Hydroxyl chemical reactions in the troposphere provide a very efficient scavenging mechanism for natural as well as human-made trace constituents. As an example let us take a look at the oxidation of methane:

$$CH_4 + {}^\bullet OH \rightarrow CH_3^\bullet + H_2O$$

$$k = 6.18 \times 10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (4.2a)$$

$$CH_3^\bullet + O_2 \rightarrow CH_3OO^\bullet \quad (4.2b)$$

$$CH_3OO^\bullet + NO^\bullet \rightarrow CH_3O^\bullet + NO_2^\bullet \quad (4.2c)$$

$$CH_3O^\bullet + O_2 \rightarrow CH_2O + HOO^\bullet \quad (4.2d)$$

$$CH_2O + h\nu\ (\text{sunlight}) \rightarrow H^\bullet + HCO^\bullet \quad (4.2e)$$

$$H^\bullet + O_2 \rightarrow HOO^\bullet \quad (4.2f)$$

$$HCO^\bullet + O_2 \rightarrow CO + HOO^\bullet \quad (4.2g)$$

$$CO + {}^\bullet OH \rightarrow HO\text{-}CO \quad (4.2h)$$

$$HO\text{-}CO + O_2 \rightarrow CO_2 + HOO^\bullet \quad (4.2i)$$

$$4(HOO^\bullet + NO^\bullet \rightarrow {}^\bullet OH + NO_2^\bullet) \quad (4.2j)$$

If we add all ten reactions together, the overall reaction is

$$\begin{aligned} &CH_4 + 5NO^\bullet + 5O_2 + h\nu \rightarrow \\ &CO_2 + H_2O + 5NO_2^\bullet + 2^\bullet OH \end{aligned} \qquad (4.2k)$$

(The reader can check it using Hess' law).

The major source of $^\bullet OH$ radicals is ozone photolysis with short wavelength UV radiation; this produces excited oxygen atoms, $O(^1D)$, which rapidly react with water vapor, forming $^\bullet OH$:

$$O_3 + h\nu(\lambda < 320\,\text{nm}) \rightarrow O_2 + O(^1D) \qquad (4.3)$$

$$O(^1D) + H_2O \rightarrow 2\,^\bullet OH \qquad (4.4)$$

where ^1D indicates a singlet photophysical state. At night time, the nitrate radical ($NO_3^\bullet$), considered as the main oxidative chemical species under such conditions, takes over from $^\bullet OH$; although $NO_3^\bullet$ is less reactive than $^\bullet OH$, it reaches its highest concentration (approximately 400 ppt) during that period:

$$NO_2^\bullet + O_3 \rightarrow NO_3^\bullet + O_2 \qquad (4.5)$$

$NO_3^\bullet$ is easily photolyzed and therefore its daytime concentration is very low.

Peroxyacetyl nitrate (PAN), $CH_3COOONO_2$, is also a source of $^\bullet OH$ radicals when it thermally decomposes:

$$CH_3COOONO_2 \rightarrow CH_3CO_3 + NO_2^\bullet \qquad (4.6a)$$

$$CH_3CO_3 + NO^\bullet \rightarrow CH_3CO_2 + NO_2^\bullet \qquad (4.6b)$$

$$CH_3CO_2 + O_2 \rightarrow CH_3O_2 + CO_2 \qquad (4.6c)$$

$$CH_3O_2 + NO^\bullet \rightarrow CH_3O + NO_2^\bullet \qquad (4.6d)$$

$$CH_3O + O_2 \rightarrow CH_2O + HOO^\bullet \qquad (4.6e)$$

$$HOO^\bullet + NO^\bullet \rightarrow {}^\bullet OH + NO_2^\bullet \qquad (4.6f)$$

$$CH_2O + {}^\bullet OH \rightarrow CHO + H_2O \qquad (4.6g)$$

$$CHO + O_2 \rightarrow CO + HOO^\bullet \qquad (4.6h)$$

$$HOO^\bullet + NO^\bullet \rightarrow {}^\bullet OH + NO_2^\bullet \qquad (4.6f)$$

Thus, decomposition of PAN in the presence of $NO^\bullet$ can lead to the formation of $^\bullet OH$ radicals and conversion of $NO^\bullet$ to $NO_2^\bullet$ merely from thermal reactions. This could be very important because PAN can be an indicator of the urban ozone-forming potential (see Section 8.4.1) and of the organic-oxidizing capacity of the urban air mass. The thermal decomposition of PAN also leads to the formation of $NO_3^\bullet$ radicals.

4.5 Physical Principles of the Greenhouse Effect

If we consider the Earth to be in a thermal steady state (i.e., a state where the flux of energy received from the Sun equals the energy emitted by the Earth, see Figure 4.2), then

$$E_E = E_A \qquad (4.7a)$$

$$E_A = (1 - A)F \qquad (4.7b)$$

where E_A is the fraction of energy absorbed on the Earth's surface: A represents the *albedo* of the Earth, that is, the overall reflectivity of our planet (its dimensionless value is approximately 0.29); F is the solar energy flux at the top of the Earth's atmosphere (energy per unit area per unit time). F is also known as the *solar constant* and its value is approximately 1370 W m^{-2}. E_E is the energy released by the Earth as electromagnetic radiation (emitted as a black body):

$$E_E = 4\pi R^2 \sigma T^4 \qquad (4.7c)$$

R is the radius of the planet; σ is the Stefan–Boltzmann constant ($5.67 \times 10^{-8}\ \text{W m}^{-2}$), and T is the temperature of the Earth. An additional consideration has to be made: the conceptual absorbing disk perpendicular to the solar radiation has an area of πR^2, and this factor multiplies the E_A term.

The law of conservation of energy demands that both energies be equal:

$$\pi R^2 (1 - A)F = 4\pi R^2 \sigma T^4 \qquad (4.8)$$

Solving for T one gets

$$T^4 = \frac{(1 - A)F}{4\sigma} \qquad (4.9)$$

and

$$T = \left[\frac{(1 - A)F}{4\sigma}\right]^{\frac{1}{4}} \qquad (4.10)$$

Substituting the known values, one gets

$$T = \left[\frac{(1 - 0.29)1370}{4(5.67 \times 10^{-8})}\right]^{\frac{1}{4}} \qquad (4.11)$$

$$T = 256\ \text{K}$$

However, the surface temperature of the Earth is 298 K. This temperature difference is attributed to what is known as the *greenhouse effect*, where part of

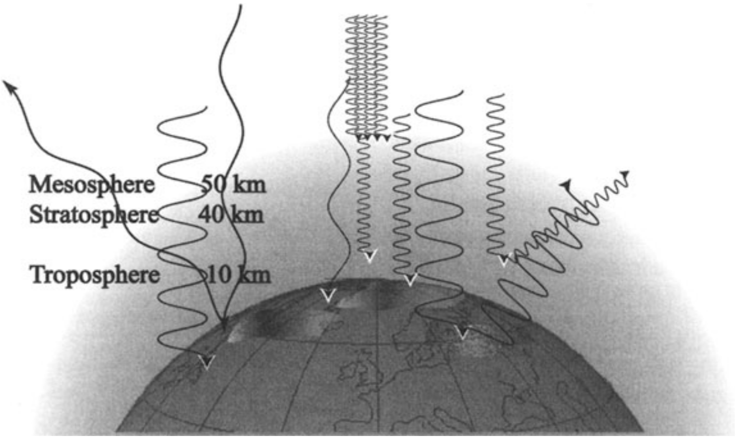


FIGURE 4.2. Behavior of incoming radiation (as noted, part of it is reflected by clouds, aerosols, and the surface of the Earth. The relative magnitudes of the wavelengths are denoted by the different peak-to-peak and valley-to-valley separations).

the emitted radiation (in the infrared region) is absorbed by gases such as water vapor, carbon dioxide, nitrous oxide, methane, CFCs, and SF_6, known as *greenhouse gases.* Their effect is further discussed in Section 8.4, and the efficiencies of some of them (relative to that of CO_2) are shown in Table 4.3.

It is worth noting that O_2 and N_2 are IR transparent as they do not posses a dipole moment and thus cannot undergo a change in it (because their only vibrational mode is symmetrical).

TABLE 4.3. Greenhouse efficiency of key gases.

Component	Greenhouse efficiency per molecule
CO_2	1
CH_4	21
N_2O	206
CFC-11	12400
CFC-12	15800

4.6 Stratospheric Chemistry

Stratospheric ozone protects life on the surface of the Earth by screening the harmful UV light coming from the Sun through a photodissociation mechanism:

$$O_3 + h\nu \rightarrow O_2 + O^\bullet \qquad (4.12)$$

$$O^\bullet + O_2 \rightarrow O_3 \qquad (4.13)$$

Thus ozone absorbs UV radiation without being consumed; the net result is to convert UV radiation into heat. This is why temperature increases with altitude in the stratosphere, giving rise to the *inversion layer* that traps molecules in the troposphere. Ozone is consumed if an $O^\bullet$ atom collides with an O_3 molecule:

$$O^\bullet + O_3 \rightarrow 2O_2 \text{ “recombination”} \qquad (4.14)$$

This reaction is slow, and if it were the only mechanism for ozone loss, the ozone layer would be thicker than it really is. Certain trace chemical species, mainly free radicals such as the oxides of nitrogen ($NO^\bullet$ and $NO_2^\bullet$), atomic hydrogen ($H^\bullet$), oxygen species ($^\bullet OH$ and $HO_2^\bullet$), and chlorine species ($Cl^\bullet$, $ClO^\bullet$ and $ClO_2^\bullet$) are responsible for catalyzing the recombination reaction. The thickness of the ozone layer is then the result of a competition between the photodissociation and recombination mechanisms.

In the 1930s, S. Chapman proposed the following set of reactions to explain the chemistry of oxygen species in the stratosphere:

$$O_2 + h\nu \rightarrow O^\bullet + O^\bullet \qquad (\lambda < 240\,\text{nm}) \qquad (4.15a)$$

$$O^\bullet + O_2 \rightarrow O_3 \qquad (4.15b)$$

$$O_3 + h\nu \rightarrow O_2 + O^\bullet \qquad (\lambda < 320\,\text{nm}) \qquad (4.15c)$$

$$O^\bullet + O_3 \rightarrow 2O_2 \qquad (4.15d)$$

Figure 4.3 shows the ozone distribution within the stratosphere, before 1984. (The problemetic *ozone hole* is dealt with in Chapter 8).

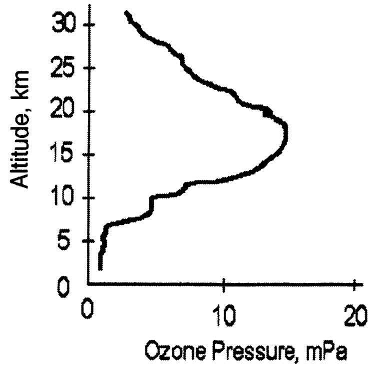


FIGURE 4.3. Ozone distribution in the stratosphere.

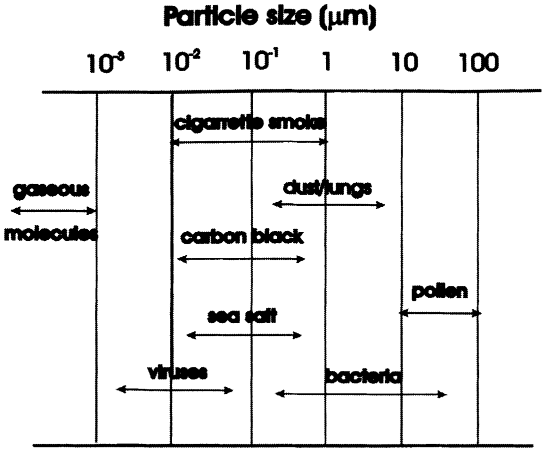


FIGURE 4.4. Size ranges of particles in the atmosphere.

4.7 Aerosols

In addition to gaseous species in the atmosphere, there are solid and liquid particulates as well. These are known as *aerosols* and their sizes vary from micrometers to millimeters. Sea salt, dust, and volcanic emissions are natural sources of aerosols. Figure 4.4 illustrates the sizes of some particulates in the atmosphere.

Aerosols alter the Earth's radiative process and thus affect its temperature and climate. A very important component of aerosols is black carbon (soot) that is released from the burning of fossil fuels and biomass.

Related Experiment in the Companion Book

10. Halogenated hydrocarbons and the ozone layer depletion

Additional Related Experiments/Activities

Driscoll, J. A. "Ultraviolet Absorption of Ozone," *J. Chem. Educ.* **1977**, *54*, 675.

Chasteen, T. G. "Ozone's Problem with Polar Stratospheric Clouds," Sam Houston State University. Chemistry-Based QuickTime, Shockwave Flash, http://www.shsu.edu/~chm_tgc/sounds/sound.html

Fang, C. H. "A Simplified Determination of Percent Oxygen in Air," *J. Chem. Educ.* **1998**, *75*, 58–59.

Gordon, J.; Chancey, K. "The Determination of the Percent of Oxygen in Air Using a Gas Pressure Sensor," *J. Chem. Educ.* **2005**, *82*, 286–287.

Koubek, E.; Glanville, J. O. "The Absorption of UV Light by Ozone," *J. Chem. Educ.* **1989**, *66*, 338.

Lisk, G. M. "Lecture-Demonstration: Ozonizer," *J. Chem. Educ.* **1931**, *8*, 2429.

Ransford, J. E. "Demonstration of Ozone from Bottled Oxygen," *J. Chem. Educ.* **1951**, *28*, 477.

Whisnant, D. M.; Lever, L.; Howe, J. "Cl_2O_4 in the Stratosphere: A Module from the Physical Chemistry On-Line Project," *J. Chem. Educ.* **2005**, *82*, 334–335.

References and Further Reading

Alloway, B. J.; Ayres, D. C. *Chemical Principles of Environmental Pollution*, 2nd ed.; Chapman & Hall: London, 1997.

Brooks, B. O.; Davies, W. F., *Understanding Indoor Air Quality*; CRC Press: Boca Raton, FL, 1992.

Heicklen, J., *Atmospheric Chemistry*; Academic Press: New York, 1976.

IUPAC (International Union of Pure and Applied Chemistry). Commission on Atmospheric Chemistry, "Glossary of Atmospheric Chemistry Terms," *Pure Appl. Chem.* **1990**, *62*, 2167–2219.

IUPAC (International Union of Pure and Applied Chemistry). Compendium of Chemical Terminology. http://www.iupac.org/publications/compendium/R.html

IUPAC (International Union of Pure and Applied Chemistry) Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F. Jr.; Hynes, R. G.; Jenkin, M. E.; Kerr, J. A.; Rossi, M. J.; Troe, J. "Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry". http://www.iupac-kinetic.ch.cam.ac.uk/summary/IUPACsumm_web_March2005.pdf

Kay, J. G.; Keller, G. E.; Miller, J. F. *Indoor Air Pollution*; Lewis Publishers: Michigan, 1991.

Leslie, G. B.; Lunan, F. W. *Indoor Air Pollution, Problems and Priorities*; Cambridge University Press: Cambridge, 1992.

Macalady, D. L., Ed., *Perspectives on Environmental Chemistry*, Oxford University Press: Oxford, 1998.

Newman, L., Ed., *Measurement Challenges in Atmospheric Chemistry*; Advances in Chemistry Series 232, American Chemical Society: Washington, D. C., 1993.

Roan, S. *Ozone Crisis*; Wiley: New York, 1989.

Singh, H. B., Ed. *Composition, Chemistry and Climate of the Atmosphere*; Wiley: New York, 1995.

Spiro, T. G.; Stigliani, W. M. *Chemistry of the Environment*; Prentice Hall: New Jersey, 1996.

The Ozone Secretariat of the United Nations. http://www.unep.ch/ozone/

Wayne, R. P. *Chemistry of Atmospheres*; Oxford Press: New York, 1991.

5

The Chemistry of Processes in the Lithosphere

In this chapter we give a brief overview of the structure and composition of the Earth, discuss some properties of rocks and minerals, explain the origin of minerals and the consequences of weathering, analyze the dissolution and precipitation of solids, and present key soil phenomena and components.

5.1 The Lithosphere and its Components

5.1.1 Structure of the Solid Earth

The mass of the Earth is estimated at 6×10^{24} kg. The structure of its solid mass is mainly a result of a process called *differentiation* that includes both physical (e.g., thermal) and chemical processes. As deduced from geophysical data, this structure is divided into three spherical layers: core, mantle, and crust.

5.1.1.1 Core

The *core* is at the center of our planet and has a diameter of approximately 2500 km. It is believed that it has two physical states: solid in the inner core and liquid in the outer core. The core as a whole is composed primarily of Fe and Ni. With respect to the association of Fe and Ni, we can say that probably because of the high temperatures, the rotations of the Earth, and its density, molten iron moved at some point toward the center of the Earth. As it moved in this direction, the iron came in contact with elements of less negative (i.e., more positive) reduction potentials and reduced them to the elemental state. For this reason, such elements are called *siderophiles* (iron-loving elements) and nickel is one of them. Two alternative definitions for a *siderophile* involve (1) any element that has a weak affinity for oxygen and sulfur and that is readily soluble in molten iron, or (2) an element concentrated in the metallic rather than in the silicate and sulfidic phases of meteorites. We will adhere to the initial definition given above.

5.1.1.2 Mantle

Surrounding the core, the *mantle* has a thickness of about 2900 km. Its mass is estimated at 4×10^{24} kg. It is composed mainly of high-density silicates of Mg and Fe. It is divided into three layers: lower (2000 km), transition (500 km), and upper mantle (360 km). The lower mantle is predominantly formed by Mg-perovskite, Mg-wurstite, and Ca-perovskite, which contain water in their crystal structures. Incredibly as it may seem, because of this water content the lower mantle is believed to contain more water than the oceans.

5.1.1.3 Crust

Encompassing the mantle lies the outermost—and thinnest—layer called the *crust*. It is only about 8 km beneath the oceans (*oceanic* crust) and an average of about 40 km under the continents (*continental crust*). Its mass is estimated at 2.4×10^{22} kg, and is constituted primarily of (oxygenated) compounds of Si (approximately 60%) and Al (approximately 15%): silica, quartz, silicates, silicoaluminates, and others (e.g., metal oxides). As can be deduced from these compositions, crust materials are predominantly oxidized, whereas materials in the core are predominantly present in their reduced form. A more detailed classification of rocks is given below.

In general, siderophiles tend to be less concentrated on the crust and the surface of the Earth. Other siderophiles—besides Fe and Ni—include elements in the center-bottom of the periodic table (Co, Mo, Ru, Rh, Pd, W, Re, Os, Ir, Pt, Au).

Elements with more negative reduction potentials than Fe are typically grouped according to their relative affinity for oxygen or sulfur. Those with a higher affinity for oxygen (*lithophiles*) and more negative potentials include most elements in groups 1–5, 17, as well as some second and third row elements. Those having a higher affinity for sulfur (*chalcophiles*) include most of the heavier elements in groups 11–16. Such differences in affinity generally follow the HSAB theory discussed earlier (Chapter 2), since oxygen is a harder base than sulfur.

5.1.2 Classification of Rocks

Rocks can be "genetically" classified as igneous, metamorphic, and sedimentary.

5.1.2.1 Igneous Rocks

Cooling and solidification of molten magma or lava give rise to igneous rocks (*intrusive* and *extrusive*, respectively). Because their primary component is SiO_2, its percent content is what accounts for their classification. However, it must be borne in mind that actual SiO_2 (and other oxide) moieties do not truly exist within rocks but are part of the more complex structures described above. Nonetheless, minerals containing oxygen may be conceptualized as combinations of single oxides (e.g., the composition of perovskite can be written either $CaTiO_3$ or else $CaO{\cdot}TiO_2$). In this same sense, the slightly acidic—but rather insoluble—SiO_2 (as well as other oxides) is more like a *virtual* rather than an individual species. Modern geology describes a quartz-rich rock as *felsic* or *silicic* (as opposed to the term *acidic* that was used in older approaches), and basic rocks and minerals as *mafic*. Interestingly enough, a decrease in SiO_2 content is often accompanied by an increase in MgO and CaO content (basic oxides). The average SiO_2/MgO percent contents of the following rocks are used for their classification: granite (felsic, 72.0/0.5), diorite (intermediate, 54.5/3.8), basalt (mafic, 48.4/8.1), and peridotite (ultramafic, 43.5/34.0). See Figure 5.1.

5.1.2.2 Sedimentary Rocks

Sedimentary rocks are typically a result of erosion and the interaction of the environment on igneous and metamorphic rocks; they are formed by the aggregation of mineral particles or sediments. Their SiO_2/CaO percent composition can be quite varied: for example, from 74.3/4.9 (sandstones) down to 8.2/40.5 (limestones). On the average, sedimentary

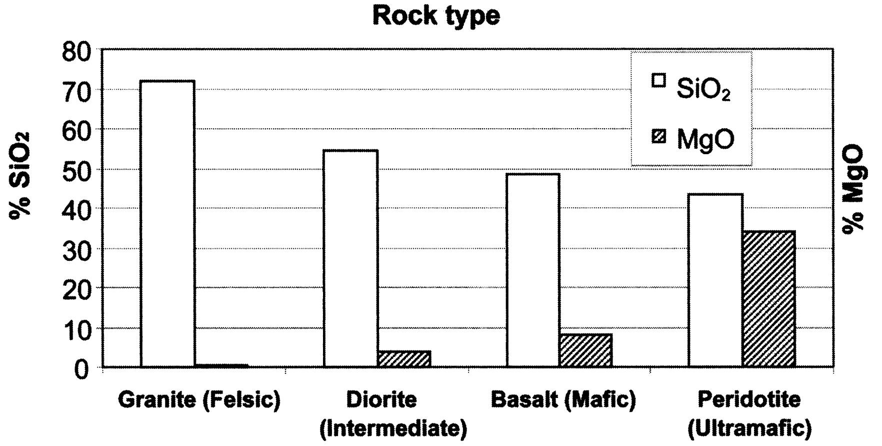


FIGURE 5.1. Relationship between the SiO_2 and MgO contents of igneous rocks.

rocks have a lower silicate content than igneous and metamorphic rocks.

5.1.2.3 *Metamorphic Rocks*

Metamorphic rocks originate from physical or chemical changes produced in igneous or sedimentary rocks by high temperatures and pressures. They distinctively appear in zones where geological phenomena involving huge amounts of energy occurred (e.g., the formation of mountains). An example of such a chemical change is the production of wollastonite from quartz and calcite:

$$SiO_{2(s)} + CaCO_{3(s)} \xrightarrow{\Delta T,P} CaSiO_{3(s)} + CO_{2(g)} \tag{5.1}$$

This type of solid state reaction can be understood in light of the reaction between SiO_2 and CaO (produced by the thermal decomposition of $CaCO_3$ into CaO and CO_2). See Section 2.2.3.

5.1.2.4 *Rock-Forming Minerals*

Although there are more than 2,000 minerals identified, only a few are the most common rock-forming minerals. These are listed in Table 5.1.

The structural classification of silicates is based on the polymerization of silicon tetrahedra (SiO_4) and on the proportion of silicon-to-oxygen atoms (Si:O) as follows:

- 1:4 = nesosilicates (orthosilicates)
- 2:7 = sorosilicates
- 1:3 = cyclosilicates
- 1:3 and 4:11 = inosilicates
- 2:5 phyllosilicates
- 1:2 tectosilicates (quartz and feldspars)

5.2 Formation and Differentiation of Minerals and Ores

Physical, chemical, and biochemical phenomena gave rise to a wide variety of minerals. As indicated above, minerals originally differentiated according to their reduction potentials relative to iron (siderophiles, lithophiles, and chalcophiles). In a second stage, they differentiated according to their ionic radii, bonding preferences, lattice energies, and densities. The third stage—an ongoing process—contributes to such differentiation

TABLE 5.1. The most common rock-forming minerals.

Mineral	Type	Formula
Olivine		$(Fe,Mg)_2SiO_4$
Quartz		SiO_2
Feldspar	Plagioclase feldspar	$NaAlSi_3O_8$ to $CaAl_2Si_2O_8$ (continuous series)
	Potassium feldspar	$KAlSi_3O_8$
Mica	Muscovite	$KAl_2(AlSi_3O_{10})(F, OH)_2$
	Lepidolite	$KLi_2Al(Al,Si)_3O_{10}(F, OH)_2$
	Staurolite	$(Fe,Mg,Zn)_2Al_9(Si,Al)_4O_{22}(OH)_2$
	Biotite	$K(Fe,Mg)_3AlSi_3O_{10}(OH)_2$
Pyroxene	Enstatite series	$(Mg,Fe)_2Si_2O_6$
	Augite	$Ca(Mg,Fe)Si_2O_6$
Amphibole	Hornblende (an inosilicate)	$(Ca,Na)_{2-3}(Mg,Fe,Al)_5[(Si,Al)_8O_{22}](OH)_2$
	Actinolite	$Ca_2(MgFe)_5Si_8O_{22}(OH)_2$
	Glaucophane	$Na_2(Mg_3Al_2)(Si_8O_{22}(OH)_2)$ or $Na_2(Mg,Fe)_3Al_2Si_8O_{22}(OH)_2$
Other common minerals:		
Magnetite		Fe_3O_4
Garnet		$(Ca,Mg,Fe^{2+})_3(Al,Fe^{3+})_2Si_3O_{12}$
Calcite		$CaCO_3$
Dolomite		$CaMg(CO_3)_2$

by the interaction of the minerals in the crust with both pristine and polluted environments; these phenomena are generically called *weathering* and are discussed in more detail below. But before discussing this further, we will briefly go over the phenomena that caused the formation of ore minerals.

An ore is a metal-bearing mineral that is valuable enough to be mined. Ore formation is primarily due to temperature and pressure effects (e.g., magmatic concentration, deposition upon cooling, evaporation, hydrothermal processes), weathering and transport phenomena (e.g., sedimentation, metamorphism, mechanical concentration, residual concentration), and chemical processes (e.g., abiotic and biotic oxidations, and reductions). These effects, phenomena and processes are illustrated in Figures 5.2–5.4.

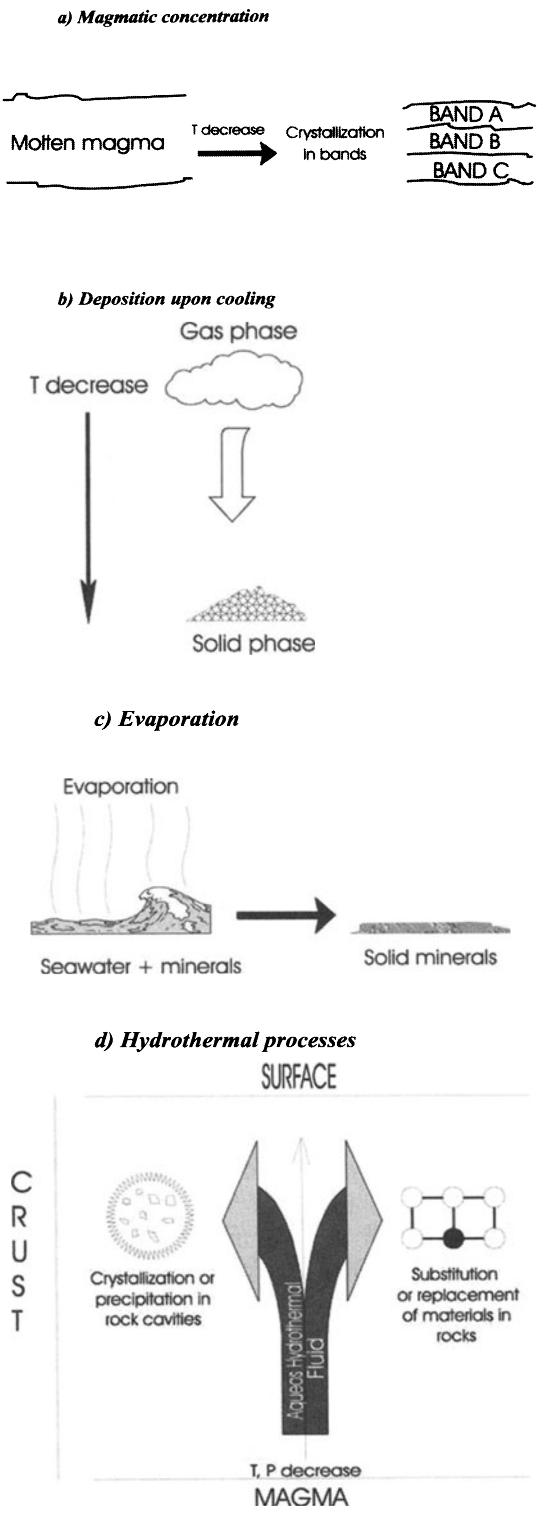
5.3 Weathering

The interaction of crust minerals with both pristine and polluted environments is called *weathering*. Such interaction can be of a physical, chemical, or biochemical nature (or a combination of these). A brief description of each type is given below.

5.3.1 Physical Weathering

Physical phenomena bring about weathering as a result of temperature gradients, abrasion, erosion, mechanical forces, and other similar conditions.

- *Temperature gradients.* These gradients produce cracks in rocks as a result of expansion–contraction cycles. The degree of expansion–contraction is dependent on the individual thermal expansion coefficients. Interestingly, it is believed that ancient civilizations took advantage of the expansion–contraction cycle of water/ice to split rocks apart for decorative and construction purposes.
- *Abrasion.* Wind carries dust and solid particulate matter capable of abrading rocks and soils.
- *Erosion.* This condition, for example, can be brought about by water physically washing away soil particles.


a) Magmatic concentration

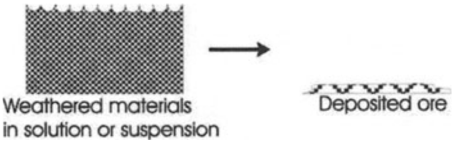
b) Deposition upon cooling

c) Evaporation

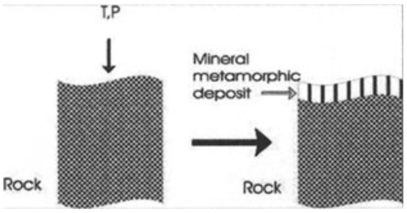
d) Hydrothermal processes

FIGURE 5.2. Ore formation phenomena: Temperature effects.

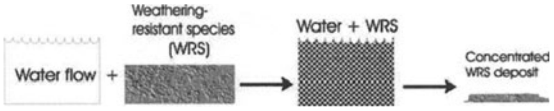
a) Sedimentation



b) Metamorphism



c) Mechanical concentration



d) Residual concentration

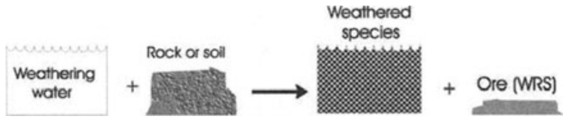


FIGURE 5.3. Ore formation phenomena: Weathering and transport.

- *Mechanical forces.* Plant roots and earthquakes are examples of phenomena that indirectly give rise to weathering by exposing larger surfaces of rocks.

5.3.2 Chemical Weathering

The migration of compounds on the Earth's surface is part of the minor or exogenous cycling of matter on Earth. This cycling of matter depends largely on water cycling and atmospheric processes. The movement of matter and the transformation of compounds in natural aqueous reservoirs are responsible for the chemical composition of natural water. The main processes involved are the weathering of rocks and the transformation of soils.

Weathering reactions are caused by the interaction of water and air with the near surface of compounds contained in the crust of the Earth. Such reactions are slow, and the rates are sensitive to water flow and/or to the rate of mineral surface reactions. Surface runoff interacts minimally, but infiltrating and percolating water has an intense interaction.

When minerals are bathed with a film of water, many tend to dissolve. This process will depend on the solubility of the mineral or soil ions in water, and on the composition, pH, redox potential, and frequency of renewal of the aqueous film surrounding the mineral.

Rock-forming minerals and igneous rocks react with water and the species contained in it, and with ambient oxygen, thereby weakening rocks through solubilization (e.g., hydrolysis of silicates), redox, and precipitation reactions; the rocks are transformed in this manner into soils and sediments that are further broken up through physical weathering that favors the transport processes.

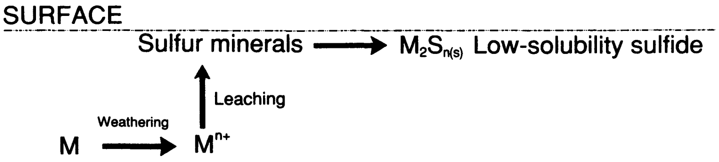
The dissolution and precipitation processes and equilibria taking place between the aqueous and soil phases determine their final composition and the mobility of ions in both phases.

As a "rule of thumb," chemical weathering is predominant in warm, moist regions, where vegetation is abundant. The most chemically stable minerals may also undergo chemical weathering by being physically weathered in the first place, so that a higher surface is exposed to the chemical action of water and the atmosphere (see *Physical weathering*, above).

The change in natural conditions from dry events or seasons to extremely wet seasons modifies and complicates the weathering reactions. During the dry seasons the solute concentrations in the water films increase, the total surface covered with these water films decreases, and the chemically active sites become less reactive. New equilibria are established due to the elevated concentration of solutes, and precipitation reactions may occur.

(a) Abiotic

1. Oxidation



2. Reduction

In the above scheme, M^{n+} may be chemically reduced to $M^{(n-1)+}$ with subsequent (insoluble) sulfide formation.

(b) Biotic

Different bacteria (mainly autotrophic, i.e., not dependent on organic material for their carbon supply) can effect oxidation or reductions of minerals.

1. Oxidation

$$2FeCO_3 + \tfrac{1}{2}O_2 + 3H_2O \xrightarrow{\textit{ferrobacillus}} \underset{\textit{Iron ore}}{2Fe(OH)_3} + 2CO_2$$

2. Reduction

$$\begin{tikzcd} nSO_4^{2-} + 2C_nH_{2n}O_n + 2nH^+ \arrow[r, "\textit{desulfovibrio}", "\textit{desulfuricans}"'] & nH_2S + 2nCO_2 + 2nH_2O \arrow[d, "2M^{x+}"] \\ & M_2S_x \text{ \textit{Sulfide ore}} \end{tikzcd}$$

FIGURE 5.4. Ore formation phenomena: Chemical processes.

In a subsequent wetting event the primary minerals, the precipitates, and the secondary minerals formed under dry conditions may react. As new low-concentration water films come in contact with the minerals, the dissolution processes are activated once again.

Examples 5.1, 5.2 and 5.3 deal with different aspects of physical and chemical weathering.

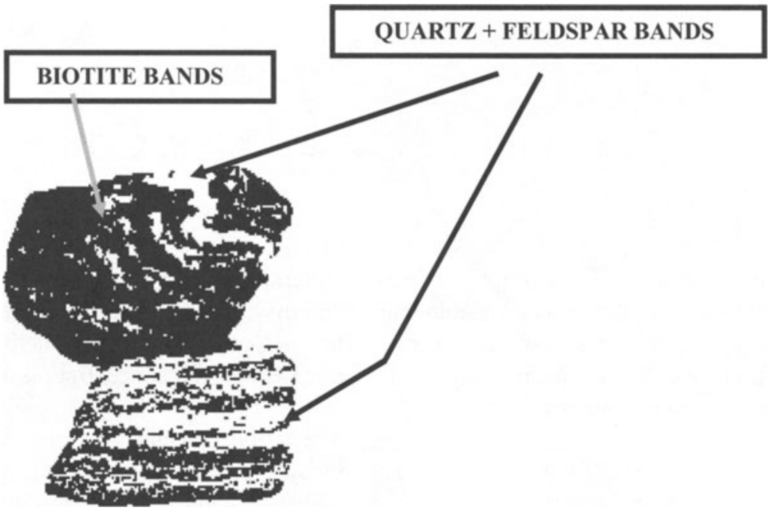
Temperature, CO_2, and oxygen levels also have an impact on the weathering processes and on water composition. Vegetation activity determines to a great extent the concentration of oxygen and CO_2 in the soil and in the water films surrounding it. Vegetation consumes oxygen and liberates CO_2, thereby increasing soil acidity and decreasing the oxidative nature of its environment. On the other

Example 5.1 Weathering of oxides. To better understand its weathering process, the chemical composition of a quartz-feldspar-biotite gneiss was analyzed as a fresh rock, and also after weathering (see the figure below). The weights (w_0) of five oxides (labeled A, B, C, D, and E) found in 100 g of the fresh rock, and their weights after weathering (w_t), are reported in the following table (see Krauskopf, 1967).

Oxide	**w_0, g**	**w_t, g**
A	71.48	55.59
B	14.61	14.61
C	0.69	1.23
D	3.84	0.07
E	0.32	4.68

With this information and knowing that the selected oxides (not in order) are those of the elements Na, H, Al, Si, and Fe(III):

(a) Calculate the absolute weight change (i.e., loss or gain) of each oxide for a 100 g sample of fresh rock.
(b) Calculate the % change in the weight of each oxide, relative to its initial amount.
(c) Plot the weights at the beginning and at the end of the weathering process vs the relative degree of weathering. Suggestion: Use a log scale for the *y*–axis, and plot a relative degree of weathering as the *x*–axis (i.e., only the initial and final points).
(d) Write the chemical formulas of the natural oxides of Na, H, Al, Si and Fe(III).
(e) Assuming that the aluminum oxide is not weathered, assign the formula of each oxide to its label. Hint: table 5.1 can give an idea of which oxide should be present in the largest amount.



A weathered quartz-feldspar-biotite gneiss (Adapted from: http://geology.csupomona.edu/).

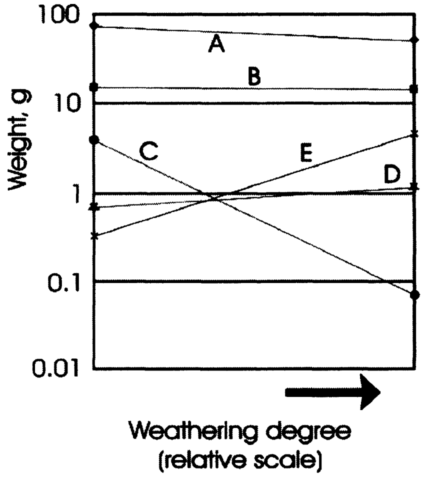
Answer

(a, b)

	w_0, g	w_t, g	Absolute weight change, g	Percent change
A	71.48	55.59	−15.89	−22.2
B	14.61	14.61	0	0
C	0.69	1.23	0.54	78.26
D	3.84	0.07	−3.77	−98.2
E	0.32	4.68	4.36	1363

Note that the absolute weight change (in grams) is numerically identical to the weight percent change in a 100 g sample.

(c)



(d) The oxides to be labeled are Na_2O, H_2O, Al_2O_3, SiO_2, and Fe_2O_3.

(e) Because Al_2O_3 is not weathered, then its weight remains constant (i.e., **oxide B**).

- From the type of the rock, from Table 5.1 it is clear that the main component (and thus the highest in composition) must be SiO_2 (i.e., **oxide A**). The observed loss is probably due to hydrolysis.
- H_2O gets incorporated into the weathered rock, and thus it shows a large percentage increase (i.e., **oxide E**).
- Na_2O is fairly soluble, and it is lost during weathering (i.e., **oxide C**).
- The only one remaining is Fe_2O_3 (i.e., **oxide D**). The observed increase is probably due to hydration.

hand, temperature greatly affects the vegetative activity as well as the evaporative processes.

In summary, the main weathering reactions that contribute to the introduction or removal of solutes in water and to the transformation of rocks are dissolution, precipitation and redox reactions. Because redox reactions were treated in Section 2.3, we now proceed to analyze more in depth the chemistry of dissolution and precipitation reactions.

Example 5.2 Erosion rates.

The Rhine River (above Lake Constance) averages a Mg^{2+} composition of 9 mg L^{-1} (see Stumm, 1996). If the annual runoff in that area is approximately 1 m^3 per m^2 of geographical area, estimate the erosion rate of Mg^{2+} (as $MgCO_3$), in g m^{-2} y^{-1}.

Answer

Erosion rate = (9 mg Mg^{2+}/L) (1 m^3/m^2y) (1 mmol $MgCO_3$/1 mmol Mg^{2+}) (74.3 mg $MgCO_3$/1 mmol $MgCO_3$) (1 mmol Mg^{2+}/24.3 mg Mg^{2+}) (10^3 L/m^3) (1 g/10^3 mg) = 31.2 g $MgCO_3$ $m^{-2}y^{-1}$

Example 5.3 Determination of stable species upon weathering.

The composition of the weathering water often determines the composition of the final stable mineral product. For example, the potassium feldspar/mica/gibbsite system under weathering can be simplified as follows (see Fergusson, 1985):

$$\underset{\text{potassium feldspar}}{KAlSi_3O_{8(s)}} \xrightarrow{H_2O} \underset{\text{mica}}{KAl_3Si_3O_{10}(OH)_{2(s)}} \xrightarrow{H_2O} \underset{\text{gibbsite}}{Al_2O_3{\cdot}3H_2O_{(s)}}$$

The corresponding *unbalanced* reactions in this process are

1. $KAlSi_3O_{8(s)} + H_2O_{(l)} + H^+_{(aq)} \rightleftarrows KAl_3Si_3O_{10}(OH)_{2(s)} + H_4SiO_{4(aq)} + K^+_{(aq)}$

   followed by

2. $KAl_3Si_3O_{10}(OH)_{2(s)} + H_2O_{(l)} + H^+_{(aq)} \rightleftarrows Al_2O_3 \cdot 3H_2O_{(s)} + H_4SiO_{4(aq)} + K^+{}_{(aq)}$

Using Le Chatelier's principle, one can see that water with high H^+ content and low K^+ content will favor the existence of gibbsite. Likewise, a high silicic acid content will favor feldspar. With this in mind,

(a) Balance reactions 1 and 2.
(b) Using the thermodynamic data of the table below, calculate ΔG^0 and K for each reaction.
(c) Find the equation that relates the log of the ratio $\{[K^+]/[H^+]\}$ and the log $[H_4SiO_4]$ for each reaction.
(d) Find the solubility limit of $[H_4SiO_4]$, knowing that

$$SiO_{2(s)} + H_2O_{(l)} \rightleftarrows H_4SiO_{4(aq)} \qquad K_{sp}^{25°C} = 1 \times 10^{-2.7}$$

(e) Draw an x-y diagram of log $\{[K^+]/[H^+]\} = y$, vs log $[H_4SiO_4] = x$ (called *stability field diagram*) containing both equations from part (c) for the region where $2.7 < x < -6$ and $0 < y < 10$.
(f) Which is the most stable species (potassium feldspar, mica, or gibbsite) at the point where $\{[K^+]/[H^+]\} = 10^2$ and $[H_4SiO_4] = 10^{-3}$?

Free energies of formation (The physical states are those in the two equations above).

Substance	ΔG_f^0 (kJ mol^{-1})
$KAlSi_3O_8$	−3582
$KAl_3Si_3O_{10}(OH)_2$	−5439
$Al_2O_3{\cdot}3H_2O$	−2322
H_4SiO_4	−1255
H_2O	−238
K^+	−280
H^+	0

Answer

(a) By performing normal mass and charge balances, the stoichiometric coefficients are

Eq. 1: [3, 12, 2] = [1, 6, 2]
Eq. 2: [2, 18, 2] = [3, 6, 2]

(b) $\Delta G_1^0 = \Delta G_{\text{Prod}}^0 - \Delta G_{\text{React}}^0 = [-5349 + 6(-1255) + 2(-280)] - [3(-3582) + 12(-238) + 0] = 73\,\text{kJ}$

Because $\Delta G_1^0 = -RT \ln K_1$, then

$$\begin{aligned} K_1 &= \exp(-\Delta G_1^0/RT) \\ &= \exp[-73000\,\text{J}/(8.314\,\text{J/K mol}) \times 298\,\text{K}] \\ &= 1.4 \times 10^{-13} \end{aligned}$$

In the same manner, $\Delta G_2^0 = 106$ kJ and $K_2 = \exp[-106000/(8.314 \times 298)] = 2.6 \times 10^{-19}$

Example 5.3 (*Continued*)

(c) Eq.1:

$$K_1 = [K^+]^2[H_4SiO_4]^6/[H^+]^2 = \{[K^+]/[H^+]\}^2[H_4SiO_4]^6$$

From here,

$$[H_4SiO_4]^6 = K_1/\{[K^+]/[H^+]^2\}$$

Taking log on both sides, and using the properties of logarithms

$$6\log[H_4SiO_4] = \log K_1 - 2\log\{[K^+]/[H^+]\}$$
$$\log\{[K^+]/[H^+]\} = 1/2\log K_1 - 3\log[H_4SiO_4]$$

By substituting and rearranging one gets

$$\log\{[K^+]/[H^+]\} = -3\log[H_4SiO_4] - 6.41$$

This line gives the equilibrium between *feldspar* and *mica*.

Now, for Eq. 2 one uses the same procedure and

$$\log\{[K^+]/[H^+]\} = -3\log[H_4SiO_4] - 9.3$$

This line gives the equilibrium between *mica* and *gibbsite*.

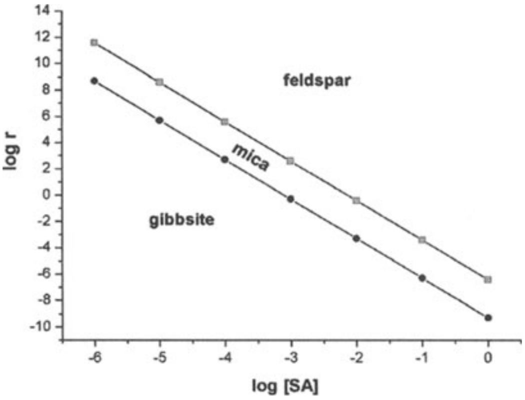
(d) Because SiO_2 is a solid and $H_2O_{(l)}$ is the reaction medium, one has that

$$K_{sp} = 1 \times 10^{-2.7} = [H_4SiO_{4(aq)}]$$

and thus the solubility limit for $[H_4SiO_{4(aq)}]$ is $1 \times 10^{-2.7}$ M (in the absence of other silica containing species).

(e) By using the equations of the two straight lines just calculated, and making [SA] = silicic acid concentration, and $r = [K^+]/[H^+]$ for each equation one can plot the corresponding log r vs log[SA] in the requested region:

[SA]	log [SA]	log r_1	r_1	log r_2	r_2
1.00E+00	0	−6.41	3.89045E-07	−9.30E+00	5.01187E-10
1.00E-01	−1	−3.41	0.000389045	−6.30E+00	5.01187E-07
1.00E-02	−2	−0.41	0.389045145	−3.30E+00	0.000501187
1.00E-03	−3	2.59	389.045145	−3.00E-01	0.501187234
1.00E-04	−4	5.59	389045.145	2.70E+00	501.1872336
1.00E-05	−5	8.59	389045145	5.70E+00	501187.2336
1.00E-06	−6	11.59	3.89045E+11	8.70E+00	501187233.6



(f) At the point where $[K^+]/[H^+] = 10^2$ and $[H_4SiO_4] = 10^{-3}$, we have log [SA] = −3, and log $r = 2$. From the plot one can see that the stable species at (−3, 2) is mica.

5.3.2.1 Dissolution and Precipitation of Solids

As introduced above, the interaction between the hydrosphere and the lithosphere frequently results in mass exchange. In this way rocks get dissolved, sediments build-up, stalactites and stalagmites form, materials get transported, and so on. The pH of water and of sediments determines the mobility and solubility of different elements, which may in turn modify the redox potential of the aqueous medium. For example, aluminum, calcium, magnesium, iron, manganese, and other metals become more soluble at low pH; if pH increases, their solubility decreases and precipitation occurs.

Using the ideas discussed in Section 2.1, the following equilibrium applies to an ionic solid in equilibrium with its ions in pure water:

$$M_xA_{y(s)} \rightleftarrows xM^{m+} + yA^{n-}$$
$$K_{sp} = [M^{m+}]^x[A^{n-}]^y \qquad (5.2)$$

(The conditions for this equation to be reasonably accurate are that the solid be of uniform composition and large grain size. In addition, it is assumed that no protolysis reactions nor ion pairing occur and that no complexes nor multinuclear species are formed).

Taking negative logs on both sides of equation 5.2,

$$-\log K_{sp} = pK_{sp} = -x\log[M^{m+}] - y\log[A^{n-}] \qquad (5.3)$$

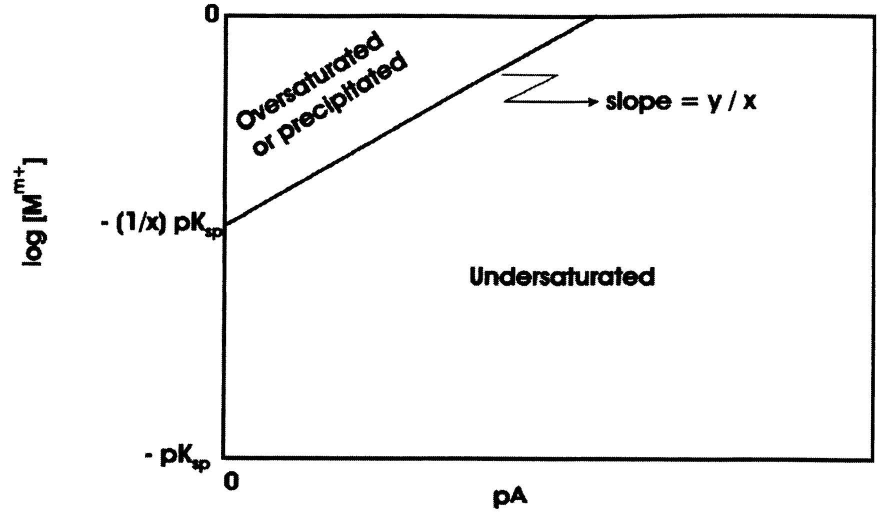


FIGURE 5.5. Precipitation diagram for an ionic solid in equilibrium with its aqueous ions.

From the general definition of $pZ = -\log Z$, one gets upon rearrangement:

$$x \log [\mathrm{M}^{m+}] = -\mathrm{p}K_{sp} + y\,\mathrm{pA} \qquad (5.4)$$

$$\log [\mathrm{M}^{m+}] = -(1/x)\mathrm{p}K_{sp} + (y/x)\,\mathrm{pA} \qquad (5.5)$$

This is a straight line with a slope y/x and an intercept equal to $-(1/x)\ \mathrm{p}K_{sp}$. The plot of this equation is actually the *precipitation diagram* for the system and is shown in Figure 5.5.

For salts of different stoichiometries (e.g., M_2A, MA, or MA_2), the equilibrium lines can be obtained from eq. 5.5 as shown in Example 5.4.

To calculate the solubility of a salt, let us use the ionic salt MA with a 1:1 ionic stoichiometry. For

Example 5.4 Slopes and intercepts in precipitation diagrams.

For the following ionic solids, find the slope and intercept of each precipitation line (eq. 5.5) in terms of the corresponding pK_{sp}:

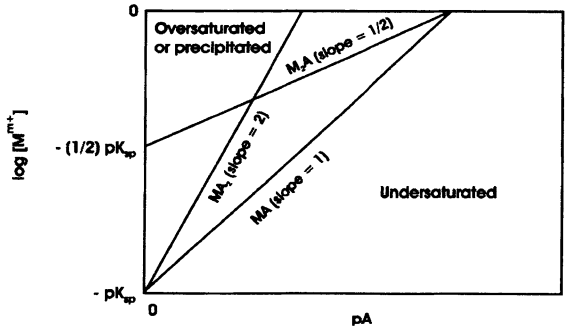
(a) $BaSO_4$, (b) CaF_2, and (c) Ag_2CrO_4

Answer

Using equation 5.5, one gets:

Salt	x	y	Slope $= y/x$	Intercept
$BaSO_4$	1	1	1	$-\mathrm{p}K_{sp}$
CaF_2	1	2	2	$-\mathrm{p}K_{sp}$
Ag_2CrO_4	2	1	1/2	$-1/2\mathrm{p}K_{sp}$

The corresponding plots are shown in the following figure.



Note: These lines become less valid as $[\mathrm{M}^{m+}]$ and $[\mathrm{A}^{n-}]$ increase, i.e., toward the extremes of each equilibrium line because the concentrations become more and more different than the activities.

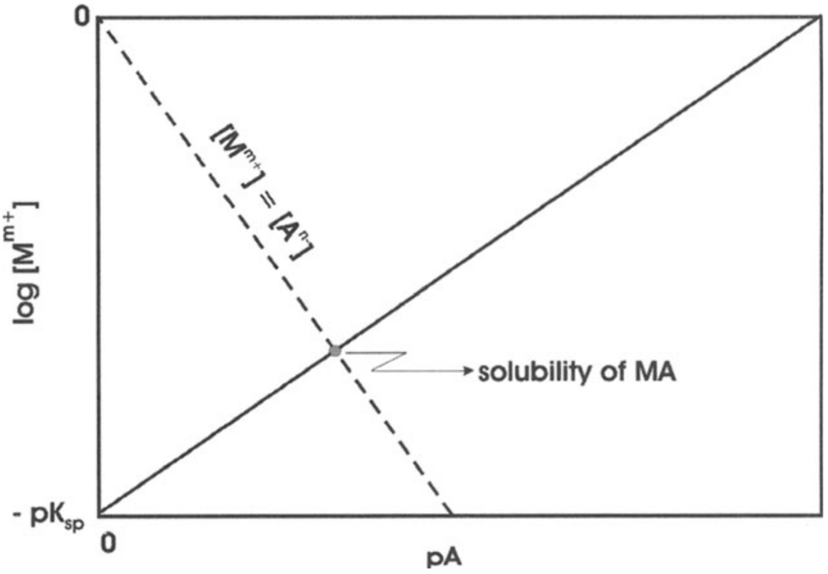


FIGURE 5.6. Solubility of the salt MA.

this salt,

$$[M^{m+}] = [A^{n-}] \tag{5.6}$$

Assuming that the concentration of any other ions possibly present (including H^+ and OH^-) is very small compared to $[M^{m+}]$ or $[A^{n-}]$, then

$$\log [M^{m+}] = \log [A^{n-}] = -pA \tag{5.7}$$

The dashed line in Figure 5.6 represents this condition. The solubility of this 1:1 salt is given by the concentrations of $[M^{m+}]$ and $[A^{n-}]$ at the intersection. In the general case, the solubility is given by equation 5.5.

Another way of looking at solubility equilibria to find out whether a solution is oversaturated, saturated, or unsaturated consists of calculating the free energy for the system in eq. 5.2. From eq. 2.58 and 2.69–2.72 one can write the free energy change for this equilibrium as

$$\Delta G^0 = -RT \ln K_{sp} + RT \ln Q = RT \ln(Q/K_{sp}) \tag{5.8}$$

where $Q = \{\Pi[\text{Products}]^{\text{products}}\}/\{\Pi[\text{Reactants}]^{\text{reactants}}\}$. Then, the following conditions apply:

If $Q < K_{sp}$, then $\Delta G^0 < 0$ and the solution is *undersaturated*
If $Q = K_{sp}$, then $\Delta G^0 = 0$ and the solution is *saturated*
If $Q > K_{sp}$, then $\Delta G^0 > 0$ and the solution is *oversaturated* (or in equilibrium with a *precipitate*)

Under real circumstances equilibrium conditions are difficult to attain, and kinetic criteria (which are often hard to predict) play a key role. To complicate matters, the stoichiometries of some of these reactions do not obey their theoretical chemical equations. In addition, the formation of a solid phase can be the result of successive reactions with varied rates. See, for example, the simplified precipitation pathway of ferric ions with hydroxide ions, depicted in Figure 5.7.

5.3.2.2 Dissolution of Natural Oxides

Ligands and metal complexes present in aqueous systems in contact with natural oxides can affect their dissolution either by promoting or inhibiting it. For example, some metal—EDTA complexes react with Fe_2O_3 and dissolve it, producing [Fe(III)EDTA]. Other minerals like Co(III)OOH and Mn(III)OOH reductively dissolve by oxidizing ligands and metal complexes. Dissolution rates can

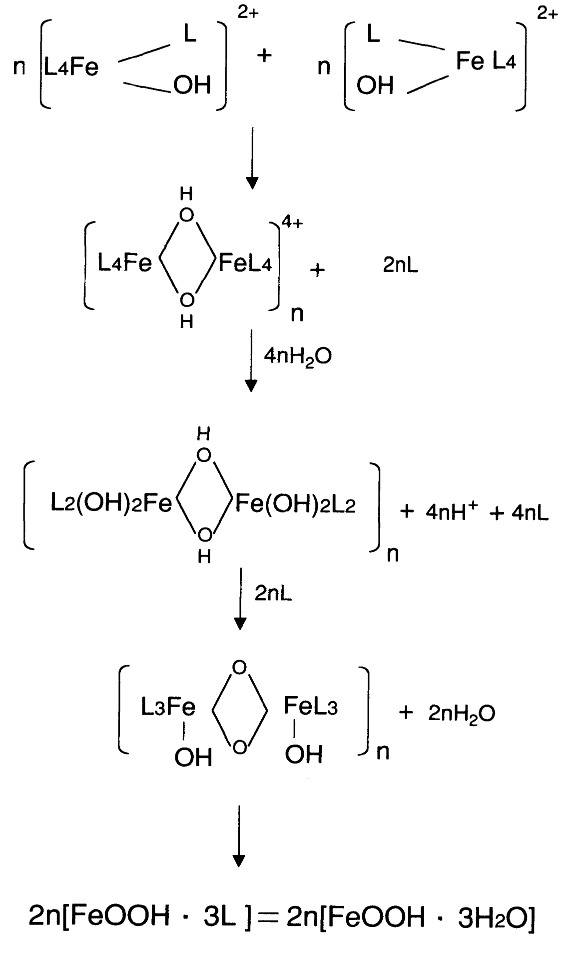


FIGURE 5.7. Simplified precipitation scheme of Fe^{3+} + OH^-. Here, L denotes H_2O.

be linear functions of the surface concentration of the ligands. The action of polyphosphate anions on the dissolution of solid metal oxides is discussed in Chapter 8.

Soil components often retain complexes more strongly than they retain metal ions alone. For example, the general description of a surface reaction for the complex of a divalent metal (e.g., Pb^{2+}) with a typical tetravalent ligand (e.g., $EDTA^{4-}$) is depicted by

$$\equiv SOH + ML^{2-} + H^+ \rightarrow \equiv S{-}L{-}M^- + H_2O \quad (5.9)$$

5.3.2.3 Stable and Metastable Solid Phases

To circumvent such seemingly insurmountable difficulties, approximations and simplifications can often be made. For example, even though the formation of a solid from a saturated solution can involve several successive reactions, one may judiciously select for analysis or prediction the one that presents the slowest rate. The so-called *Ostwald's phase rule* states that a supersaturated solution that undergoes a sudden alteration that takes it out of such a state will produce a *metastable* solid (instead of the expected thermodynamically stable solid). It is a very useful rule, although it is not always obeyed. Three limiting cases are shown in Figure 5.8 for different values of the overall crystallization rate (nucleation + crystal growth), v.

It is then clear that under a given set of conditions, metastable and/or stable phases can exist. To find the conditions for precipitation/dissolution of a stable solid, one can use the corresponding thermodynamic constants as shown in the following example.

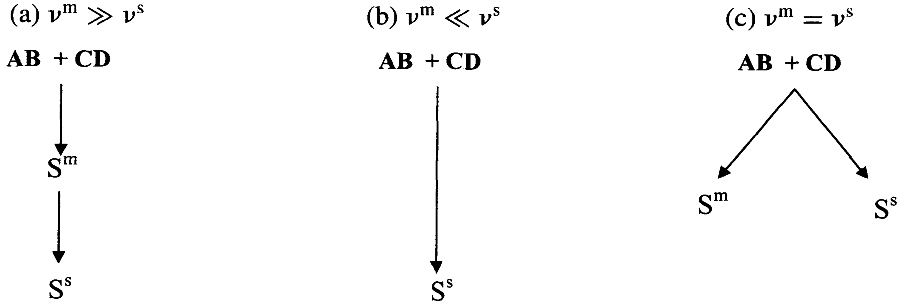


FIGURE 5.8. Formation of *metastable* (super index *m*) or *stable* (super index *s*) phases by precipitation of the solid S from an aqueous solution.

Example 5.5 With the following data, establish the four main equilibrium equations involved in the solubility/precipitation of iron (III) hydroxide, in the form: log [X] $= f$(pH). Then, plot the complete solubility diagram for this substance. Lastly, show the predominance zone of the insoluble $Fe(OH)_3$.

$$\begin{array}{llll}
\text{(A)}\ Fe(OH)_{3(s)} & \rightleftarrows & Fe(OH)_2^+ + OH^- & K_1 = 10^{-16.5} \\
\text{(B)}\ Fe(OH)_{3(s)} & \rightleftarrows & Fe(OH)^{2+} + 2OH^- & K_2 = 10^{-27} \\
\text{(C)}\ Fe(OH)_{3(s)} & \rightleftarrows & Fe^{3+} + 3OH^- & K_{sp} = 6.0 \times 10^{-38} \\
\text{(D)}\ Fe(OH)_{3(s)} + OH^- & \rightleftarrows & Fe(OH)_4^- & K_3 = 10^{-4.5}
\end{array}$$

Answer

(A) $Fe(OH)_{3(s)} \rightleftarrows Fe(OH)_2^+ + OH^-$

$$K_1 = 10^{-16.5}$$

$$[Fe(OH)_2^+][OH^-] = 10^{-16.5}$$

$$[Fe(OH)_2^+] = \frac{10^{-16.5}}{[OH^-]} = \frac{10^{-16.5}}{10^{-14}/[H^+]}$$

$$= 10^{-2.5}[H^+]^{-1}$$

$$\log[Fe(OH)_2^+] = -2.5 - \text{pH}$$

(B) $Fe(OH)_{3(s)} \rightleftarrows Fe(OH)^{2+} + 2OH^-$

$$K_2 = 10^{-27}$$

$$K_2 = 10^{-27} = [Fe(OH)^{2+}][OH^-]^2$$

$$[Fe(OH)^{2+}] = \frac{[H^+]^2}{10^{27}(10^{-14})^2}$$

$$[Fe(OH)^{2+}] = \frac{[H^+]^2}{10^{-1}} = 10[H^+]^2$$

$$\log[Fe(OH)^{2+}] = 1 - 2\text{pH}$$

(C) $Fe(OH)_{3(s)} \rightleftarrows Fe^{3+} + 3OH^-$

$$K_{sp} = 6.0 \times 10^{-38}$$

$$K_{sp} = [Fe^{3+}][OH^-]^3 \rightarrow [Fe^{3+}] = \frac{K_{sp}}{[OH^-]^3}$$

At 25°C, $[H^+][OH^-] = K_w = 10^{-14}$. Then,

$$[Fe^{3+}] = \frac{6.0 \times 10^{-38}}{(10^{-14}/[H^+])^3}$$

$$= \frac{6.0 \times 10^{-38}[H^+]^3}{10^{-42}}$$

$$= 6.0 \times 10^4 [H^+]^3$$

$$\log[Fe^{3+}] = 4.78 + 3\log[H^+]$$

$$= 4.78 - 3\text{pH}$$

(D) $Fe\ (OH)_4^- \rightleftarrows Fe(OH)_{3(s)} + OH^-$

$$K_3 = 10^{-4.5}$$

$$10^{4.5} = \frac{[OH^-]}{[Fe(OH)_4^-]}$$

$$[Fe(OH)_4^-] = \frac{[OH^-]}{10^{4.5}}$$

$$= \frac{10^{-14}/[H^+]}{10^{4.5}}$$

$$[Fe(OH)_4^-] = 10^{-18.5}/[H^+]$$

$$\log[Fe(OH)_4^-] = -18.5 + \text{pH}$$

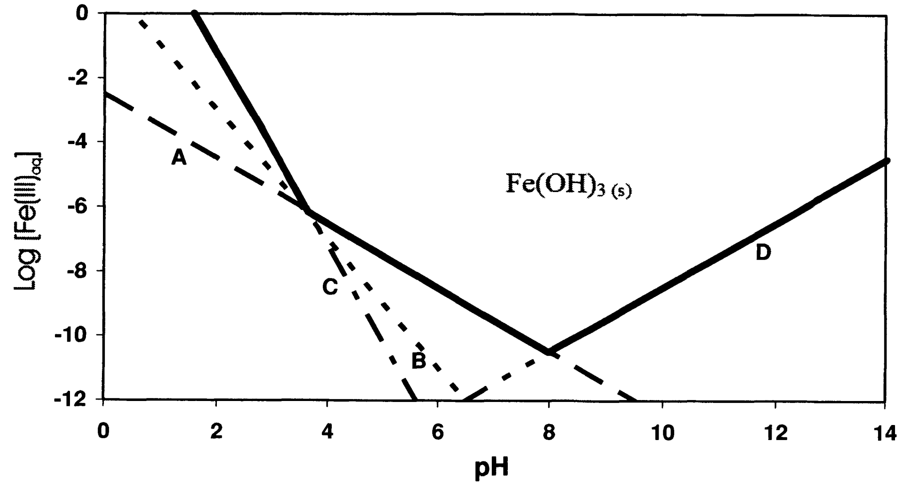
The corresponding plots are shown in the solubility diagram for iron (III) oxide, see below. In order to assign the different species to the correct side of their corresponding equilibrium lines, one can do the following reasoning for each (based on Le Chatelier's principle):

(a) For equations A, B, and C:
If one moves along the pH axis in the diagram toward higher pH values (which means higher $[OH^-]$), then the equilibrium shifts towards the *left*, and the solid $Fe(OH)_{3(s)}$ predominates.

(b) For equation D:
If one moves along the pH axis in the diagram toward higher pH values (which means higher $[OH^-]$), then the equilibrium shifts towards the *right*, and the soluble negative ion ($Fe(OH)^-_{4(aq)}$) predominates (not shown here).

Note: Precise diagrams involve nonlinear functions (as opposed to the straight lines drawn here in this simplified plot). This is due to at least three reasons:

1. The solubility lines in the present diagram are drawn considering only the *predominant* species, and not the *total* species.
2. No polynuclear species are considered here.
3. The soluble fraction of $Fe(OH)_3$ is considered too small as to be taken into account in our calculations.



5.3.3 Biological Weathering

Partially responsible for weathering phenomena are the biological processes that contribute to the emission of CO_2 through respiration and photosynthesis, modifying the pH and alkalinity conditions in the surrounding water. Biological processes also generate organic matter, which may serve to chemically reduce some inorganic species and produce organic ligands that increase the solubility of metallic ions and therefore their mobility (see Sections 3.1 and 7.4)

5.4 Soil Characteristics

The nature of soils is extremely complex, as they are formed by or contain minerals (e.g., clays, oxides, and carbonates), humic substances, other humidified organic matter, debris, leaves, etc. Clay minerals are hydrous aluminosilicates with a Si:O ratio of 1:2.5 (or 2:5). Structurally speaking, they are based on composite layers (i.e., $[Si_2O_5]_m^{2m-}$ or $[Si_4O_{10}]_n^{4n-}$) built by silica tetrahedral units that sandwich a sheet of octahedrally coordinated Al plus alkali and/or alkaline earth ions. Common examples include kaolinite, $Al_2(OH)_4Si_2O_5$ and the montmorillonite group, with the general empirical formula $R_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$ (here, $R = Na^+, K^+, Mg^{2+}, Ca^{2+}$; ions of other elements as Fe and Cr may exist as well). Clays constitute a large percentage of the sediments in water bodies.

The composition of soils leads to the following taxonomy.

5.4.1 Soil Taxonomy

Soil taxonomy distinguishes between *mineral* and *organic* soils. This distinction is not so easily applied in practice, and somewhat complicated rules need to be established. The different strata in soils are called *horizons* and practically all soils have both mineral and organic components. Those horizons that have less than 20–35% organic matter show properties that are closer to mineral soils, and vice versa.

Some examples of soil composition, arranged in decreasing order of organic content, are given in Table 5.2.

TABLE 5.2. Examples of soil composition

Soil type	Total organic carbon, TOC, %	Soluble organic matter, SOM, %	Moisture, %	pH
Peat	41.1	4.3×10^{-4}	50.2	7.0
Sand	3.0	1.7×10^{-4}	13.0	7.4
Clay	1.52	6.8×10^{-5}	22.0	7.3
Cambisols	0.22	4.6×10^{-5}	24.4	5.4

Data from Kozuh, 2000.

5.4.2 Humic Substances (HS)

Organic matter in soil contains abundant proportions of humic substances (HS), which are natural biogenic soil organic macromolecules that have high molecular weights, are typically refractory (i.e., resistant to biodegradation), and are yellow to black in color. They consist mainly of modified lignins as a consequence of microbial attack on vegetable decaying matter. Other HS precursors include leaf polyphenols, proteins and amino acids, lipids, as well as cellulose and other polysaccharides. HS are subdivided in humic acids (HA), fulvic acids (FA), and humines or kerogen (HU). HA form brown hydrogels after solvent extraction from a soil sample, followed by acidification with HCl, extraction with NaOH, and further acidification. On the other hand, FA remain soluble after this same reaction sequence as they tend to be more aliphatic and possess a higher functional group density than HA. HU are composites of HA + clays + minerals, and tend to be insoluble. Because HS typically aggregate as hydrophilic globular particles, they are easily hydrated in aqueous media. Representative formulas for HA include $C_{10}H_{12}O_5N$ and $C_{36}H_{30}O_{15}N_2 \cdot xH_2O$ ($x = 0\text{–}15$); for FA the formula is $C_{12}H_{12}O_9N$, with a small percentage of S. The largest HS are the HU and the smallest are the FA.

HA and FA are more likely than HU to be soluble owing to the presence of acidic groups. The main functional groups present in these substances are carboxyl, acidic phenolic hydroxyl, hydroxyl, quinone, and ketone; there are also some nucleic acids and their derivatives, as well as chlorophyll and chlorophyll-degradation products, phospholipids, amines, and vitamins. It is remarkable that in spite of their varying compositions, HA have a fairly constant carboxylic acid content of ca. 3 mmol/g of HA. At the same time, their total acidity typically varies from ca. 6 to 12 mmol/g of HA. Also, their hydrogen-to-carbon mole ratio (H/C) tends to be in a narrow range (ca. 1.3 ± 0.3), as does their oxygen-to-carbon mole ratio (ca. 0.6 ± 0.2). HS are sometimes found as ligands in metal complexes.

5.4.3 Decomposition of Organic Materials Adsorbed on Soil

Sorption refers to the acquisition of a chemical species from the aqueous phase by a contiguous solid phase. The three principal sorption mechanisms are *adsorption*, *precipitation*, and *absorption* (or incorporation).

For example, certain soil components can act as adsorption sites for organic materials and facilitate their photodecomposition upon exposure to sunlight. In the case that the soil component is a semiconductor, this process can occur through the formation of electron–hole pairs (i.e., *photocatalysis*, see Chapter 10). Photochemical processes may then affect soil components and composition.

Related Experiments in the Companion Book

4. Aqueous carbonate equilibria and water corrosiveness.
5. The point of zero charge of oxides.
7. Air oxidation of metal ions.
11. Acid mine (or acid rock) drainage.
14. Electrochemical treatment of polluted soils.

Additional Related Experiments/Activities

Bauer, R.; Birk, J.; Sawyer, D. *Laboratory Inquiry in Chemistry*, 2nd ed.; Brooks-Cole: Stamford, CT, 2005.

- Should we mine this ore? (Experiment 20)
- What is the pH of soil? (Experiment 37)

Blume, R.; Bader, H. J. *Environmental Chemistry in Classroom Experiments;*, IUPAC Publication, S.M.V. Traders and Printers: Delhi, 1990.

- Measurement of the pH of soils. Experiment 51.

Brouwer, H. "Acid Volatile Sulfides (AVS) in Sediment—An Environmental Experiment," *J. Chem. Educ.* **1995**, *72*, 182–183.

Christensen, J. K.; Høyer, B.; Kryger, L.; Pind, N.; Kong, L. S. "Sulfides in the Anaerobic Environment: The Determination of Hydrogen Sulfide and Acid-Soluble Metallic Sulfides in Sea-Floor Sediment," *J. Chem. Educ.* **1998**, *75*, 1605–1608.

Clemson University. *Introductory Chemistry Lab Experiments in Environmental Chemistry*; Environmental Chemistry Library. National Science Foundation, 2002. http://www.ces.clemson.edu/ecl/labs/general/index.html

- Analysis of soil

Davies, G.; Ghabbour, E. A.; Steelink, C. "Humic Acids: Marvelous Products of Soil Chemistry," *J. Chem. Educ.* **2001**, *78*, 1609–1614.

Davranche, M.; Lacour, S.; Bordas, F.; Bollinger, J.-C. "An Easy Determination of the Surface Chemical Properties of Simple and Natural Solids," *J. Chem. Educ.* **2003**, *80*, 76–78.

Fannis, L. N.; Jacobsen, E. K. "Soil Testing: Dig In!," *J. Chem. Educ.* **2006**, *83*, 240A–B.

GEPEQ-IQ-USP, "Experiences about Soils," *Quim. Nova Escola* (Brazil, in Portuguese) **1998**, *8*, 39–41.

Lunsford, S. K.; Slattery, W. "An Interactive Environmental Science Course for Education Science Major," *J. Chem. Educ.* **2006**, *83*, 233-236.

Moraes Pitombo, L. R.; Ribeiro Marcondes, M. E. "Experiences with Soil," *Quim. Nova na Escola* (Brazil, in Portuguese) **1998**, *8*, 39–41.

Vidal, M. M.; Filipe, O. M. S.; Cruz Costa, M. C. "Reducing the Use of Agrochemicals: A Simple Experiment," *J. Chem. Educ.* **2006**, *83*, 245–247.

Walczac, M. M. "Should we Build a Copper Mine?," *214th. Am. Chem. Soc. Nat. Meet.*, Chem. Ed. Division Paper #003. Las Vegas, NV, Sept. 7–11, 1997.

Willey, J. D.; Brooks Avery Jr., G.; Manock, J.; Skrabal, Stephen A.; S. C. F. "Chemical Analysis of Soils: An Environmental Chemistry Laboratory for Undergraduate Science Majors," *J. Chem. Educ.* **1999**, *76*, 1693–1694.

References and Further Reading

Baur, I.; Johnson, C. A. "Sorption of Selenite and Selenate to Cement Minerals," *Environ. Sci. Technol.* **2003**, *37*, 3442–3447.

Bureau de Recherches Géologiques et Miniéres, Paris. http://webmineral.brgm.fr:8003/mineraux/Caldwell.

Bernadette. "Digging Up Earth Day Resources," *J. Chem. Educ.* **2006**, *83*, 201–204.

Darling, D. Encyclopedia of Astrobiology, Astronomy & Spaceflight. http://www.daviddarling.info/encyclopedia/

Deer W. A.; Howi, R. A.; Zussman, J. *An Introduction to the Rock Forming Minerals*; Longman: London, **1971**. pp. 250–274.

e-Rocks: Berkshire, England. http://webmineral.com/data/Montmorillonite.shtml

Fassbender, H. W.; Bornemisza, E. *Chemistry of Soils*; Interamerican Institute for Cooperation in Agriculture (IICA) : San Jose, Costa Rica, 1987 (in Spanish).

Fergusson, J. E. *Inorganic Chemistry and the Earth;* Pergamon Series on Environmental Science, Vol. 6, Pergamon Press: Oxford, 1985.

Freixedas, F. G.; Bauza, A. C.; Sohnel, O. *Crystallization in Solution*; Reverte: Barcelona, 2000. (in Spanish).

Glossary of Geology, 4th ed.; American Geological Institute: Alexandria, VA, 1997.

Kozuh, N.; Stupar, J.; Gorenc, B. "Reduction and Oxidation Processes of Chromium in Soils," *Environ. Sci. Technol.* **2000**, *34*, 112–119.

Krauskopf, K. B. *Introduction to Geochemistry.* McGraw-Hill: New York, 1967. p. 103.

Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 84th, ed.; CRC Press: Boca Raton, FL, 2003–2004.

Mcardell, C. S.; Stone, A. T.; Tian, J. "Reaction of EDTA and Related Aminocarboxylate Chelating Agents with $Co^{III}OOH$ (Heterogenite) and $Mn^{III}OOH$ (Manganite)," *Environ. Sci. Technol.* **1998**, *32*, 2923–2930.

Mindat.org. The Mineral and Location Database. http://www.mindat.org/

Ministry of Energy, Mines and Petroleum Resources. British Columbia, Canada. http://www.em.gov.bc.ca/mining/geolsurv/Publications/InfoCirc/IC1987-05/rockmin.htm

Skinner, B. J.; Porter, S. C.; Park, J. *Dynamic Earth. An Introduction to Physical Geology*, 5th ed.; Wiley: New York, 2004.

Stumm, W.; Morgan, J. J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters.* 3rd ed.; Wiley Interscience: New York, 1996. Chapter 7.

Summers, D. B. *Chemistry Handbook*, 2nd ed.; William Grant Press: Boston, 1975.

Science and Technology Concentrates. *Chem. Eng. News* March 11, 2002. p. 40.

U.S. Department of Agriculture. Natural Resources Conservation Service. "Keys to Soil Taxonomy," 8th ed.; 1998. www.nssc.nrcs.usda.gov

Wikipedia. http://en.wikipedia.org/wiki/

Wordreference. English Dictionary. http://www.wordreference.com/definition/ore

6

The Chemistry of Processes in the Hydrosphere

Water is by far the most abundant liquid on Earth. It comprises between 70% and 90% of the weight of living organisms and covers nearly 71% of the Earth's surface. It is obvious that without liquid water, life as we know it would not be possible.

6.1 Natural Waters: Types and Composition

The water molecule can be viewed both as the dihydride of oxygen, as well as the oxide of hydrogen. It is a bent molecule due to the two oxygen–hydrogen bonds and the two unshared electron pairs in the oxygen atom. Because of their higher electronegativity, oxygen atoms attract the electron density from the O–H bond, creating strong dipoles that attract each other and form new bonds—known as *hydrogen bonds*—that maintain a strong adhesion among the molecules. This confers very special characteristics to water, making it an excellent solvent with a high surface tension and a wide temperature range in which it remains in the liquid state (0–100°C at normal pressure).

Water may be found in nature as vapor and humidity in the atmosphere; as a liquid in rain; as surface water in rivers, streams, ponds, lakes, watersheds, and interior seas; or forming part of seas and oceans. It is also found as groundwater, in vadose or unsaturated zones, occluded as interstitial water in the free spaces of soil and sediments, in springs and aquifers, or forming part of minerals as hydrates. It exists as a solid in glaciers, icebergs, hail, snow, and ice. Natural water may contain varying amounts of a myriad of chemical compounds that come from natural or anthropogenic sources, or both. In this sense, it is considered as a multicomponent electrolyte solution.

Water cycles, distributes, and purifies itself through the hydrological cycle over and over again . . . the same water, for centuries. Its distribution (considered as average static water storage) is shown in Figure 6.1.

Water is partially responsible for the cycling of elements within the global biogeochemical cycle through two main functions: (1) as a reagent in the chemical transformations of matter, and (2) as a transport medium for the dissolved and solid compounds to the different receiving bodies. The cycling of water (*hydrological cycle*, or simply, the *water cycle*, shown in Figure 6.2) is the dynamic part of the resource as it establishes the paths that different compounds may follow on their water-promoted movement. This cycling involves a water turnover of about 600,000 km^3 of water per year. Water separates from its solutes through evaporation or freezing processes, purifying itself to mix and react again with other compounds in its course as it moves and condenses as rain or snow. It returns to land, flowing over the surface or underground, until it reaches the oceans. This renews the cycling process. From this short discussion, it is clear that pure water is virtually impossible to find in nature.

6.1.1 Processes That Affect Water Composition

The composition of water in each site depends on its geological environment, as well as on the dissolution and chemical reactions of this solvent with

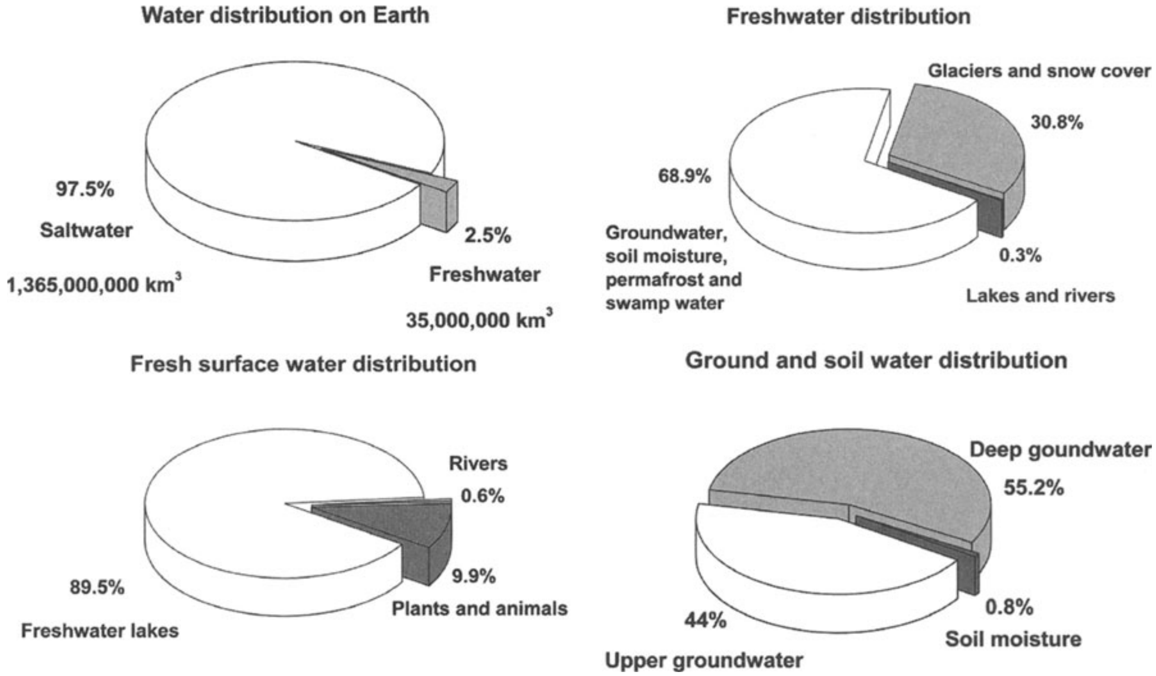


FIGURE 6.1. Water distribution. (Data from Shiklomanov, 1999).

solids, liquids, and gases during the water cycle. Many interdependent variables are thus involved, and no generalizations or correlations can be easily established for the composition of natural waters.

Several individual or combined processes contribute to the presence of different species that affect the composition and properties of natural waters. Examples include:

- Rain and dry deposition due to atmospheric inputs.
- Dissolution of gases from natural biological processes or from interfacial phenomena with the atmosphere or geological emissions.
- Deposition of airborne compounds derived from volcanic eruptions, and the presence of sulfur compounds brought about through hydrothermal activity (i.e., hot springs).
- Evaporation–precipitation processes, drainage, and leacheates due to rain and runoff.
- Gas exchange and dissolution reactions of atmospheric gases.
- Weathering processes (see definition in Section 5.3).
- Solubilization and suspension of minerals and salts in surface and underground water (caused by natural solubilization and movement of water through the Earth's crust and the erosion of rocks and minerals).
- Dissolution, precipitation, and deposition processes (e.g., those present during the formation of limestone caverns or in the formation of brines or high-salinity waters).
- Decomposition and decay of natural organic matter.
- Natural excretes, secretions, and metabolic products, as well as uptakes of aquatic and soil biota.
- Adsorption and ion exchange processes with sediments and colloids.

Consequently, the *composition* of water depends on

a. the geochemical nature of the bedrock
b. the weathering regimes
c. the environmental climatic conditions
d. the biogeochemical processes taking place in the zone
e. the chemistry of the components of the bedrock

The *concentration* of substances in surface and groundwater depends on the climatic, geological, and biological environments and regimes within

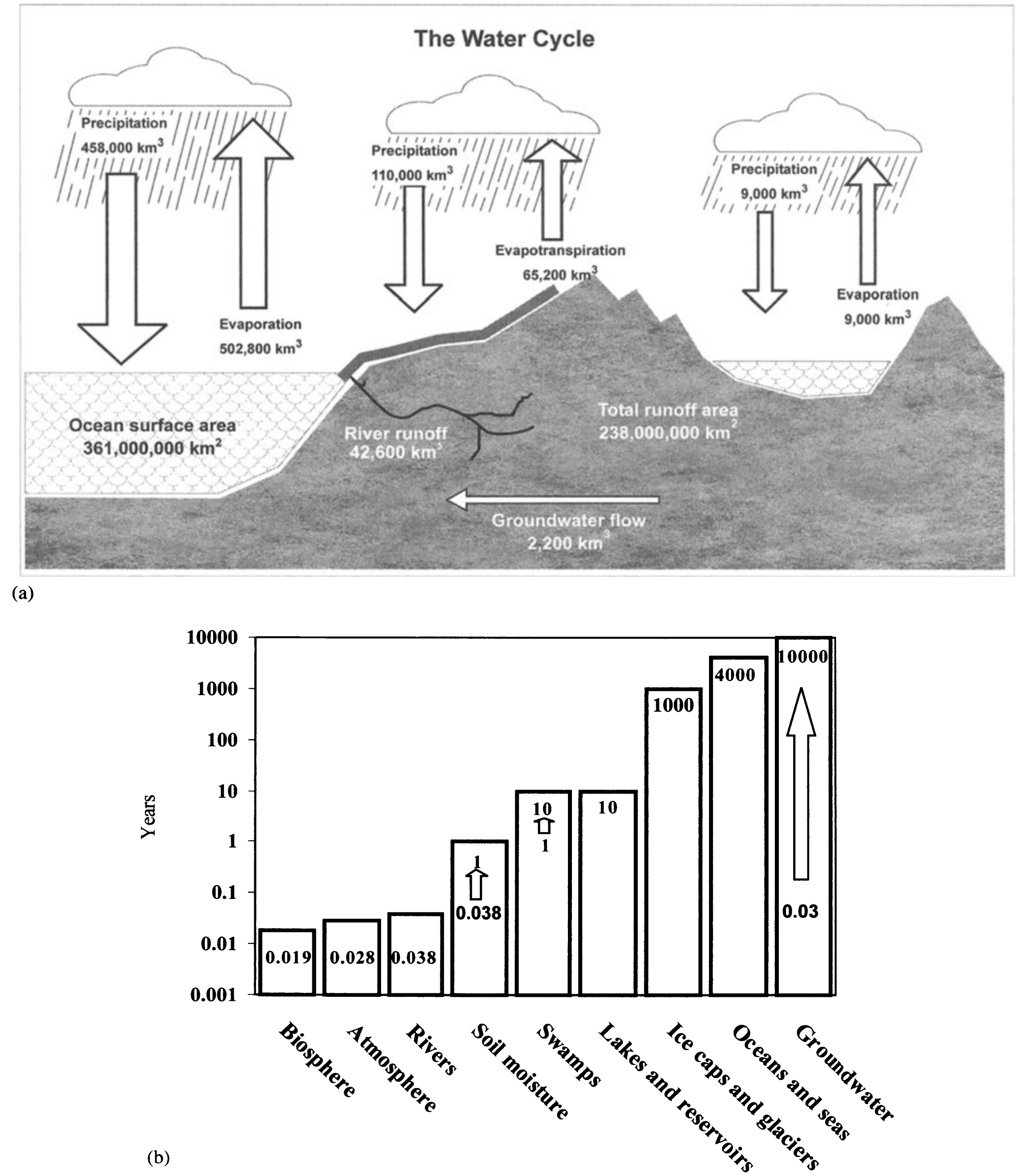


FIGURE 6.2. (a) Hydrological cycle, and (b) estimated residence times of water turnover. (Data from Shiklomanov, 1999).

specific drainage basins and zones. The predominant processes primarily affect the varying compositions of surface waters in different zones of the planet.

The most common parameters that define chemical/environmental characteristics of natural waters are pH, alkalinity, ionic strength, conductivity, salinity, hardness, and the composition and concentration of the different ions or compounds present, usually expressed as parts per million (ppm). *Water hardness* relates to a high concentration of Ca^{2+} and Mg^{2+} ions, mainly as bicarbonates, that tend to form deposits in ducts and form precipitates with soap and dirt; it is generally reported as ppm of $CaCO_3$. *Alkalinity* is defined in Section 6.3.

Another key parameter is the ratio of the sodium ion concentration to that of the calcium ion. Their relative concentrations indicate the predominant processes taking place in a given aquatic body.

6.1.2 Rainwater

Rainwater is responsible for the washing and cleaning processes of the atmosphere by means of dissolution of gases and salts, and the transport of substances and particles onto the surface of the Earth. The particles of minerals and salts washed out by rain usually have diameters below 1 μm. Other particles included in the washout are microorganisms, such as bacteria, that are suspended in air through wind erosion and carryover.

Rainwater is the consequence of several steps in the water cycle brought about by evaporation, condensation, and precipitation. The water in the atmosphere has a residence time of approximately 8–9.6 days before precipitating as rainfall. As mentioned above, in this cycling the global volume of precipitation that falls onto the Earth each year is of the order of 5.8×10^5 km^3, from which approximately 21% falls onto the land and about 79% onto the sea (see Figure 6.2).

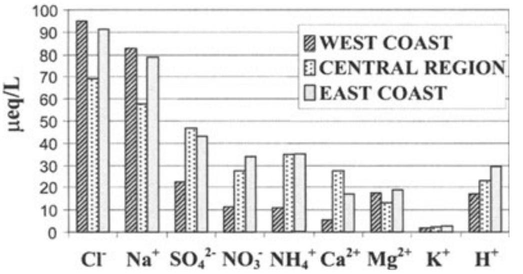
Rainwater composition is determined by the atmospheric composition of the precipitation zone and by that of the zone of origin of the clouds and the winds that carry them to the precipitation site. It varies geographically and depends on the natural and anthropogenic input of gases and particles into the atmosphere, as well as on the atmospheric reactions that may transform them. Activity of the local *biomes* (see definition in Section 7.3) also affects rainwater composition as does the local weather, which in turn defines the amount of precipitation and therefore the concentration of components.

The dissolution of CO_2 in rainwater makes it slightly acidic ($pH = 5.7$, see the calculation in Section 6.2.1). The theoretical content of CO_2 in rainwater, based on Henry's constant, is approximately 0.5 ppm at 20°C, but real contents are up to four times higher due to pollution and fossil fuel burning. The pH of rainwater may also be modified by dissolution and reactions of other air pollutants or compounds present in air, such as NH_3, SO_2, and NO_2. For example, SO_2 and NO_2 from natural or anthropogenic sources may undergo oxidation and dissolution processes to produce sulfuric and nitric acids as particles. Such oxidations occur in air or in rainwater by hydrogen peroxide and ozone. This produces what is known as *acid rain* or, in a broader sense, *acid deposition* that includes snow, hail, and the like (the phenomenon is discussed further in Section 8.4). Ammonia dissolves in water and forms ammonium ions that may react with the sulfuric and nitric acids formed, which produce the salts $(NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3.

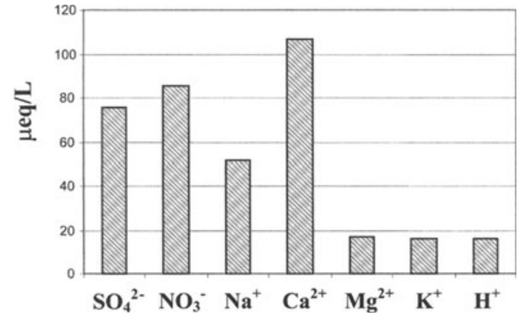
Marine-generated aerosols and gases released from the sea surface in near-coastal areas and over the sea enrich rainwater, thereby modifying its composition. Seawater aerosols are injected into the atmosphere through the bursting of sea foam, the breaking of waves, or the impact of rain over the sea surface. These aerosols then become dry due to evaporation, and the resulting salt particles are transported by the wind and dissolved by rain. When suspended in air, these particles may be carried far away from the seacoast through atmospheric transport (even across continents!), falling onto the land either by themselves or with the rain. The salinity content in this rainwater is considerably high, although not as much as that of seawater.

Sulfate concentration may also increase in rainwater due to the oxidation of volatile sulfide compounds produced by surface algae and liberated from the oceans as $(CH_3)_2S$ (dimethyl sulfide), CS_2 (carbon disulfide), and COS (carbonyl sulfide), and through the oxidation of H_2S generated in shallow coastal waters overlying anoxic sediments. The oxidation of these species is sometimes dependent on the equilibria with other compounds present (e.g., NH_3), thus generating NH_4HSO_4 aerosols. Greater amounts of sulfate ions favor the lowering of rainwater pH in these zones. Rainwater is also responsible for the washing out of organic volatile compounds from air such as formaldehyde, HCHO (considered of natural origin), and several others of anthropogenic origin.

The most common inorganic ions in rainwater are: NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^-, and HCO_3^- (it also contains some dissolved silica,



A **Precipitation weighted annual mean concentrations from three sites in the UK**



B **Average rainwater composition in Mexico City**

FIGURE 6.3. Mean concentrations of the principal ions in rainwater: (a) in the UK and (b) in Mexico City. (Sources: National Environmental Technology Centre, U.K., 2002, and DGPCC/DRAMA, Mexico City, 1996).

SiO_2). As discussed above, the distribution of these ions in rainwater may vary according to the zone of origin of the clouds and the zone of washout. In general, the order of concentrations is: $Cl^- > Na^+ > SO_4^{2-} > NO_3^- \sim NH_4^+ > Mg^{2+} \geq Ca^{2+} > K^+$.

In Figure 6.3 we see the distribution of these ions in samples from coastal and central sites in the United Kingdom, where the effect of sea emissions and the predominance of the different ions are evident. For example, the pH range in UK rainwater is approximately 4.7–6.5. The concentration of Cl^- is typically 10–20% higher than Na^+, and up to 200–300% higher than the next ion (SO_4^{2-}). The concentrations of NO_3^- and NH_4^+ are similar here, as is usually the case, but lower than the SO_4^{2-} concentration. The K^+ concentration is normally the lowest among the most common ions (1–5 μeq/L). All of these concentrations also depend on the anthropogenic contributions in the zone.

In the same figure we see the rain quality data for Mexico City. Compared to the UK data, records show noticeably larger concentrations of nitrate, sulfate, and calcium ions in the Mexican samples. It is then clear that one cannot assume a global average rainwater composition.

6.1.3 Surface Water

Surface water is that contained in streams, rivers, ponds, lakes, swamps, marshes, and springs. Approximately 0.014% of the water on Earth is found on continental land, while the rest is contained in the oceans and ice caps, glaciers, "permanent snow," groundwater, and as water vapor in the atmosphere.

Approximately one-half of the water contained in land is in the upper 1 km of the Earth, and the other half is in the next 4 km, as deep groundwater. Much of the surface water comes from precipitation. When the precipitation rate exceeds the infiltration rate into the soil, an excess of water builds up on the soil surface and moves overland as surface runoff, contributing to the streams, rivers, and other surface water sources. Part of the surface water is a contribution from *spring water* (i.e., groundwater that flows out to the surface owing to a physical condition that obstructs its flow under the Earth, or when the water table intersects the surface).

Approximately 0.007% of the total water on Earth is contained in freshwater lakes, 0.006% in saline lakes, 0.002% in rivers, and 0.0008% forms part of swamp water. The rest of the surface water (approximately 0.0011%) is present as soil moisture or as a part of biological matter (see Figure 6.1).

The composition of surface water depends on the predominant processes taking place in the geographic zone as follows:

- If weathering reactions prevail (see Section 5.3), the ions present in water depend on both local soil and mineral composition. The concentration of total dissolved salts (and thus the ionic strength) will be moderate in surface waters, and the main ions will be Ca^{2+}, HCO_3^-, and silicates, due to the presence of silica (as silicic acid) and calcite or limestone (i.e., crystalline $CaCO_3$), one of the most common and abundant minerals in soil.
- If rainfall is the dominant contribution—as in tropical rainforest rivers—the total dissolved solids or salts will be low, thus yielding a low ionic strength because weathering reactions will

not predominate. As discussed in the previous section, rainfall is responsible for the washout of atmospheric compounds and aerosols (e.g., sea salt aerosols), which contribute Na^+, Mg^{2+}, Cl^-, and SO_4^{2-} ions to its composition. Additional atmospheric inputs that may contribute to surface water composition include products of eolian erosion and volcanic fallout, which contribute dust rich in Ca^{2+}, HCO_3^-, SO_4^{2-} and acid deposition.

- If there is abundant vegetation and animal excretes in the surrounding zone, as in tropical rainforest zones, weathering processes and runoff will increase the presence of organic and inorganic material in water as well as products from the decomposition of organic matter. In this case, there will be a noticeable presence of particulate (solid) and dissolved organic matter (POM and DOM, respectively). Decomposition of forest soil components (i.e., biodegradation of organic matter and animal excretes and decay) contributes with organic matter composed mainly of carbohydrates, proteins, amino acids, and an acidic black to brown solution containing humic substances (see Section 5.4.2). Table 6.1 shows some of the characteristics of these substances as present in rivers, lakes and other surface waters.

  Surface waters fed with the drainage of soils rich in organic components (where there is intense biological activity) generally have abundant aquatic fauna and flora, and therefore abundant nutrients such as ammonia, nitrates, and orthophosphates are constantly discharged and consumed.
- If the evaporative/precipitation processes have a strong influence in the geographic zone, as in warm and arid zones, the dissolved salts derived from weathering and erosive processes become concentrated. This increases the ionic strength and the concentration of dissolved solids, thus increasing the sodium ion concentration. On the other hand, the calcium ion concentration decreases due to precipitation reactions under oversaturation conditions (see Section 5.3.2).

In addition, the amounts of dissolved oxygen and CO_2 affect several processes in surface water. For example, carbon dioxide can determine the pH and the extent of dissolution reactions, while dissolved oxygen levels determine the redox conditions. When oxygen is present in the upper stratum of surface water, it provides an oxidizing medium, causing oxidation processes and aerobic biological processes to take place. By contrast, near the bottom of deeper reservoirs (close to the sediments), the conditions are reductive and give rise to electron-donating reactions.

All of these complex processes largely define the composition of surface water in the hydrosphere.

6.1.3.1 Stream and River Water

River water results mainly from two contributions: surface runoff of falling rainwater and groundwater upflow. Surface overland runoff is the consequence of precipitation on saturated or impervious surfaces; its behavior is cyclical because it depends on the wet and dry spells on Earth.

On the average, of the nearly 120,000 km^3 of rain that fall on land each year, about one-third becomes river runoff. Because of the changing climatic conditions during the last few decades, there has been an increase in river runoff in South America and a decreasing runoff in Africa.

Tropical regions tend to exhibit greater river runoffs due to precipitation, while in the coldest zones of the Earth the runoff is mainly a result of snow and ice-melting processes. The total volume of water in the world's rivers is estimated to be slightly higher than 2000 km^3. Again, the predominant processes in a given geographical zone define the composition of river water. Solutes vary with the soil and precipitation characteristics of the drainage basin, and in the case of groundwater

TABLE 6.1. Characteristics of natural complex organic acids found in surface water

Organic complex acids	Typical color	Average formula	Average molecular weight
Fulvic acids (soluble)	Light yellow to brown	$C_{12}H_{12}N_{0.2}O_6$	1×10^3
Humic acids (dissolved)	Dark brown	$C_{10}H_{11}N_{0.3}O_6$	$2–5 \times 10^3$
Humic acids (insoluble)	Grey-black	$C_{10}H_{13}N_{0.9}O_5$	Variable (ca. 10^6)
Humin or kerogen (insoluble)	Black	$C_{10}H_{19}N_{0.5}O_{11}$	$1 \times 10^3–2 \times 10^5$

upflow, with the level of the Earth's crust at which the water entering the stream has flowed or permeated, and surfaced. Hence, the range of compositions may vary between two extremes: one where the soil-weathering processes predominate, and the other where the rainfall contributions predominate.

The surrounding vegetation or biota richness of the zone, the presence of wetlands, marshes, or peat bogs, and the biological activity in rivers also contribute complex organic compounds and nutrients (containing N and P). Soils rich in organic materials contribute acidic or neutral brown solutions containing humic or fulvic organic acids. Furthermore, the overland surface runoff always has a lower ionic strength than the groundwater upflow.

The overland surface runoff that feeds streams generally carries suspended particles as sand, silt, clay, and organic matter. The solid organic particles or POMs may be biopolymers, as proteins, lignin ($C_{10}H_{11}N_{0.1}O_3$), cellulose, or other complex lignins or plant-decay products such as humin. Together with the subsurface runoff, soluble nutrients and organic matter, SOM will also be present due to the degradation processes of organic matter, which can increase through the contribution of soil erosion from riverbanks and from direct input of plant leaves and other natural debris.

When the source of water flows upward through the soil, the mineral composition and the weathering reactions determine the final water composition. In this case, the water flowing into a river contains small amounts of particles, solubilized inorganic compounds of alkaline nature, H_4SiO_4 in varying amounts, and sometimes sulfates and sulfides due to the weathering of gypsum and sulfide mineral deposits. The rate of weathering determines the concentration of such compounds (i.e., greater concentrations with higher rates). Water will then have a low organic content (or none at all) as well as little PO_4^{3-}, Al^{3+}, and Fe^{n+} because these species tend to precipitate or form solid complexes. When the runoff zone is over limestone as a predominant component, the rivers tend to have higher alkalinity and calcium ion concentrations. This is the case of rivers in some humid and dry areas of North America, Europe, and Asia, where most of the areas rich in calcareous materials and limestone (or *karst* material) are located, but not in South American or African rivers, where such types of soils or rocks are not abundant.

Because atmospheric and evaporative processes are mainly determined by the climatic characteristics of the corresponding zone and by seasonal changes, they also influence water composition sometimes even more strongly than runoff and soil water flushing. In small streams and rivers, the biological processes do not influence the water composition significantly because the rapid flow will dilute their effect. This is not the case in large, slow moving rivers, where the biological processes have enough time to alter their composition through biodegradation and excretion products. In general, the turnover in medium-flow rivers is approximately 16–20 days.

On the other hand, the contribution of ions to river water in wet climates by soil weathering is very low, whereas the direct rainwater contribution is higher. In contrast, dryer climates have much higher rainwater runoff and weathering contributions and, as a consequence, the concentration of dissolved and particulate matter is much higher. As a result, dissolved Na^+ may predominate over Ca^{2+}, and there may be an increase in NO_3^- and Cl^-.

The average composition of selected major rivers is presented in Table 6.2. Although this is an average of various extreme compositions, it is worthwhile to compare the concentration of the major components.

The order of predominance of the four main metals present as simple cations in the majority of rivers is $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ (and sometimes they contain important amounts of Al^{3+}). The corresponding order of the anions is $HCO_3^- > SO_4^{2-} > Cl^- > F^- > Br^-$. There are also small amounts of silicic acid, H_4SiO_4, N as NO_3^-, P as

Table 6.2. Average concentrations (mg/L) of the main dissolved constituents in major rivers

HCO_3^-	Ca^{2+}	SiO_2	SO_4^{2-}	Cl^-	Na^+	Mg^{2+}	K^+	Fe^{n+}	Total
30.5–58.4	8–15	10.4–13.1	4.8–11.2	3.9–7.8	3.7–6.3	2.4–4	1.0–2.3	0.04–0.67	100 to ~120

See Berner, 1987; Livingston, 1963; and Maybeck, 1989.

PO_4^{3-}, and Fe^{n+}. When the weathering process is intense, the silica content increases although reactions with Al^{3+} may form insoluble compounds that lower its concentration.

Freshwater in rivers and streams typically has low ionic strengths (between 10^{-4} and 10^{-3} M); the pH ranges from 6 to 8.5, and the total dissolved solids, TDS, may vary from approximately 4 ppm (in zones where rainfall predominates) to an extreme of 5000 ppm (in rivers where evaporation predominates). The TDS average is between 50 and 200 ppm, with a predominance of $Ca(HCO_3)_2$. Nevertheless, one can find rivers with extreme concentration variations as compared to these average values. For example, the Horocallo River in Ethiopia is strongly affected by evaporation processes and exhibits a pH = 9.2 and Na^+, SiO_2, HCO_3^{2-}, Cl^-, and SO_4^{2-} ion concentrations of 480, 79, 975, 195, and 65 ppm, respectively. In comparison, the Black Amazon River, where precipitation and biogenic contributions dominate, has a pH of 3.7 and only traces of these ions.

With regard to the concentration of nutrients (N and P content) in river water, there is considerable variability in part due to the biological activity taking place in the river (which adds and removes nutrients) and to the effect of human activities increasing their discharge. Average N and P values in pristine river waters are 5 μmoles/L of total inorganic nitrogen (as NO_3^-, NO_2^-, NH_4^+) and 0.4 μmoles/L of PO_4^{3-}. Considering both pristine and polluted rivers, a global N:P mean ratio of 23–31 is observed. Examples of N, P, and silicic acid concentrations (as well as N:P ratios) in selected rivers are given in Table 6.3. The composition of these rivers shows important differences primarily due to the influence of human activities. As expected, considerably lower concentrations are present with decreased human activity.

6.1.3.2 *Lake Water*

A lake is an enclosed body of generally fresh water with or without direct input and with or without direct output; these inputs and outputs have important effects on its quality and composition.

The volume of water in lakes is estimated at 176×10^3 km^3. Of this amount, approximately 52–54% is in freshwater lakes. The main sources of lake water are generally rainfall, river runoff, and groundwater (either surfacing as seepage or point springs). An additional water source in alpine and glacial lakes is glacial and snow melting. The composition of lake water depends on the characteristics of the sources that supply the lake and the processes that take place in it. Such a composition is affected by runoff, atmospheric deposition and washout, biological activity, the presence or absence of outflow, and by interactions between water and sediments. In addition, the reactions that begin in the rivers and streams that feed them will continue in the lakes, especially those related to biological activity, affecting the characteristics of the water content as well.

For example, lakes in drainage basins of easily weathered soils such as calcareous rocks (calcite, dolomite, gypsum, halite) generally have high values of pH, alkalinity, total dissolved solids, conductivity, and hardness. Such is the case for lakes located in cavities formed through the gradual dissolution of water-soluble rocks (*solution* or *Karst* lakes). On the other hand if the drainage basin is in an acidic rock basin (i.e., where silicates predominate and are difficult to weather), the water has an acidic pH, low alkalinity, and low total dissolved solids.

The chemical composition, biological activity, and renewal time are also influenced by the morphometric characteristics of the lake (i.e., area and depth) and the climate. This is so because the

TABLE 6.3. Nutrient and silicate concentrations in selected rivers, in μmoles/L

River	N as NO_3^-/NO_2^-	N as NH_4^+	Total inorg. N	P as PO_4^{3-}	N:P ratio	Silicates
Amazon	3.7	–	3.7	0.4	7.5	187
Niger	7.6	1	8.6	0.4	21.5	250
Mississippi*	156	<4	160	2.8	57	83
Upper Rhine	30	2.5	32.5	0.5	65	61
Lower Rhine*	230	90	320	11.4	28	90

* Highly polluted rivers due to human activity. (Source: Bolin, 1983).

temperature, precipitation, wind activity, as well as the evaporation and capture area, all influence the rates of weathering, evaporation, biological activity, and runoff volume. These characteristics affect the input, output, distribution, circulation, and suspension or sedimentation of the chemical substances.

Because water in lakes is more static and there is minor mixing (produced by the wind), it tends to stratify as a result of density differences due to thermal effects. The resulting strata are called *epilimnion* (the less dense upper strata), *hypolimnion* (the denser lower strata) and *thermocline* (the intermediate, transition zone). This stratification is more common and pronounced in deep lakes. Mixing is only present at seasonal change when the strata are overturned. In addition, water renewal in lakes takes place after long intervals (from 1 to more than 100 years), depending on the size of the lake and on the input and output balance. For example, Lake Superior takes 100 years to renew its capacity while Lake Erie (which is smaller) takes only 2–3 years; smaller, shallower lakes—less than 5 m deep—may take 1 year or less. Renewal rates are important as they normally allow time for reactions to reach equilibrium; a disadvantage is that the removal of contaminants takes much longer because the turnover is much slower.

The two predominant processes that affect lake water composition are evaporation and biological processes. In dry zones, evaporation has important effects on the composition of lake water, concentrating one type of ion more than others and favoring precipitation reactions of other ions, sometimes deriving in highly saline lakes. Approximately 46–48% of the water in lakes is contained in saline lakes. In most freshwater lakes, salinity ranges from 0.1 to 0.5 g/L.

The pH of healthy lakes is 6.5–8.5, and their pH-controlling system is generally the carbonate system. When evaporation processes dominate, the pH tends to increase, whereas, when the biological processes dominate, it tends to decrease. In addition, when human activities impact the surroundings (especially through air pollution and mining), the pH of the lakes may be acidified. The ability of a lake to resist such an impact depends on the water composition and on the terrain characteristics of the watershed.

An interesting volcanic contribution to lakes and rivers comes from hydrothermal sources (hot water vents) or from volcanic vents or fumaroles, which are sources of CO_2, CH_4, H_2S, and other volcanic gases. When the main emission is CO_2, the HCO_3^- content increases considerably, resulting in *soda lakes*. The same may happen in volcanic lakes occurring in craters (*maars* or *caldera lakes*), where the CO_2 levels are very high. They may be further enriched with the leachates generated by hot water, increasing the levels of silicates, chlorides, sulfides, and iron. Many of these lakes are found in Africa, Japan, the Philippines, Central America, Indonesia, and Western Europe. The dissolved CO_2 seeps from beneath the lake, sometimes as gaseous water springs (a common feature of old volcanic areas), and is trapped in deep water by the high hydrostatic pressure. If CO_2 reaches the saturation level, bubbles appear and a rich mixture of gas and water may surface.

A special case of CO_2 discharge from volcanic vents at the bottom of a maars lake caused a major disaster in the area surrounding Lake Nyos in West Cameroon, in 1986. This was due to the gradual seeping up, dissolution, and accumulation of carbon dioxide in the 35,000-year-old deep, stable lake water. A sudden explosive release of the accumulated gas to the surrounding area discharged a deadly gas blanket of approximately 1 km^3, tens of meters thick, which resulted in the death of 1700 people and 3000 livestock up to 27 km away from the lake in the surrounding valleys. A hypothesis of what triggered the event is that an overturning of the lake strata changed the temperature and pressure that had kept the gas dissolved at the bottom of the lake (see also Section 6.2.1.3). Two years earlier, a similar phenomenon happened in neighboring Lake Monoun (another maars lake in the same area), killing 37 people.

Another important process in lakes and rivers that contributes to their composition is *eutrophication*, which consists in the internal generation or autotrophic production of organic matter through biological processes or primary productivity (see also Section 7.3.2). This process is determined by the input of organic matter and nutrients. When the organic matter input is very high due to runoff from the watershed, the lakes are rich in humic substances and are called *dystrophic* or *brown water* or *polyhumic lakes*, because of the color of water. They do not favor internal production of organic matter because their dark brown color is so strong that

TABLE 6.4. Classification of eutrophic lakes

Productivity	Trophic status	Mean total P, μg/L	Mean annual chlorophyll, μg/L	Oxygen concentration, as % of saturation	Secchi disk depth,* m
Low	Oligotrophic	<10	2.5<	<80%	>6
Medium	Mesotrophic	10–35	2.5–8	40–80%	6–3
High	Eutrophic	35–100	8–25	<40%	3–1.5
Extra high	Hypereutrophic	>100	>25	<10%	1.5

Source: Thomas, 1992.

**Note:* The *Secchi depth* (m) is the depth at which a white disk submerged into the water body disappears from view. It is directly related to the turbidity, and therefore to the organic colloidal matter or biomass present.

photosynthetic processes are hampered; here, the DOM is generally of low biodegradability.

Eutrophic lakes favor the internal production and decay of organic matter, and rely on the primary producers present (plants and algae) and the available nutrients. These nutrients derive from external inputs through weathering of soil or from the decay of organic matter and dissolution of bottom sediments. The effects of eutrophication can be highly detrimental to a lake's water quality: higher biomass production, higher amounts of organic colloidal matter, increased turbidity, increased oxygen depletion, occurrence of anaerobic processes in the sediments with gas liberation, and more N and P liberation into the water column. The phosphate ion is the limiting reagent in this process.

Eutrophic lakes are classified according to their productivity, their phosphorus and chlorophyll content (the first ranging from 0.004 to 0.1 mg/L of P, and the latter related to the primary biomass production), or to the clarity of their water. See Table 6.4.

Eutrophic to hypereutrophic conditions in lakes result in growth and death of the phytoplankton, its decay and deposition at the bottom. Oxygen is then depleted in the hypolimnion, and, in extreme conditions, anoxic conditions may occur. This will result in the generation of reducing conditions that favor the release and solubilization from the bottom sediments of manganese, iron, and trace elements as well as phosphorus. In extreme cases, CH_4, CO_2 and H_2S gases will be generated, and nitrogen will be predominantly present as NH_4^+. These conditions are favored in warm tropical zones.

6.1.4 Groundwater

Groundwater is water that occupies voids and spaces between soil, sand and/or gravel particles, clay silt, and rocks. It is also present within cracks in the bedrock, and can be found under the Earth's surface, either flowing slowly or as underground lakes or ponds. The latter are common when consolidated limestone forms caverns containing considerable amounts of water. In Figure 6.4 one can see the different forms in which groundwater is found and recharged, as well as its flows.

Although fresh groundwater constitutes less than 2% of the total amount of water on Earth, it is of paramount importance as it comprises approximately 98% of the fresh water suitable for final human consumption. It originates from precipitation as rainfall that infiltrates through the soil, percolating downward into a saturated zone where all the spaces between the rock and soil are filled with water. Beneath such a zone there may be a watertight rock layer (confining layer). The top level of the saturated zone filled with groundwater is known as the *water table*, and the large groundwater reservoirs are known as *aquifers*. Water that eventually reaches the saturated zone is known as *recharge*; its characteristics depend on those of the precipitation in the zone, the nearby surface water, the type and amount of vegetation and soil, the rate at which water enters the soil, and the permeability and depth of the unsaturated zone (i.e., the zone above the groundwater reservoir).

The composition of soil and rocks through which groundwater percolates on its way to the reservoir, and the materials it contains affect its quality. Normally, groundwater has pH values in the range of 6.0–8.5, and a higher concentration of dissolved salts than that in surface water (and consequently a higher ionic strength). A significant percentage of groundwater (55%) is highly mineralized; this is classified as *brackish* or *saline water* (see Section 6.1.6). Nevertheless, groundwater is

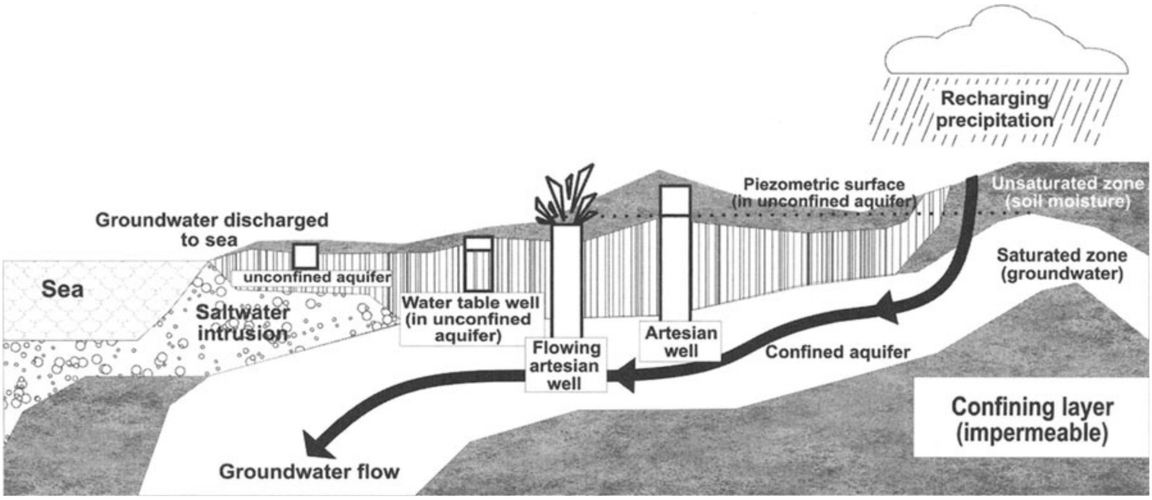


FIGURE 6.4. Types of aquifers, wells, and groundwater flow. (Adapted from: Environment Canada).

generally considered a good-quality water source for human use and consumption. The most common naturally occurring cations present in groundwater are Ca^{2+}, Mg^{2+}, K^+, Fe^{x+}, and Na^+; the anions are Cl^-, SO_4^{2-}, and HCO_3^-. Dissolved solids in groundwater can exceed 1000 ppm, and up to 10,000 ppm in some cases, when groundwater is considered as saline. On the other hand, aquifers are also common on sandstone or shale beds, which are sedimentary rocks that contain high amounts of carbonates. For example, sandstone bed aquifers tend to have a higher pH ($pH > 8$–9). When groundwater is in contact with limestone ($CaCO_3$) or dolomite beds [$CaMg(CO_3)_2$], hardness tends to be very high.

Groundwater may also contain dissolved CO_2 due to respiration processes and to degradation of terrestrial organic matter in soil, which in turn depend on temperature and seasonal conditions. Although it is estimated that only 0.77% of the CO_2 generated through such processes goes to groundwater (the rest goes to the atmosphere), this is nevertheless a significant contribution to the characteristics and processes that take place in groundwater.

The CO_2 content in warmer zones is higher due to an increase in the metabolic rates and CO_2 production, which in turn favors an increase in water hardness in surface and groundwaters surrounded by calcareous rocks. For example, average values of pH, HCO_3^- and hardness of groundwater in the state of Texas (USA) are 6.9, 316 ppm, and 264 ppm of $CaCO_3$, respectively, whereas these values are 7.0, 456 ppm, and 408 ppm of $CaCO_3$ in the state of Yucatan (Mexico).

The variation in composition—especially in alkalinity, saturation, and speciation—is extremely dependent on the time that water spends in contact with the confining rocks (i.e., whether there is enough time to reach equilibrium), on flow rate (involving dilution and mixing), and on temperature effects (e.g., kinetic effects).

In deeper groundwaters that have very long residence times (i.e., 1,000–10,000 years) and are subject to high pressures, the equilibrium reactions are different from those in the more superficial aquifers that have more movement and shorter residence times.

Soluble humic substances are found in groundwater when the source of recharge flows through rich organic soil; this also depends on the biological activity (affected by temperature and seasonal changes). As discussed in Chapter 5, these humic substances or natural organic acids are ligands that favor complexation reactions with metals in water. Such reactions sometimes favor solubilization; in other cases they favor precipitation and adsorption processes that are generally pH-dependent and affect the composition of water.

6.1.5 Seawater

Seawater comprises approximately 97% of the global water reserve. Seas and oceans constantly interact with the lithosphere, atmosphere, and biosphere; they are the natural recipients of all drainage from rivers, Earth's runoff, water from glaciers, and hydrothermal effluents, as well as dissolved salts and suspended solids carried away from land by wind and rain. Almost all the elements pass through the oceans at some point in their life cycles; in fact, ocean water and sediments are the receptacles of most elements and compounds, so much so, that they may be considered their largest reservoirs.

Oceans are remarkably big reactors, and the different physical, chemical, geochemical, and biological processes taking place in them will affect their composition. Ocean water renewal takes place approximately every 2500–4000 years. The spatial distribution of ocean contents is determined by water movements resulting from thermal and density differences, which in turn depend on salinity and temperature, and those arising from wind-initiated mixing processes on the surface.

The presence of the different ions and compounds in ocean water is determined by their residence time, which in turn is a result of the reactivity of the elements. Chemically reactive elements tend to change their speciation and have shorter residence times, therefore being present in lower concentrations. These are generally termed *non-conservative* elements. The most stable elements and compounds behave in the opposite manner and are accordingly termed *conservative* elements. The same happens with those elements involved in biological processes (such as N and P), which tend to be rapidly removed from aqueous media when used by microorganisms, generally in the well-mixed aerobic upper strata of the oceans. As a consequence of organic matter decay, such elements are released back into the aqueous phase as solutes in the deeper parts. This creates concentration differences up to 10-fold between surface and deep waters for N and P.

Seawater is normally high in salinity (mainly as NaCl, at an average of 35 g/L) and in dissolved solids content, with a relatively constant concentration of the major ions. Its average ionic strength is consequently high (approximately 0.7 M). It is a complex, well-buffered system with a pH between 8.0 and 8.4, with a density at the surface between 1.020 and 1.029 g/cm^3 and an average global temperature of 17°C. Although surface water temperature varies with latitude from −2°C to > 35°C, there is also a temperature gradient with depth.

TABLE 6.5. Major ions that define salinity in ocean water

Ion	M (mol/L)	ppm
Cl^-	5.6×10^{-1}	19,000–19,500
Na^+	4.8×10^{-1}	10,500–10,805
Mg^{2+}	5.4×10^{-2}	1,290–1,350
SO_4^{2-}	2.89×10^{-2}	2,688–2,700
Ca^{2+}	1.05×10^{-2}	401–410
K^+	1.05×10^{-2}	391
HCO_3^-	2.4×10^{-3}	142–146
Br^-	8.6×10^{-4}	67
BO_3^{3-}	4.1×10^{-4}	24
Sr^{2+}	9.51×10^{-5}	8
F^-	7.5×10^{-5}	1.4

Salinity is defined here as the grams of dissolved solids (or inorganic dissolved compounds) per kg of seawater, or parts per thousand (or as a *per thousand‰*). Alternatively, it can be defined as the mg/L or mmol/L of the major ions (i.e., those present in concentrations above 1 ppm). The total concentration of dissolved solids ranges from 7,000 ppm for the Baltic Sea, to an average of 35,000 ppm in large oceans, and up to 40,000 ppm in regions where evaporation is high and inputs are low, such as the Red Sea.

Interestingly, the relative proportions of the major ions are approximately constant throughout the oceans as observed in Table 6.5. These ions are not very reactive, and as such they are more permanent in solution. As discussed above, NaCl is the major compound present at a typical (although not constant) concentration of 500–560 mmol/L, which accounts for about 75% of the total dissolved solids. The rest of salinity comes mainly from Mg, Ca, and K chlorides and sulfates.

From equilibrium studies it is known that the major cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}, and the anion Cl^-) are mostly present in their non-complexed form, but other minor elements (at <1 ppm) primarily exist as complex ions or ion pairs. The metal cations predominantly form hydroxo complexes and, to a smaller extent, carbonato and chloro complexes.

The concentration and speciation of minor and trace elements vary considerably, depending on the particular zone where the ocean is located. Their presence or absence is due to atmospheric input, river drainage, chemical speciation, hydrothermal input, redox reactions, adsorption, and removal through settling particles, as well as biological uptake and release.

The intense surface and current movements of seawater as well as density differences also affect gas dissolution and biological processes taking place in the different ocean strata, which in turn affect the presence and removal of the trace elements and nutrients. The strong mixing processes promote good gas transfer and dissolution in the upper stratum of the ocean. In this case, relatively high dissolved oxygen levels can reach equilibrium with air, and a highly oxidative medium will be present. This favors oxidation reactions and aerobic biological processes. On the other hand, the dissolved oxygen levels are very low in the deeper strata, thus favoring anaerobic biological processes and reductive phenomena.

A certain variation in composition is present in *estuaries* (i.e., the ocean zones near the coasts where rivers discharge). Consequently, estuaries play an important role in the transportation and transformation of river drainage. This creates dilution processes and sharp gradients of composition, ionic strength, and pH that are determined by the hydrodynamic regimes. These processes are strongly affected by tidal movements and discharge regimes of river water, sometimes producing stratified layers of fresh, less dense water over denser saline water. When the tidal movements are strong compared to the river discharge, the mixing regime dominates and the chemical composition is not significantly affected. Estuaries are responsible for the destabilization and precipitation of river colloidal particulate matter and sediments, and of precipitation reactions of dissolved riverine species (see Section 6.3.1.5). The removal of dissolved nutrients is due to biological processes, whereas the removal of Al, Fe, and Mn is due to precipitation reactions promoted by particle formation and destabilization.

6.1.6 Brackish/Saline Water

Brackish water is water with a salt content greater than that of fresh water but smaller than that of seawater. It contains 0.5–30 g/L of salt, often expressed as parts per thousand. For analytical convenience, salinity is also measured as conductivity in μSiemens/m (μS/m), μmhos/m, or dS/m at 25°C. The approximate equivalence is 1 dS/m = 700 mg/L of TDS.

There may be waters that are more saline than brackish water, containing much higher concentrations of TDS. Such a high salt concentration may be toxic to plants, inhibit biological activity, or accumulate in plants, placing their consumers at risk. This water is found either as superficial water in saline lakes, in saline marshes, or in estuaries where there has been river drainage dilution, in coastal wetlands, or as saline groundwater.

Extremely saline or *hypersaline* water (also known as *hyperhaline* water) has a total content of dissolved solids or salts higher than that of seawater. It is dominated by the following ions: (a) cations: Ca^{2+}, Mg^{2+}, Na^+, K^+, and (b) anions: CO_3^{2-}, HCO_3^-, SO_4^{2-}, Cl^-. The ionic composition of a saline water may vary depending on its origin and evaporation rate. When the origin of salinity is seawater or a similar ionic solution, the initial ionic composition of the saline water will be very similar to that of its origin. Such brines are generally known as *thalassohaline brines*. They have a neutral to slightly alkaline pH (i.e., 7–8). Monovalent cations predominate in them (just as in seawater); therefore, higher concentrations of Na^+, K^+, and SO_4^{2-} ions will be present. When the origin of the salinity is different, the evaporative process (or the concentration of salts) generate a different composition. These saline waters are known as *athalassohaline brines*. Here, when the evaporative process is not as intense, the divalent cations predominate in solution and the pH will tend to be lower (pH = 5.8–6). Then, Ca^{2+}, Mg^{2+}, Cl^-, and Br^- ions will predominate, and the SO_4^{2-} ion concentration will be low. In the case of *alkaline athalassohaline brines* (present in what is known as *soda lakes*), intense evaporative processes occur and the salt composition will be dominated by the monovalent cations Na^+ and K^+, because the pH is basic (>10–11) and the solubility of the divalent Ca^{2+} and Mg^{2+} is very low in this pH range. The anion predominance in this case will be HCO_3^-, $CO_3^{2-} > Cl^-$, SO_4^{2-}. This water is mainly found in locked inland seas or lakes where the evaporative processes are intense. Examples include the Dead Sea in the Middle East, and Mono Lake and the Great Salt Lake in Utah (USA). The Dead Sea is an inland sea, which is in the lowest dry point on Earth; it is six times saltier than seawater, and it becomes saltier with depth. Its surface is diluted with the Jordan River inflow, but at a depth of approximately 100 m its salinity reaches 320 g/L, which is a saturation condition that forces salts to precipitate and settle at its bottom. The Dead Sea was formed through crustal spreading of the continents, and its bottom keeps sinking with time (about 30 cm each year). The high concentration of salts is due to two processes: the constant and strong evaporation, and the continuous feeding of river drainage (from the Jordan River and other streams) with its own salt content. There is no drainage out of the Dead Sea, and as a result all the incoming salts remain there. Owing to its composition, it cannot support life and there are no biological processes to remove compounds. The only removal processes are precipitation and evaporation.

A similar case is that of the Great Salt Lake, whose origin is Lake Bonneville (a remnant of a huge freshwater lake that lost its outlet to the sea), which receives inputs from several rivers and streams but with no outflow other than evaporation. It receives 2 million tons of dissolved salts each year, leached from soils and rocks, and its salinity fluctuates from 5% (similar to seawater) to 27% (near saturation) depending on the water inflow and rain input.

Mono Lake is another closed, saline lake with a unique chemistry. It is alkaline ($pH = 10$), and almost three times as salty as the ocean. Its salinity is approximately 81 g/L (in 1913 it reached a record salinity of 133 g/L). Its waters contain dissolved sodium salts (as chlorides, carbonates, and sulfates); in contrast, the Great Salt Lake contains abundant chlorides but very few carbonates. Mono Lake is also rich in borate and potassium ions (among the highest concentrations ever recorded). The salinity of the first two cases is compared to that of the ocean in Table 6.6 (as weight % of dry TDS).

Some inland marshes and small inner wetlands are also salty and have poor drainage. As a result, they accumulate salts in drought periods, which may be partially washed out during wet seasons. If these water systems are not well drained, the salts will accumulate especially in the form of $NaCl$, $CaCl_2$, Na_2SO_4, and $CaSO_4$, sometimes leaving a white salt crust on the soil during dry seasons.

TABLE 6.6. Average water composition of the Dead Sea, Great Salt Lake, and the ocean

	Wt % of dry TDS					
Source	Cl^-	Na^+	Mg^{2+}	Ca^{2+}	SO_4^{2-}	K^+
Dead Sea	67.2	12.3	12.8	5.3	0.4	2
Great Salt Lake	54.5	32.5	3.3	0.2	7.2	2.3
Open ocean	55.5	30.8	3.7	1.2	7.7	1.1

It is very common to find saline groundwater. Sometimes there is saline water underlying fresh water aquifers. The salinity in groundwater can be due to several causes:

- Seawater intrusion. This is especially common in unconfined or shallow-confined aquifers that flow toward the sea. It occurs when the water table of the aquifer is lowered (due to over extraction or insufficient recharge), and a change in gradients causes seawater to flow inward.
- Seepage into a saline environment.
- Strong weathering of minerals in the confinement area. This may be why water trapped within sedimentary generated strata becomes more saline at greater depths. It is interesting to observe that
    i. in the upper part, near the surface, it is richer in sulfates
    ii. in the intermediate level it is richer in bicarbonates, and
    iii. at greater depths it is richer in chlorides.
- Upconing, whereby saline water that is underlying fresh groundwater upflows at a rate sufficiently high so as to cause the salt water to be drawn into the aquifer well in an upward-shaped cone. About two-thirds of the United States freshwater aquifers could become contaminated by underlying saline water.

Surface water can be salinized through upflow of saline groundwater, although sometimes the saline water stays at the bottom due to density differences and the average salt concentration changes. In coastal areas, the water composition can be modified by saline water intrusion and tidal movements traveling inland on surface water systems (such as rivers). In other cases the saline groundwater upflows naturally, forming natural saline lakes; with further evaporation their salt content increases even more. This is the case of the so-called *playas* where, if intensive evaporation occurs, the salts will remain in the shallow zones.

Such types of saline lakes occur in arid and semiarid climates where the water table is very close to the surface. Strong evaporation causes groundwater to evaporate through the thin unsaturated zone,

TABLE 6.7. Classification of saline waters

Water type	Electrical conductivity, dS m^{-1}	Salt concentration, mg L^{-1}	Examples
Non-saline	<0.7	<500	Drinking, irrigation, and surface water
Slightly saline	0.7–2	500–1,500	Surface and irrigation water, and ground water
Moderately saline	2–10	1,500–7,000	Runoff and groundwater
Highly saline	10–25	7,000–15,000	Saline groundwater and runoff
Exceptionally saline	25–45	15,000–35,000	Very saline groundwater and seawater
Brine	>45	>45,000	Saline inland lakes and seas

forming highly saline brines beneath the surface of salt lakes. This is very common in arid zones. For instance, the saline lakes in Australia range from low to high salinity (from 1,500 to 50,000 mg/L of TDS), while saline groundwater may vary from 3,500 to 60,000 mg/L of TDS.

The main differences in composition between saline lakes and saline groundwater – compared to seawater – are the following: saline groundwaters more commonly tend to have compositions similar to the athalassohaline brines (i.e., a higher proportion of divalent ions, higher concentrations of HCO_3^- and SO_4^{2-}, a lower proportion of K^+, and a high concentration of silica and Fe^{n+} ions). In contrast, in saline lake waters there is a higher concentration of HCO_3^- ions, a somewhat higher concentration of Ca^{2+}, a much lower concentration of SO_4^{2-} ions, and no silica or Fe^{n+} ions. It is also common to find Br^- ions in saline lakes. Nevertheless, there is no average composition for saline lakes.

Classification of saline waters is important because a good portion of the groundwater and surface waters are used for irrigation. One such classification, based on their salinity characteristics, is shown in Table 6.7.

6.2 Interactions of Water with Air and Sediments; Effects on Aquatic Chemistry

Surface waters in pristine condition are affected by the dissolved and particulate loads that come from soil weathering and erosion processes, atmospheric gas dissolution, and dry deposition. Human activity has increased weathering and erosion rates as well as the concentration of gases and particulates in the atmosphere, thereby contributing to a greater amount of particles and compounds present in surface waters.

6.2.1 Gas Dissolution and Acidification of Natural Waters

Air components in contact with surface water tend to dissolve to reach equilibrium (i.e., gas saturation conditions). The amount dissolved depends on water temperature, ambient pressure, and the absorbing or reacting capacity of water for each gas. At low pressures, most gases are poorly soluble in liquids and are even less soluble with increasing temperature (as long as it is far from their critical temperature). Other sources of gases dissolved in water include the evolution of gaseous products from chemical or biochemical reactions taking place in water or in the sediments, mainly through decomposition of organic matter or from photosynthetic processes. The main sources for gases that can dissolve in and react with water are summarized in Table 6.8.

The *amount* of a given gas in water depends on its ability to react chemically with water molecules or to dissolve as a free molecule, on its partial pressure in the atmosphere, and on its vapor pressure; it also depends on both temperature and the amount of dissolved salts.

Mass transfer phenomena govern the *rate* of dissolution of a gas due to the exposed water surface, local turbulence, and the degree of air and water mixing. Consequently, large water surfaces under turbulence (as the rapids in a river) favor gas dissolution; in this way, a turbulent cold river is richer

TABLE 6.8. Main sources of gases found in natural waters

Source/gas	CO_2	O_2	NH_3	N_2O/NO	N_2	H_2S	CH_4
Air	X	X		X	X		
Biological decomposition (aerobic and anaerobic) of organic matter	X		X	X	X	X	X
Gas evolution from the Earth's crust or volcanic action	X					X	
Photosynthetic reactions	X	X					

in oxygen than a warm static lake. In addition, the higher the concentration of dissolved salts, the lower the concentration of dissolved oxygen. Oxygen does not ionize in water nor reacts with it and it is essentially present as the free dioxygen molecule. It differs from other gases such as carbon dioxide and ammonia in that they ionize to a certain extent, and their ions may react forming new compounds.

6.2.1.1 Henry's Law

When the amount of a dissolved gas is small—as in the case of covalent, non-reactive gases in water under normal conditions—Henry's law governs this amount. This law states that the solubility of a non-reactive gas in water (or in any other liquid) at constant temperature is directly proportional to the partial pressure p_i of that gas above the liquid. Because a higher dissolution means a higher concentration of the gas in the aqueous phase, one can write a simple mathematical expression for this law as:

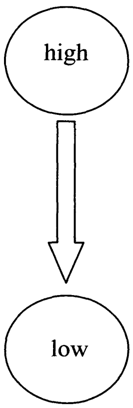
$$M_{i,w} = \text{constant} \cdot p_i = K_{H,i} \cdot p_i \text{ (moles L}^{-1}\text{)} \tag{6.1}$$

where $M_{i,w}$ is the molar gas concentration in aqueous solution, and $K_{H,i}$ is its Henry's law constant. If p_i is given in atm, then $K_{H,i}$ is given in mol L^{-1} atm^{-1}. Table 6.9 shows the values of $K_{H,i}$ for several gases commonly found in air and dissolved in water, arranged in order of their $K_{H,i}$ value. Note that the higher the $K_{H,i}$, the lower the vapor pressure (equivalent to its tendency to escape from solution).

Non-polar compounds such as CH_4 or N_2, do not easily dissolve in a polar medium like water, and they have small Henry's law constants. On the other hand, compounds such as SO_2 and NH_3 have large constants due to their polar characteristics and their chemical reactivity in aqueous media.

Henry's law works best with gases that are not too soluble, do not associate or dissociate in solution, and do not react chemically with the solvent. The components in a gas mixture act separately, and the mass of each gas that dissolves at a constant temperature is directly proportional to its Henry's law constant and to its partial pressure in the gas mixture. In addition, Henry's law is sometimes used in conjunction with the inverse process,

TABLE 6.9. Henry's law constants for the gases most commonly found in water (at 25°C and 1 atm)

Gas	$K_{H,i}$ (mol L^{-1} atm^{-1})	p_{vap}
N_2	6.5×10^{-4}	
H_2	7.8×10^{-4}	
CO	9.8×10^{-4}	
O_2	1.3×10^{-3}	
CH_4	1.4×10^{-3}	
O_3	1.3×10^{-2}	
CO_2	3.5×10^{-2}	
H_2S	1.0	
SO_2	1.2	
NH_3	5.3	

Example 6.1 Conversion of units in Henry's law

Write Henry's law so as to:

(a) Obtain the aqueous concentration, $C_{i,w}$ of the gas i in mg/L
(b) Obtain the mole fraction of the gas i in the aqueous solution, $X_{i,w}$
(c) Obtain the aqueous concentration of the gas i in the aqueous solution, in parts per million (ppm)

Answer

(a) $C_{i,w}$ in mg/L $= (K_{H,i} \cdot p_i,\ \text{mol/L})\ (\text{MW}_i,\ \text{g/mol})\ (10^3\ \text{mg/g}) = 10^3\ K_{H,i} \cdot p_i \cdot MW_i$

(b) $X_{i,w} = \text{mol}_i/\text{mol}_T$. We can assume that the solution is so dilute that its density can be approximated to that of water (i.e., 1000 g/L), and that the total number of moles (n_T) can be taken approximately as the number of moles of pure water. Thus, for a volume of 1 L, knowing the molecular weight of water ($\text{MW}_w = 18$), one gets

$$n_T = \text{weight}/\text{MW}_w \text{ in g/(g/mol)}$$
$$= 1000\ \text{g}/(18\text{g/mol}) = 55.6 \text{ moles}$$

and

$$\begin{aligned} X_{i,W} &= (n_i/n_T) = (M_{i,w}V)/n_T \\ &= (K_{H,i} \cdot p_i,\ \text{mol/L})(1\ \text{L})/(55.6\ \text{mol}_T) \\ &= (K_{H,i}/55.6) \cdot p_i \\ &= K'_{H,i} \cdot p_i \end{aligned}$$

where

$$K'_{H,i} = K_{H,i}/55.6\ \text{atm}^{-1}$$

Also note that

$$M_{i,w} = (X_{i,w}\ n_T/V)$$

(c) ppm $= (M_{i,w},\ \text{mol/L}) \cdot (\text{MW}_i,\ \text{g/mol}) \cdot 1000\ (\text{mg/g}) = \text{mg}_i/\text{L}$
(The results of this example are summarized in Table 6.10).

evaporation:

$$M_{i(\text{aq})} \rightleftarrows M_{i(\text{g})} \qquad (6.2)$$

and the value of the corresponding equilibrium constant is $K_{H,i}^{-1}$. An exercise to convert $K_{H,i}$ to different units is given in Example 6.1.

The two natural gaseous compounds that have the strongest influence in aquatic reactions, oxygen and carbon dioxide, have preponderant effects on redox reactions and on the pH of aquatic media, respectively. A more quantitative discussion is now presented.

6.2.1.2 *Dissolved Oxygen in Water*

Dissolved oxygen is essential for aquatic life because all aerobic organisms, including green plants, require oxygen for their metabolic processes (as respiration). In addition, it oxidizes organic and inorganic compounds present in water, allowing their breakdown into basic nutrients utilized by aquatic organisms. For aerobic life to exist, a minimum of 2–4 mg/L of dissolved oxygen is normally required. The amount of dissolved oxygen determines the type of aquatic organisms that may survive. For example, trouts need approximately 6.5 mg/L of dissolved oxygen, while carps need only 2.5 mg/L. Waters that have a good oxygen level maintain good water quality.

In addition to the oxygen dissolved from air, photosynthetic processes taking place in aquatic flora during daylight hours, contribute to increase the dissolved oxygen with the concomitant consumption of carbon dioxide present in water, as shown in the reaction:

$$6\text{CO}_{2(\text{g})} + 6\text{H}_2\text{O}_{(\text{l})} + h\nu \xrightarrow{\text{algae}} \text{C}_6\text{H}_{12}\text{O}_{6(\text{s})} + 6\text{O}_{2(\text{g})} \qquad (6.3)$$

When dissolved oxygen is depleted, the aerobic organisms cannot survive and non-oxygen (anaerobic) organisms thrive, giving water different

TABLE 6.10. Different formulas and units for Henry's law

Desired concentration units	Formula
$M_{i,w}$, mol_i/L	$K_{H,i} \cdot p_i$
$C_{i,w}$, mg_i/L	$(10^3\ K_{H,i} \cdot \text{MW}_i) \cdot p_i$
$X_{i,w}$, $\text{mol}_i/\text{mol}_T$	$(K_{H,i}/55.6) \cdot p_i$
ppm, mg_i/kg	$10^3\ M_{i,w} \cdot \text{MW}_i$

Example 6.2 Show that although oxygen is present *in air* at a relatively *high mole fraction* ($y = 0.21$), it only dissolves *in water* to a very *small mole fraction* (use T = 25°C, P = 1 atm).

Answer

$$O_{2(g)} \rightleftarrows O_{2(aq)}$$

The mole fraction in water can be calculated from Table 6.10 by using

$$X_{i,w} = (K_{H,i}/55.6)\cdot p_i$$

Substituting $K_{H,i}$ and p_i under the stated conditions (see Table 6.9), one then obtains

$$X_{i,w} = X_{O_2,w} = (1.3\times10^{-3}/55.6)\,0.21 = 4.9\times10^{-6}$$

which is a rather *small* mole fraction. From the definition of mole fraction, one gets

$$X_{O_2,w} = n_{O_2}/(n_{O_2}+n_w) = n_{O_2}/(n_{O_2}+55.6)$$

$$n_{O_2} = (4.9\times10^{-6})(n_{O_2}+55.6)$$

$$n_{O_2} = 2.7\times10^{-4}\ \text{mol/L}$$

Note that this is the *saturation concentration* of oxygen in water, C_s. In terms of mg/L,

$$C_s = (2.7\times10^{-4}\text{mol/L})(32\ \text{g/mol})(1000\ \text{mg/g})$$

$$C_s = 8.7\ \text{mg/L (at 25°C and 1 atm).}$$

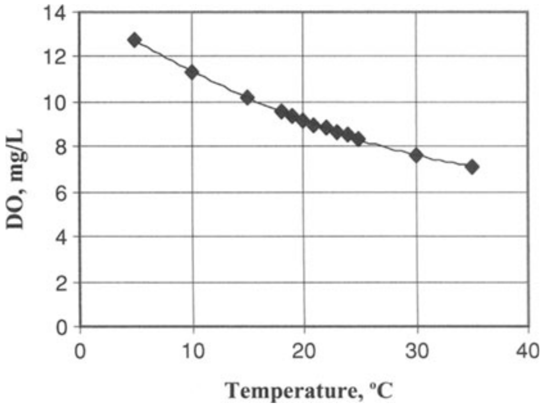
characteristics: it becomes dark in color, foul odors and gas bubbles are liberated (H_2S, CO_2 and CH_4), aquatic vertebrates are absent, and mosquitoes proliferate. These characteristics are typical of swamps, which are mainly anaerobic systems. An exercise to calculate the amount of dissolved oxygen is given in Example 6.2.

The dissolution of oxygen in water is also affected by ambient temperature, pressure, and the salinity of water or the dissolved salt content. This level of oxygen affects the oxidation processes, biological or not, taking place there. At higher temperatures the volatility of oxygen is higher, and for that reason lower values of dissolved oxygen are found in warmer climates. In addition, oxygen is consumed more rapidly because the rate of the metabolic processes taking place with the biota in water increases with temperature. This is one of the problems often present during summers, when oxygen levels sometimes decrease causing the death of aquatic organisms. The tendency of the dissolved oxygen concentration with temperature and pressure is shown in Figure 6.5.

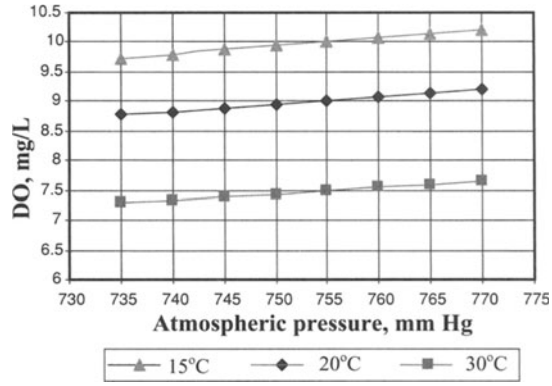
An approximate equation to calculate the mg/L of oxygen in fresh waters at 1 atm, as a function of temperature (in degrees Celsius) is

$$\text{Dissolved } O_2 \text{ (in mg/L)} = 0.033\,T^2 - 0.3201\,T + 14.258 \quad (6.4)$$

As shown in Figure 6.5, pressure affects the amount of dissolved oxygen as well; thus, at higher



(a) The effect of temperature



(b) The effect of pressure

FIGURE 6.5. (a) Effect of temperature and (b) pressure on the amount of dissolved oxygen in water. (Data from Peavy, 1985).

Example 6.3 Calculate the equilibrium concentration of $CO_{2(aq)}$ in water, in ppm.

Answer

From Table 6.10, and using consistent units, we get:

$$\begin{aligned}\text{ppm} &= 10^3 M_{i,w} \cdot \text{MW}_i = 10^3\,(K_{H,i} \cdot p_i) \cdot \text{MW}_i\\ &= 10^3(3.5 \times 10^{-2} \cdot 3 \times 10^{-4}) \cdot 44\\ &= 0.46\ \text{ppm}\end{aligned}$$

altitudes, lower concentrations of oxygen will be present. The figure also shows that there is less change in the amount of dissolved oxygen with pressure as temperature increases. This amount is also affected by the degree of salinity of water: it decreases with solute concentration. For example, as salinity goes from 0 to 45 g/L (at 20°C and 1 atm), the dissolved oxygen concentration decreases from 9 to 7 mg/L. This is why the dissolved oxygen concentration in surface waters is in the range of 7–12 mg/L (i.e., near-saturation or even over-saturation values). In surface seawater the level of dissolved oxygen is lower (of the order of 6–9 mg/L) due to the salinity, and it decreases with depth. Owing to its strong temperature dependence, cold higher-latitude ocean waters are richer in oxygen than those near the equator. Groundwaters may have DO levels as low as 0 mg/L to near-saturation. Groundwaters in recharge areas in zones of permeable, fractured rocks possess the highest DO values.

6.2.1.3 *Dissolution of CO_2 in Water*

Carbon dioxide in water comes from the following main sources:

- Dissolution from air
- Production and dissolution from photosynthetic processes in the absence of light
- Aerobic processes taking place in the main body of water
- Anaerobic processes in the sediments at the bottom of the water body
- Underground volcanic emissions as volcanic vents

The amount of dissolved CO_2 in water can be obtained from Henry's law, but its dissolution behavior is more complex than that of O_2 because CO_2 reacts with water to form carbonic acid. This is a weak acid with two dissociation constants that determine the aqueous concentrations of protons, carbonate, and hydrogen carbonate ions. Such an acid–base system has an enormous influence on all aquatic processes, because it affects the pH and alkalinity balance, and, indirectly, also the redox potential of the system.

The typical percentage of CO_2 in air is 0.03% (and up to 0.06%), and thus its partial pressure approximately equals (0.03/100) atm $= 3 \times 10^{-4}$ atm. Its concentration in ppm is calculated in the Example 6.3.

The reactions and the corresponding equilibrium constants for the carbonic acid dissociation are as follows:

$$\begin{gathered}H_2CO_3 + H_2O_{(l)} \rightarrow H_3O^+ + HCO_3^-\\ K_1 = 4.2 \times 10^{-7}\ \text{mol/L}, \quad pK_1 = 6.38\end{gathered} \tag{6.5a}$$

$$\begin{gathered}HCO_3^- + H_2O_{(l)} \rightarrow H_3O^+ + CO_3^{2-}\\ K_2 = 4.8 \times 10^{-11}\ \text{mol/L}, \quad pK_2 = 10.32\end{gathered} \tag{6.5b}$$

As a reasonable approximation, we will consider that the main source of $CO_{2(aq)}$ is its dissolution from air, and that the CO_2 content in air is constant. Therefore, the concentration of H_2CO_3 under the same set of conditions is also considered as constant and equal to the concentration of dissolved carbon dioxide, given that as soon as the dissolution reaction takes place the CO_2 is replenished according to the following equilibrium:

$$CO_{2(aq)} + H_2O_{(l)} \rightleftarrows H_2CO_{3(aq)} \tag{6.6}$$

Because carbonic acid is a weak acid, its dissociation in water is poor and thus the second dissociation takes place only to a negligible extent. Nevertheless, the dissociation of carbonic acid gives an acidic nature to water in natural systems. This is further analyzed in the Example 6.4.

The total carbonate concentration in water at equilibrium with carbon dioxide is expressed

Example 6.4 Determine the pH and the concentration of the predominant carbonate ions (i.e., HCO_3^- or CO_3^{2-}) in water in an open system in equilibrium with the carbon dioxide contained in air (e.g., rainwater). Consider the equilibrium concentration of dissolved carbon dioxide as 1.05×10^{-5} mol/L (as calculated from Example 6.3).

Answer

From the equilibrium equation for the first dissociation of carbonic acid

$$\begin{aligned} K_1 &= [HCO_3^-][H_3O^+]/[H_2CO_3] \\ &= 4.2 \times 10^{-7} \text{ mol/L} \end{aligned}$$

Given that the second dissociation is much smaller than the first one, we will consider that the HCO_3^- does not dissociate further and thus there is no other source of protons. Then, this is the predominant carbonate ion. Furthermore, we will also consider that the amount of protons provided by the self-dissociation of water is much smaller than that provided by the first dissociation of carbonic acid. In this way,

$$[HCO_3^-] = [H_3O^+] = y$$

Then,

$$4.2 \times 10^{-7} = y^2/[H_2CO_3]$$

and

$$\begin{aligned} y^2 &= (4.2 \times 10^{-7})(1.05 \times 10^{-5}) \\ y &= 2.1 \times 10^{-6} \text{ mol/L} = [HCO_3^-] = [H_3O^+] \end{aligned}$$

Lastly,

$$pH = -\log[H_3O^+] = -\log(2.1 \times 10^{-6})$$

and

$$pH = 5.7$$

which shows that rainwater will be slightly acidic, even under non-polluted conditions. The proton concentration thus calculated (2.1×10^{-6}) is indeed considerably larger than that provided by the self-dissociation of water (i.e., 1×10^{-7}), and thus our assumption can be considered appropriate.

through a mass balance:

$$C_t = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \qquad (6.7)$$

and it is highly dependent on pH. From the value of $pK_2 = 10.32$, one can see that the predominance of $[CO_3^{2-}]$ will only occur at $pH > 10.32$. Common practice considers that the predominant species that determines the alkalinity of water in the pH range 6.38–10.32 is $[HCO_3^-]$. Carbonate equilibria are further discussed in Experiment 4.

Another interesting result of carbon dioxide solubility in water is that it constitutes the basis for the phenomenon of spontaneous and violent liberation of dissolved CO_2 to the atmosphere in a stratified lake, as in the case of Lake Nyos in Cameroon mentioned above (see Section 6.1.3). When dissolved CO_2 seeps from a hydrothermal vent into a stratified lake, the pressure and low temperature favor the dissolution and saturation in the lower strata of the lake. Because of its high solubility, more than five volumes of CO_2 can dissolve in one volume of water. As for any other gas, however, its solubility depends on temperature and pressure, making the stratification intrinsically unstable. The long stability of such accumulation stems from the fact that CO_2-rich water is denser than pure water, as long as gas bubbles do not nucleate. The horizontal layering is due to the diffusion of the CO_2 and the temperature of the lake stratum. Thus, it seems that there are two possible reasons for the release of the dissolved gases: one is that an external trigger upsets the lake stratification (e.g., landslide, earthquake, or heavy rain); another is that CO_2 bubbles nucleate within a saturated layer of the lake water, then they rise and grow, attracting in their wake deeper water available for liberating the gas in solution. This may initiate a chain-like reaction, causing the entire lake to overturn through an ascending column of rising and expanding CO_2 bubbles.

6.2.2 Interactions between Water and Sediments/Soil

There are many interactions between water and sediments/soil. Some examples are discussed in Chapter 5.

6.3 Physicochemical Processes in Aquatic Systems

In addition to the influence of the gas–water equilibria discussed above, the presence and concentration of different compounds in surface water, seawater, groundwater, and the like depend on physicochemical processes such as weathering, adsorption, ion exchange, redox processes, and precipitation reactions. These reactions and processes are affected by the interactions among the different dissolved species and those with suspended constituents and sediments. Physical processes such as water flow, transport phenomena, evaporative processes, and others can also determine the composition and transformations of the different compounds.

Reactions occurring in pristine or polluted waters typically include acid–base (protolysis), electron transfer (redox), electron-sharing, complexation, ligand exchange, and light-induced reactions. The master variables here are normally pH and pE, as defined in Chapter 2. Such reactions are normally responsible for the incorporation, removal, or transformation of ions and compounds in aqueous media; these reactions are considered next. Hereafter, we will proceed to a brief discussion of other chemical and physical phenomena mentioned above.

6.3.1 Chemical Processes in Aquatic Systems

The main natural phenomenon that contributes to the presence of new compounds in water is the weathering process. Water (mainly acidic water) and gases in air or dissolved in water (mainly oxygen and carbon dioxide) can cause chemical weathering. The ions and compounds formed or removed from minerals and soil percolate and move into rivers, lakes, and groundwater, thus changing their original composition. Weathering reactions are caused by the interaction of water and air with the surface of compounds on the Earth's crust. These are normally slow reactions, previously discussed in detail in Section 5.3.2.

6.3.1.1 Acid–Base Reactions

As discussed in Section 2.2, acid–base reactions depend on the presence of proton *donors* and *acceptors*. The main natural sources of proton donors include the dissolution of atmospheric gases (mainly CO_2) and the additional CO_2 contributions from biochemical processes, some of which will also promote the presence of organic acids as decomposition products (such as fulvic and humic acids). Proton acceptors include basic substances (e.g., amines) and some alkaline or alkaline earth metal derivatives (e.g., sodium carbonate, calcium hydroxide).

Protons are sometimes released by ion exchange reactions between aqueous components and living organisms or soil, whereby protons are unconfined due to cation substitution. Another natural proton source is the oxidation of S-, N-, and P-containing compounds, as well as the oxidation and hydrolysis of hydrated polyvalent metals such as Al^{3+}, Fe^{2+}, and Fe^{3+}. For example,

$$Al(H_2O)_6^{3+} + H_2O_{(1)} \rightleftarrows Al(OH)(H_2O)_5^{2+} + H_3O^+ \tag{6.8}$$

a. The pH of Aquatic Systems

The hydrological cycle involves pH variations. In fact, most natural waters have a pH between 4 and 9 that is controlled mainly by the carbon dioxide–carbonate equilibrium. For instance, as calculated in example 6.4, the pH of rainwater is around 5.7 because of its equilibrium with carbon dioxide, but as it touches the Earth and comes in contact with decomposing organic materials, it may acidify even further. On the other hand, if water comes in contact with alkaline environments, minerals or sediments – mainly carbonates (which upon dissolution in water generate strongly basic media), its pH will rise.

Sometimes the natural oxidation of sulfur compounds exposed to air and rainwater will generate sulfuric acid that may lower the pH to extremely acidic values. This is typical of mine spoilage or acid mine drainage, AMD, where pyrite (FeS_2) is exposed to oxidation:

$$\begin{aligned} &FeS_{2(s)} + 15/4\, O_{2(g)} + \tfrac{1}{2}\, H_2O_{(1)} \rightarrow \\ &\quad Fe^{3+} + H^+ + 2SO_4^{2-} \end{aligned} \tag{6.9}$$

Acid drainage originates when the sulfidic rock is exposed to the atmosphere and oxidation processes take place, transforming the sulfur compounds of the minerals into sulfuric acid. This phenomenon is further discussed in Section 8.4.3.

The pH of a system determines the reactions that define the concentration of many dissolved chemical species in water containing salts and minerals, supplied by weathering reactions, rain, runoff, and lixiviating processes. The pH is a key parameter for biological growth and for the sustainment of life for the different aquatic flora and fauna species. As discussed in Chapter 2 the contribution of the different species will affect the final pH and vice versa (i.e., the pH on its own often determines the form of the species present). That is why the distribution diagrams of chemical species are frequently defined as functions of pH (Section 2.1.2). In summary, the main environmental processes that affect the pH and the alkalinity of natural waters include:

(a) Physicochemical processes
  - Acidification through atmospheric CO_2 dissolution
  - Atmospheric acid deposition
  - Oxidation and hydrolysis of hydrated polyvalent metals
  - Cation uptake and proton exchange
  - Acidification through air-oxidation of metal sulfides
  - Basification by partial dissolution of solid carbonates
  - Acidification by NH_4HSO_4 aerosols from ocean sources

(b) Biologically mediated processes
  - Photosynthesis and respiration (liberation of CO_2)
  - Nitrification (ammonium ion oxidation that involves proton liberation):

$$2NH_4^+ + 3O_{2(g)} \rightleftarrows 2NO_2^- + 4H^+ + 2H_2O_{(l)} \qquad (6.10)$$

  - Microbial-mediated production of sulfides and further oxidation to sulfuric acid:

$$R - SH + H_2O_{(l)} \rightleftarrows R - OH + H_2S_{(g)} \qquad (6.11)$$

$$H_2S_{(g)} + 2O_{2(g)} \rightleftarrows 2H^+ + SO_4^{2-} \qquad (6.12)$$

  - Acidification from biodecomposition of organic matter (formation of humic and fulvic acids)

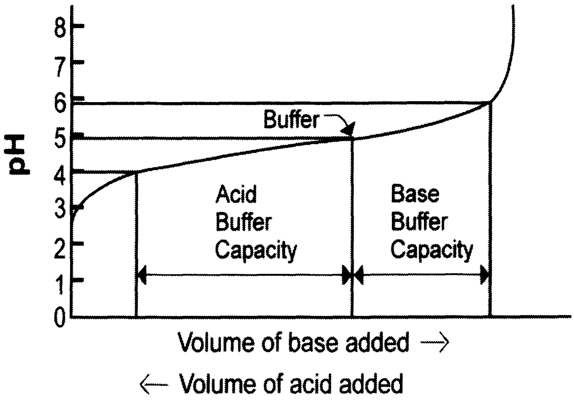


FIGURE 6.6. Schematic diagram of the buffer capacity of an aqueous system. (Source: Dartmouth University, 2005).

b. Buffering Capacity in the Environment

In an environmental aquatic system, the dissolution of ions from soils and the dissolution of atmospheric or biologically generated gases may determine its neutralizing and buffering capacities. (The action of buffers is discussed in Section 2.2.2). They consist, respectively, of the ability to neutralize and to resist pH changes resulting from acidic or basic inputs or discharges. These properties allow an aquatic system to tolerate such inputs as long as they do not surpass its buffering capacity (see Figure 6.6).

This phenomenon is mainly due to the presence of inorganic or organic conjugate acid–base pairs in natural waters, and of soluble minerals and inorganic compounds from sediments. The conjugate base neutralizes the extra acid input, while the conjugate acid reacts with the extra base. This is a common occurrence, especially in the presence of salts of weak acids or bases, because they establish equilibria between the two phases: solid (sediments) and aqueous. This allows the aquatic system to have a neutralizing and buffering capacity.

Many natural aqueous systems have ion combinations in solution that allow them to function as buffers. Other aquatic systems (e.g., some rivers and lakes) lack such ions or have a poor buffering capacity, and therefore they are vulnerable to acid or basic inputs.

The species produced by the dissolution of CO_2 in water are extremely important in regulating the pH of natural waters. Likewise, the presence of limestone, calcite (calcium carbonate), and dolomite, $CaMg(CO_3)_2$ (that are commonly present in soil and sediments) is often decisive for the neutralizing capacity of aquatic systems.

Other common species that have an effect on the pH and buffering capacity of natural systems include phosphates, borates, amino acids, and some organic compounds (generally weak acids). Phosphoric acid is a polyprotic acid that liberates one proton in each of its three dissociation steps, leaving a weaker acid in each step:

$$H_3PO_4 \rightleftarrows H_2PO_4^- + H^+ \quad K_1 = 10^{-2.14} \tag{6.13a}$$

$$H_2PO_4^- \rightleftarrows HPO_4^{2-} + H^+ \quad K_2 = 10^{-7.20} \tag{6.13b}$$

$$HPO_4^{2-} \rightleftarrows PO_4^{3-} + H^+ \quad K_3 = 10^{-12.34} \tag{6.13c}$$

The evident buffering capacity in seawater resists pH changes due to acid or base inputs and maintains a pH close to 8 because of the presence of several ions [mainly the HCO_3^-/CO_3^{2-} pair and the borate system, $B(OH)_3/B(OH)_4^-$]. Although borates and carbonates are considered weak bases, they actually act as amphoteric species (i.e., they behave as acids or bases, depending on the nature of the other species present). When a strong acid is present in the solution, the amphoteric species acts as a base; if a stronger base is present, it acts as an acid. For example, in the $H_2CO_3/NaHCO_3$ system, this conjugate pair behaves like seawater by showing a relative insensitivity to pH changes resulting from acid or base additions. As noted in the *buffering index* discussion (Section 2.2.2), this ability will be best at pH values in the vicinity of each pK_a or pK_b of the weak acid or base.

When the carbonate system is the buffer, the addition of H^+ gives:

$$CO_3^{2-} + H^+ \rightleftarrows HCO_3^- \tag{6.14}$$

This reaction prevents a large pH drop in the system. A similar buffering behavior is observed when a base is added to the buffer solution. Here, the OH^- of the base reacts with the acid, forming more hydrogen carbonate ions:

$$H_2CO_3 + OH^- \rightleftarrows HCO_3^- + H_2O \tag{6.15}$$

Because the ratio of carbonic acid to hydrogen carbonate ion decreases here, then the pH rises but only slightly. When the acid or base added to the system completely neutralizes either member of the pair, the system moves out of the buffering range and the buffering action is lost. Changing the ratio by a factor greater than 10 will have this effect, and the pH will then change directly with the amount of acid or base added.

c. Alkalinity or Acid-Neutralizing Capacity

Because the buffering capacity of a natural aquatic system is often too complex to calculate, a much simpler alternative is to determine its *alkalinity* or, alternatively, its *acid-neutralizing capacity* (*ANC*). These parameters represent the ability of an aquatic system to neutralize an acid discharge, because they measure the concentration of neutralizing ions present in the aqueous system. The difference between alkalinity and the ANC of a water sample is that the latter considers the acid neutralizing capacity of solutes plus particulate matter, whereas alkalinity only takes into account the dissolved species. Alkalinity generally gives valuable information with respect to the concentration of carbonate species because the carbonate system is the key factor for the buffering capacity in aquatic systems. Both parameters are generally reported as equivalents (or meq, or μeq) per liter, or ppm of $CaCO_3$.

Alkalinity is algebraically represented as the total concentration of basic anions present in water minus the hydrogen ion concentration; it generally considers only the basic anions associated to the carbonate system because it is the predominating species in nature. This may be expressed as mg/L (as calcium carbonate):

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{6.16}$$

Any substance contained in an aqueous system that reacts with a strong acid contributes to its ANC. Important non-carbonate species that contribute to this capacity include organic ligands (e.g., acetate and propionate), silicates, borates, ammonia, and sulfide ions.

Phosphate and arsenate ions, when found in high concentrations, may also contribute to the ANC. In average natural waters, non-carbonate contributors are not present in sufficient amounts so as to affect the alkalinity or ANC determinations.

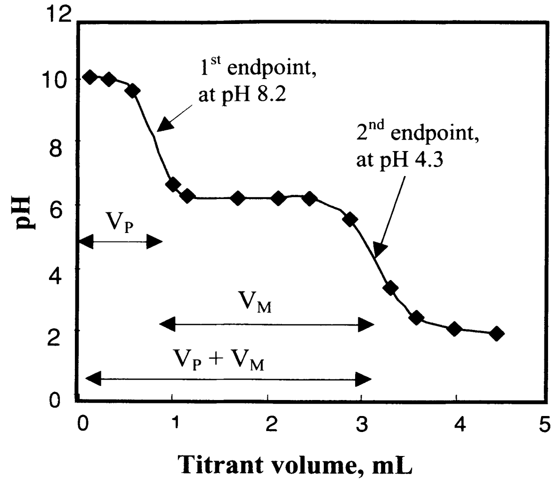


FIGURE 6.7. Experimental determination of alkalinity or ANC in a water sample.

d. Experimental Determination of Alkalinity or ANC

Alkalinity can be determined by an acidimetric potentiometric titration of a filtered sample. In the case of the ANC, a raw water sample is used. The titration involves the addition of an acid of known concentration (typically in the range 0.01 to 2 N HCl or H_2SO_4) to a given sample volume V_s. A typical plot is schematically shown in Figure 6.7.

The first endpoint (phenolphthalein endpoint, at V_p) occurs at pH $\approx$ 8.2 and indicates the neutralization of OH^- and the conversion of CO_3^{2-} to HCO_3^- as follows:

$$OH^- + H^+ \rightleftarrows H_2O \qquad (6.17)$$

$$CO_3^{2-} + H^+ \rightleftarrows HCO_3^- \qquad (6.18)$$

The second endpoint (at $V_P + V_M$, where V_M is the methyl orange endpoint) occurs at pH $\approx$ 4.3 and indicates the conversion of HCO_3^- into H_2CO_3 as follows:

$$HCO_3^- + H^+ \rightleftarrows H_2CO_3 \qquad (6.19)$$

Then, the amount of acid added at V_P provides all the H^+ necessary to neutralize the OH^- present, plus half the H^+ necessary to titrate CO_3^{2-} all the way to H_2CO_3. Similarly, the amount of acid added from V_P to the second endpoint V_M is the amount needed to titrate all the HCO_3^- (i.e., that produced in the $CO_3^{2-} + H^+ \rightleftarrows HCO_3^-$ reaction, plus the HCO_3^- initially present in the sample), to H_2CO_3. This interpretation also involves the (reasonable) assumption that the initial $[H^+]$ is small and thus H^+ is not a major component of the sample. For different alkalinity cases, see Example 6.5.

The *relative neutralization capacity* of an aquatic system to acid deposition or acid drainage may be assessed using Table 6.11.

Alternatively, the *sensitivity* of an aquatic body can be given in terms of the ANC (using the same units as in the previous table): ≤ 0 (Acidified), 0–40 (Very sensitive), 40–200 (Sensitive), >200 (Insensitive). (See Thomas, 1992.)

Although it is good for neutralizing acid deposition, the ANC in freshwater systems is one of the critical parameters for determining the risk to the flora and fauna living in those systems. For example, Scandinavian countries have limited the ANC value for freshwater lakes to 20 μeq/L since brown-lake trouts and other species respond negatively to increased alkalinity levels.

6.3.1.2 Redox Reactions

Because the pH of natural water systems is a function of their dissolved compounds (including gases), these species also confer a definite electrochemical reduction potential range to the aquatic medium. Some of the pH and *E* values typically found in natural water systems are given in Table 6.12.

Redox conditions vary in natural aquatic systems with composition and depth. The superficial or top layer provides an oxidizing environment, usually with a high dissolved oxygen content (and thus a high *E*), and as a rule the species found there will be in a highly oxidized state. The lower or bottom layer provides a reducing environment, with low dissolved oxygen concentration where reduced forms predominate; microorganisms mediate many redox reactions here (see Chapter 7).

Redox reactions affect the solubilization of certain solids and their mobility as well. Elements whose solubility strongly depends on their oxidation state include Fe, Mn, Cr, N, and S. Oxygen is normally the main oxidant or electron acceptor; however, when there is oxygen deficiency, these other elements may become the electron acceptors and their compounds change to a reduced form. In this way, Mn(III) or Mn(IV) are reduced to Mn(II); Fe(III) to Fe(II); SO_4^{2-} to S^{2-}; and NO_3^- can be

Example 6.5 Alkalinity

(A) Match each alkalinity case (as specified by the results of the corresponding titration, given in the left column) to its appropriate interpretation (right column). Note that the predominant (and only) species considered in this aqueous system before each titration are OH^-, CO_3^{2-}, and HCO_3^-.

1. $V_P = V_M$
2. $V_P = 0$
3. $V_M = 0$
4. $V_M > V_P$
5. $V_P > V_M$

a. CO_3^{2-} and HCO_3^- predominate
b. Only CO_3^{2-} is present
c. Only HCO_3^- is present
d. OH^- and CO_3^{2-} predominate
e. Only OH^- is present

Answer to (A)

1-b, 2-c, 3-e, 4-a, 5-d

(B) For cases 1 through 5 of part A, write the concentrations of the following species (in mol/L) as a function of:

- the concentration of the acid titrant (N_H, expressed in equivalents/L),
- the sample volume (V_S), and
- the parameter(s) specified in each case.

As a guide, see the solution to Case 1 below.

Case	Conc. sought, *mol/L*	Parameter (s)	Answer, *mol/L*
1	$[CO_3^{2-}]$	V_P	$\left(\frac{N_H}{V_S}\right) V_P$
2	$[HCO_3^-]$	V_M	
3	$[OH^-]$	V_P	
4	(i) $[CO_3^{2-}]$ (ii) $[HCO_3^-]$	(i) V_P (ii) V_M, V_P	
5	(i) $[OH^-]$ (ii) $[CO_3^{2-}]$	(i) V_M, V_P (ii) V_M	

Answer to (B)

CASE 1

In this case, only CO_3^{2-} is present (see the answers from part A). Because one H^+ titrates one CO_3^{2-} *to the phenolphthalein end point*, then

$$\text{moles } CO_3^{2-} = \text{moles } H^+$$

$$\left(\frac{\text{mol } CO_3^{2-}}{\text{L}}\right) V_S = \left(\frac{\text{mol } H^+}{\text{L}}\right) V_P$$

$$= \left(\frac{\text{mol } H^+}{\text{L}}\right)\left(\frac{1 \text{ equiv. } H^+}{1 \text{ mol } H^+}\right) V_P$$

$$= \left(\frac{\text{equiv. } H^+}{\text{L}}\right) V_P = N_H V_P$$

and

$$[CO_3^{2-}] = \frac{N_H V_P}{V_S} = \left(\frac{N_H}{V_S}\right) V_P, \text{ in } \left(\frac{\text{mol } CO_3^{2-}}{\text{L}}\right)$$

The other cases can be solved in the same way, as shown below. (Suggestion: try not to look at the answers until you have solved all five cases).

CASE 2

Only HCO_3^- is present. Then,

$$[HCO_3^-]V_S = N_H V_M$$

$$[HCO_3^-] = \frac{N_H V_M}{V_S} = \left(\frac{N_H}{V_S}\right) V_M$$

CASE 3

Only OH^- is present. Then,

$$[OH^-]V_S = N_H V_P$$

$$[OH^-] = \frac{N_H V_P}{V_S} = \left(\frac{N_H}{V_S}\right) V_P$$

CASE 4

CO_3^{2-} and HCO_3^- predominate.

(i) Since titration of CO_3^{2-} to the phenolphthalein end-point is independent of the presence of HCO_3^-, one can use the same expression derived in Case 1 for $[CO_3^{2-}]$:

$$[CO_3^{2-}] = \left(\frac{N_H}{V_S}\right) V_P$$

(ii) Since V_M contains the H^+ necessary to titrate both, the HCO_3^- coming from CO_3^{2-} as well as the HCO_3^- initially present, one can find this last unknown by simple substitution:

moles of H^+(in V_M)
= moles of HCO_3^- (from CO_3^{2-}) + moles of HCO_3^- (initially present)
= moles of CO_3^{2-} + moles of HCO_3^-

Then,

moles of HCO_3^-
= moles of H^+(in V_M) − moles of CO_3^{2-}

$$[HCO_3^-]V_s = [H^+]V_M - [CO_3^{2-}]V_s$$

$$[HCO_3^-]V_s = N_H V_M - [N_H/V_s]V_P V_S$$

$$= N_H(V_M - V_P)$$

$$[HCO_3^-] = [N_H/V_s](V_M - V_P)$$

CASE 5

OH^- and CO_3^{2-} predominate. One can differentiate between them by noting that the phenolphthalein end-point encompasses both species, whereas the methyl orange end-point does not measure the OH^-. Then,

(i) We subtract:

$$\begin{aligned}\text{moles of } H^+(\text{in } V_P) &= \mathrm{N_H} V_P \\ &= \text{moles of } OH^- + \text{moles of } CO_3^{2-}\end{aligned}$$

minus

$$\text{moles of } H^+(\text{in} V_M) = \mathrm{N_H} V_M = \text{moles of } CO_3^{2-}$$

$$\mathrm{N_H} V_P - \mathrm{N_H} V_M = \text{moles } OH^- = [OH^-] V_S$$

Then,

$$[OH^-] = \left(\frac{\mathrm{N_H} V_P - \mathrm{N_H} V_M}{V_S}\right)$$

$$[OH^-] = \left(\frac{\mathrm{N_H}}{V_S}\right)(V_P - V_M)$$

(ii) To find $[CO_3^{2-}]$, one simply uses the second expression from (*i*):

$$\text{moles of } CO_3^{2-} = \mathrm{N_H} V_M$$

$$\left[CO_3^{2-}\right] V_S = \mathrm{N_H} V_M$$

$$\left[CO_3^{2-}\right] = \left(\frac{\mathrm{N_H}}{V_S}\right) V_M$$

To convert a CO_3^{2-} concentration of C (mol CO_3^{2-}/ L_{solution}) into alkalinity (mg $CaCO_3/L_{\text{solution}}$), the following conversion factor is used:

$$\begin{aligned}\text{Alkalinity} &= \left(\frac{C,\ \text{mol}_{CO_3^{2-}}}{L}\right)\left(\frac{1\ \text{mol}_{CaCO_3}}{1\ \text{mol}_{CO_3^{2-}}}\right) \\ &\times \left(\frac{100\ \text{g}_{CaCO_3}}{1\ \text{mol}_{CaCO_3}}\right)\left(\frac{10^3\ \text{mg}_{CaCO_3}}{1\ \text{g}_{CaCO_3}}\right) \\ &= 10^5\ C\,\frac{\text{mg}_{CaCO_3}}{L}\end{aligned}$$

Alternatively, if one starts with the *normality* of CO_3^{2-}, the conversion is

$$\begin{aligned}\text{Alkalinity} &= \left(\frac{N,\ \text{equiv } CO_3^{2-}}{L}\right)\left(\frac{1\ \text{mol}_{CO_3^{2-}}}{2\ \text{equiv}_{CO_3^{2-}}}\right) \\ &\times \left(\frac{1\ \text{mol}_{CaCO_3}}{1\ \text{mol}_{CO_3^{2-}}}\right)\left(\frac{100\ \text{g}_{CaCO_3}}{1\ \text{mol}_{CaCO_3}}\right) \\ &\times \left(\frac{10^3\ \text{mg}_{CaCO_3}}{1\ \text{g}_{CaCO_3}}\right)\end{aligned}$$

Lastly,

$$\begin{aligned}\text{Alkalinity} &= \left(\frac{10^5}{2}\right) N\,\frac{\text{mg}_{CaCO_3}}{L} \\ &= 5 \times 10^4 N\,\frac{\text{mg}_{CaCO_3}}{L}\end{aligned}$$

reduced to gaseous N_2, passing through several oxidation states corresponding to different denitrification stages.

The actual reduction of aqueous species is limited by the potentials corresponding to the oxidation and reduction of water, respectively, given by $E = 1.23 - 0.059$ pH and $E = -0.059$ pH, as discussed in Section 2.3.4. However, thermodynamics and kinetics do not always coincide, and a more realistic potential range observed in natural waters is approximately $+0.5$ to -0.5 V.

Among the most common natural redox reactions are the oxidation and reduction of Fe species. For instance, iron is present as Fe(II) in the primary-bearing minerals. Fe(II) is liberated through weathering reactions in proton-rich media, and becomes easily solubilized and oxidized to Fe(III) in the presence of dioxygen; it is simultaneously hydrolyzed

TABLE 6.11. Classification of an aquatic system according to its capacity to neutralize an acid discharge

ANC,* μeq $CaCO_3$/L	Classification
0	No capacity – acidified
0 to 25	Low capacity
25 to 200	Moderate capacity
200 to 500	High capacity

*Determined by a Gran titration plot. Source: U.S. Environmental Protection Agency, 2003.

TABLE 6.12. Typical pH and E ranges of natural systems

System	pH	E(V vs SHE)
Waterlogged soils	3.8–5.7	−0.3 to 0.05
Rain	5–6	0.4 to 0.5
Rivers and lakes	6–7.5	0.3 to 0.4
Marine sediments	6.3–8.8	−0.5 to 0.25
Oceans (surface waters)	7.6–8.8	0.2 to 0.3

Example 6.6 A 50.00 mL water sample is titrated to the phenolphthalein end-point with 5.00 mL of 0.02 N H_2SO_4, and to the methyl orange end-point with additional 5.00 mL of the acid. What is the total alkalinity, in mg_{CaCO_3}/L?

Answer

Since $V_P = V_M$ (which corresponds to Case 1 in the previous example), one can assume that CO_3^{2-} predominates in the system. Using the equation corresponding to Case 1, one gets

$$[CO_3^{2-}] = (N_H/V_S)V_P = (0.02/50)5 = 0.002\ mol_{CO_3^{2-}}/L$$

$$\text{Total alkalinity} = 10^5 \times 0.002 \frac{mg_{CaCO_3}}{L} = 200.0 \frac{mg_{CaCO_3}}{L} = 4.0\ meq_{CaCO_3}/L$$

into an insoluble iron oxy-hydroxide product, as shown below:

$$Fe^{2+} + \frac{1}{4}O_{2(g)} + \frac{3}{2}H_2O_{(l)} \rightleftarrows FeOOH_{(s)} + 2H^+ \qquad (6.20)$$

Different oxidation states as well as different solid and dissolved compounds can be predicted from the corresponding E-pH diagrams, as discussed in Chapter 2.

6.3.1.3 Complex Formation

Metals are present in the environment in a variety of forms, including inorganic and organic complexes. The presence of complex-forming ligands in natural environments is quite varied. Examples include citrate ions (found in natural waters as a result of biological activity), humic and fulvic acids (found in soils and water), amino acids and other DOM (dissolved organic matter, i.e., simple organic acids), and the like. Additionally, many ligands are pumped into the environment as a result of a myriad of industrial and other human activities (see Chapter 8).

The importance of complex formation is exemplified by the binding of Mg, Na, Co, Mn, Fe, Cu, and Zn to fulvic acids (FA), and of Fe to humic acids. The binding capacity of these natural acids for metal ions is within the range of 0.2–0.6 mmol/g, and the order of stability of complex formation (M-FA) with some key metals is $Fe^{2+} > Al^{3+} > Cu^{2+} > Ni^{2+} > Ca^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}$ (see Schnitzer, 1970). Interestingly, some cryptogams (i.e., mosses and lichens) capture part of their essential minerals by secreting ligands to complex them from their host rocks. Other examples follow.

a. Metal Complex and Ligand Adsorption onto Solid Surfaces. Because many aqueous metal ions and complexes adsorb onto minerals such as Fe and Al oxides and hydroxides, this alters the metal partitioning between the aqueous and solid phases; consequently, their migration, mobility and bioavailability can be affected as well (Section 6.3.2).

Complexation of metal ions by ligands in solution can be in competition with the binding of metals onto solid surfaces. The final result will depend on

- the concentration of the ligand
- the concentration of active surface sites on the solid (sediment or soil)
- the stability of the metal–ligand complexes in solution
- the stability of the solid surface complexes.

For example, in the presence of strongly binding natural organic ligands in water (especially at pH > 6), metals such as Cu, Ni, and Cd remain in solution, decreasing their extent of adsorption onto solid particles (e.g., goethite). On the contrary, with weaker ligands (even in excess), and more acidic pH, the metal ions prefer to adsorb onto soil or sediment particles.

b. Natural Oxidation of Dissolved Metal Complexes Oxidation reactions of metal complexes by dissolved oxygen are relatively common. For example, Fe(II) complexes can be oxidized to their Fe(III) counterparts:

$$4[\mathrm{Fe}^{2+}\mathrm{L}^{n-}]^{(2-n)} + \mathrm{O}_{2(g)} + 2\mathrm{H_2O}_{(l)} \rightarrow 4[\mathrm{Fe}^{3+}\mathrm{L}^{n-}]^{(3-n)} + 4\mathrm{OH}^- \qquad (6.21)$$

Another example involves complex oxidation with the participation of natural catalysts such as goethite (α-FeOOH), a redox-reactive solid:

$$4[\mathrm{Co(II)EDTA}]^{2-} + \mathrm{O}_{2(g)} + 4\mathrm{H}^+ \xrightarrow{goethite} 4[\mathrm{Co(III)EDTA}]^{-} + 2\mathrm{H_2O}_{(l)} \qquad (6.22)$$

6.3.1.4 Speciation

As mentioned in Chapter 2, the form in which the elements and compounds are found in different environments depends on the medium conditions. Thus, the distribution of their species in water is highly dependent on pH, composition, temperature, and the oxidation–reduction potential of the solution. These variables define their precipitation, dissolution, and complexation reactions. For example, P in water may be present in different forms (polyphosphate, $\mathrm{H_2PO_4}^-$, $\mathrm{HPO_4^{2-}}$, or $\mathrm{PO_4^{3-}}$) but the dominant species present strongly depend on pH (see Section 8.4.3) and on the solution's ionic strength. As a case in point, $\mathrm{H_2PO_4}^-$ will be the dominant species in fresh waters (at pH $\approx$ 6), but $\mathrm{HPO_4^{2-}}$ predominates in seawater (pH $\approx$ 8, and high ionic strength).

Phenomena such as chemical and biological transformations, metal mobility, bioavailability, bioaccumulation, toxicity, and persistence in the environment frequently depend on the chemical form or speciation of a given ion, especially the metallic ions. For example, there is normally a great difference between the sorption behavior of a free metal cation and that of its anionic complexes onto mineral oxides and hydroxides.

In the same vein, ligand speciation may drastically affect the nature of the complexes they form. (For ligand speciation calculations, one can use the chemical-species distribution algorithm derived in Section 2.1.2). For example, EDTA can be present as five different chemical species depending on pH and thus its complexes can be anionic, cationic, or neutral. This can have dramatic effects on their physicochemical properties and adsorption behavior. A case in point is the EDTA complexation of Fe^{3+}, where the neutral complex formed with HEDTA^{3-} is more than 20 orders of magnitude less stable than its corresponding anionic complex with EDTA^{4-}.

Bioavailability and toxicity of metal ions in aqueous systems are often proportional to the concentration of the free metal ion and thus decrease upon complexation. However, there are some metal compounds more dangerous than the metallic element itself (e.g., mercury vs. methyl mercury).

The redox environment can also determine some of the properties of metallic and non-metallic species. For example, the toxicity of arsenic when present in oxic (oxidizing) environments such as As(V) is very low, whereas its reduced form, As(III), is highly poisonous. The opposite occurs with Cr(VI) that is much more toxic than its reduced counterpart, Cr(III).

Mobility can also be severely affected by the redox environment. For example, Fe(II) and Mn(II) species are ordinarily soluble in natural waters deficient in oxygen, but their oxidized forms precipitate quite easily. The stability regions of insoluble Mn oxides can be seen in the Pourbaix diagram depicted in Figure 6.8.

Because of these reasons, the determination of the *total* concentration of a metal in a given matrix is often inadequate as a useful characterization, and *speciation* has gained considerable ground. Speciation is the process yielding evidence of the atomic or molecular form of an analyte. It can be defined either *functionally* (e.g., the determination of species that have certain specific functions such as their availability to plants), or *operationally* (e.g., the determination of the *extractable* forms of an element).

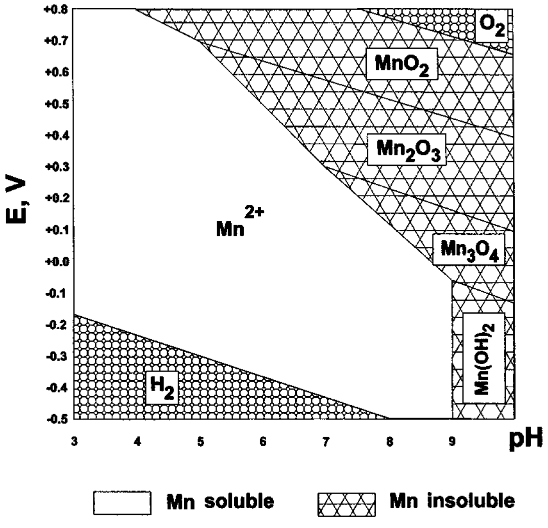


FIGURE 6.8. *E*–pH diagram for Mn.

For example, the speciation analysis of metal ions in sediments can be performed by sequential extraction, whereby each of the fractions obtained shows a different form of association of the metal in the soil matrix. As mentioned in Chapter 1, an accepted modern procedure is:

Step 1. Extraction of the *acid soluble* fraction (i.e., carbonates) with CH_3COOH
Step 2. Extraction of the *reducible* fraction (i.e., iron/manganese oxides) with hydroxyl amine hydrochloride
Step 3. Extraction of the *oxidizable* fraction (i.e., organic matter and sulfides) by H_2O_2 oxidation followed by extraction with $NH_4(CH_3COO)$

Sampling and analyzing in a way that does not affect the speciation of the sample is not always a trivial task, because the integrity of the target species can sometimes be altered quite easily. For example, a common practice is to add acid to samples to preserve species in their original form; however, this practice may lead to changes in ligand speciation as well as in the oxidation states of metal ions. Another example is the sampling and storage of Hg-containing samples because this metal can escape from containers made of certain plastics, which yields lower-than-true concentrations. Other samples are photosensitive (e.g., alkyltins and arsenobetaine) and must be isolated from light immediately after collection.

Sound knowledge of fundamental chemistry helps in most cases. For example, the analysis of Fe(II) in an aqueous sample can be accurately accomplished in an acidic environment even if it is not performed immediately, whereas the conversion of Fe(II) to Fe (III) in an alkaline environment in the presence of air is quite fast and will significantly alter the speciation results.

6.3.1.5 Colloids: Properties, Types, Sources, and Formation

The size of particles in water determines to a large extent their different physical states: large particles precipitate, small particles tend to dissolve. However, this differentiation is far from clear-cut, and as a result there are particles between these two extremes that remain *suspended* in water. Because these suspended *colloidal particles* (called *colloidal sols*) are not directly observable by the human eye, they look homogeneous and do not settle upon standing.

A colloid is a small particle separated from others by a dispersion medium (in aqueous systems this medium is obviously water). The size of colloidal particles ranges from one nanometer (nm) to one micrometer (μm). They are formed either by aggregates of small molecules or by large molecules of high molecular weight. Dispersions created with coarser materials (<10 μm) are sometimes considered *colloidal dispersions* as well.

The most common types of colloidal dispersions in aqueous systems are

- the dispersion of small solid particles
- a dispersed gas that forms a foam
- an insoluble dispersed liquid that forms an emulsion

In natural systems, solid–liquid dispersions are the most common colloidal dispersions.

Bacteria, viruses, organic polymeric substances, or inorganic solid particles of suspended sediment can also form colloids. Organic sources of colloidal particles in water include certain living and dead microorganisms, proteins, lignin, cellulose, and the natural insoluble polymeric fraction of humic substances (from kerogens to fulvic acids) that serve as ligands and form colloidal metal chelates.

Colloidal matter in water may also be a result of the weathering reactions of minerals such as hydrated iron oxides, and the disintegration and suspension of sediment clays that form coarse colloidal suspensions. Such colloids may also form by precipitation of inorganic ions due to geochemical changes (such as the formation of metal oxides, hydroxides, carbonates, and silicates, particularly into non-crystalline forms). This is especially true when the particles do not grow into larger aggregates that could increase their weight and make them settle easily, separating from water.

A typical example of colloid formation involves acidic streams containing dissolved Al^{3+} that encounter neutralizing streams, whereby aluminum hydroxide colloids form. Other cases include the formation of solid oxides and hydroxides of Fe^{3+} and Mn^{4+} through natural oxidation processes. When dissolved, the reduced species may encounter high oxygen levels in water that favor their oxidation processes, as represented in reaction 6.20 which can also occur as follows:

$$2Fe^{2+} + \frac{1}{2}O_{2(g)} + 5H_2O_{(l)} \rightarrow 2Fe(OH)_{3(s)} + 4H^+ \qquad (6.23)$$

Colloidal dispersions may appear either translucent or cloudy, depending on the type of colloid and the degree of particle concentration and dispersion. The colloidal particles cannot be easily distinguished from water. They possess properties that are very different from other solid settable suspensions and from solutions. When the colloidal particles are < 5 μm, they have erratic aleatory movements known as *Brownian movements*, caused by collisions with molecules from the dispersion medium. When a light beam passes through a colloidal dispersion, this reflects and scatters light (*Tyndall effect*).

Colloids are either *hydrophilic* (water-loving) or *hydrophobic* (water-hating). *Hydrophilic colloids* (e.g., proteins, humic substances, bacteria, viruses, as well as iron and aluminum hydrated colloids) tend to hydrate and thereby swell. This increases the viscosity of the system and favors the stability of the colloid by reducing the interparticle interactions and its tendency to settle. These colloids are stabilized more by their affinity for the solvent than by the equalizing of surface charges. Hydrophilic colloids tend to surround the hydrophobic colloids in what is known as the *protective-colloid* effect, which makes them both more stable.

Hydrophobic behavior generally occurs in inorganic colloids (e.g., silicates, carbonates, and sulfates) that have little or no affinity for water. Such colloids tend to acquire a surface charge that promotes the adsorption of oppositely charged electrolyte ions, thereby generating a mutual repulsion of similar charges.

Colloidal particles are also characterized by a large surface area/mass ratio (called *specific surface*), and by a strong surface charge that favors adsorption. For example, montmorillonite clays and some organic colloids may have specific surfaces of up to 800 m^2/g.

Colloids are either negatively or positively charged as a result of dissociated surface groups that create unbalanced charges, and of the ions of opposite charge in the surrounding medium. The magnitude and type of charge of colloids in a suspension is particularly difficult to predict.

The most abundant colloids in water (including sea water) are clay minerals (see Section 5.4). These colloids typically display a negative charge that can be partially neutralized by the electrostatic adsorption of surrounding cations in solution. Such negative charges are mainly due to two effects: one that defines a *permanent charge* and another which is a *variable effect* (pH-dependent) that promotes the deprotonation of the outer OH groups, leaving the negative charge of oxygen on the surface. This variable effect is very common in other types of mineral particles such as metal oxides, oxyhydroxides, hydroxides, and the like.

The permanent charge in clays is due either to uncompensated internal charges, or to the loss or substitution of interlayer cations in the lattice structure; the latter is known as *isomorphous substitution* which occurs during mineral formation. This consists in the substitution of one cation by another of similar size and coordination number in the crystal lattice, without disrupting the crystal structure of the mineral. In this way, a Si^{4+} moiety may be substituted by an Al^{3+}, or an Al^{3+} may be replaced with Fe^{2+}, Ni^{2+} or Mg^{2+}; this unbalances the charges and leaves a net negative charge.

Organic colloids (mainly humic substances) also possess large specific surfaces and are generally negatively charged due to the acidic functional groups that tend to dissociate or polarize. Examples of such groups include carboxyls (R-COOH), quinones (-Ar=O), phenols (-Ar-OH), and enols (R-CH=CH-OH). (See Section 5.4.2 for a more complete discussion of humic substances.)

The net charge in colloidal particles results largely from the adsorption of ions, favored by the large surface area, that tends to neutralize the colloidal charge. This effect creates a *double layer* of counter ions around the particles. The sign and magnitude of the net charge on the colloid is mainly due to its chemical nature and to the characteristics of the dispersion medium (i.e., ionic strength and pH). The double layer is formed by a fixed, *inner* layer and an *outer*, diffuse and mobile layer of freely moving counter ions (see Figure 6.9). The double layer is responsible for some of the properties of colloids. It generates a surface potential called *zeta potential*, usually expressed in millivolts.

The colloidal particles are subject to two forces: *Van der Waals' attractive forces* and *repulsive forces* caused by the electrostatic repulsion of similar charges. While these particles remain suspended in colloidal form, the repulsive forces predominate; the

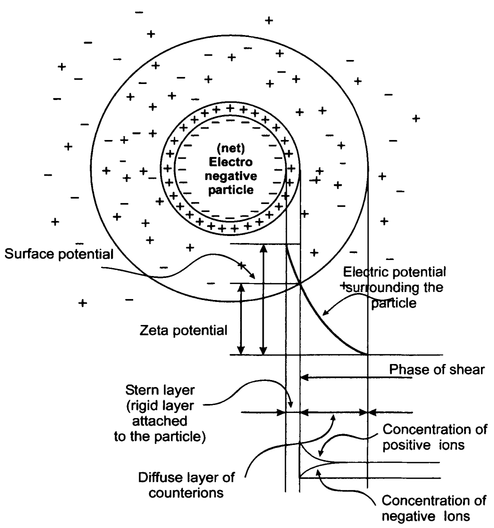


FIGURE 6.9. Double layer of charges in a colloidal particle.

colloids may or may not come together, depending on the net repulsive or attractive nature of their interaction. In turn, this depends to a large extent on the ionic strength of the medium, whereby one of the two opposing interactions will predominate. At higher ionic strength, the repulsion forces diminish due to the compression and contraction of the double layer. Such a phenomenon reduces the surface potential, allowing the colloids to come together and aggregate. On the other hand, at low ionic strengths, the repulsive forces become dominant and prevent aggregation.

The flocculation and formation of colloidal particle aggregates is an example of how ionic strength modifies the forces interacting on the colloidal particles. This is the case of clay minerals or sediments discharged by rivers into estuaries. Here, the river drainage containing sediments and colloidal particulate matter encounters a strong electrolytic medium in the estuary. This increases the concentration of counter ions that neutralize practically all the surface charges, thus reducing the size of the double layer. Van der Waals' forces then predominate, and the colloids will form aggregates and settle as sediments.

The presence of organic matter (especially particulate organic matter, *POM*, common in seawater) promotes the coagulation of colloids by serving as binding material that favors their aggregation. Nevertheless, tidal movements re-suspend these settled sediments, creating a region in the estuaries with a high concentration of the re-suspended sediments called *turbidity maxima*. Here, many other important reactions take place (especially at the solid-liquid interphase).

TABLE 6.13. Charges on common natural colloids

Colloid	Charge
Clay minerals	(−)
Silica	(−)
Manganese dioxide	(−)
Sulfides	(−)
Carbonates	Usually (+)
Ferric hydroxide	Usually (+), but it may also be (−), depending on pH
Organic colloids	(−)

Source: Krauspkopf, 1979.

Some of the most typical charges in common natural colloidal particles are shown in Table 6.13.

One of the most relevant environmental consequences of the existence of colloids derives from their ability to adsorb different species and to exchange ions. Examples include radionuclides, organics, and metal derivatives that may be toxic pollutants. Colloids that retain these species may participate in transforming them into catalysts, after which they transport them into aqueous systems located far from their original discharge points.

6.3.1.6 Photochemical Reactions

As discussed in Section 2.6, natural light can induce a variety of processes of environmental importance either *directly* (when light is absorbed by the species of interest) or *indirectly* (when the species of interest reacts with an intermediate called *mediator*, previously excited or produced by light).

The best conditions for photolysis in natural aqueous bodies involve low turbidity, low concentrations of dissolved organic compounds, bright sunny days, and quiescent waters or slow-moving streams. For example, the rate of photoproduction of $^{\bullet}OH$ radicals from nitrate photolysis (see below) is lower at higher latitudes. For example, at a latitude 0 N (like in Lake Victoria, in Tanzania) this rate is more than twice that for latitude 60 N (like in lake Tyrifjorden, in Norway). Likewise, at this last latitude the rate can vary by a factor of 40 from mid-summer to mid-winter. In deep-water bodies (i.e., lakes) the photoprocesses are generally much slower. Some examples of natural photoprocesses in aquatic media now follow.

a. Photodegradation of Dissolved Organic Matter

Most organic compounds absorb strongly only at wavelengths below 250 nm. Under irradiation in aqueous media, the net result is usually their oxidation into simpler compounds, because initial photoexcitation is typically followed by reaction with dissolved O_2:

$$R \xrightarrow{h\nu} R^* \tag{6.24}$$

$$R^* + O_2 \rightarrow R^{+\bullet} + O_2^{-\bullet} \tag{6.25}$$

$$R^{+\bullet} \rightarrow \text{products} \tag{6.26}$$

or

$$R - X \xrightarrow{h\nu} R^\bullet + X^\bullet \tag{6.27}$$

$$R^\bullet + O_2 \rightarrow RO_2 \tag{6.28}$$

Since dissolved organic matter involves considerable amounts of humic substances (HS), which contain 3–6% nitrogen that may undergo recycling, they can act both as sources and sinks for ammonium in natural waters. Their natural photodegradation produces significant concentrations of nitrite, NO_2^-; this anion plays a crucial role in many biological processes in water within the nitrogen cycle. In addition, trace amounts of nitrite usually indicate the extent of pollution and eutrophication in natural waters. The rates of direct photolysis are often much slower than those of indirect photolysis. For example, the rate of direct photooxidation of atrazine (a herbicide) is six times slower than that of its indirect, nitrate-mediated photooxidation (see below).

b. Photolysis of Nitrates and Nitrites

Nitrate is the most thermodynamically stable aqueous nitrogen species in oxic (i.e., oxidizing) environments. However, it can be photolyzed by natural sunlight to produce hydroxyl radicals, $^\bullet OH$, that are known to be powerful oxidizing agents. The net result involves rapid nitrate-induced photooxidations. Other species (ozone, hydrogen peroxide, nitrite, dissolved organic matter, and $FeOH^{2+}$) also produce $^\bullet OH$ upon photolysis, although that of nitrates is believed to be the key source of $^\bullet OH$ in natural waters. Such a photolysis can follow three pathways:

$$\text{(a) } NO_3^- + h\nu \rightarrow NO_2^- + O\,(\text{atomic}) \tag{6.29}$$

$$\text{(b) } NO_3^- + h\nu \rightarrow NO_2 + {}^\bullet O^- \tag{6.30}$$

followed by

$$^\bullet O^- + H_2O_{(l)} \rightleftarrows {}^\bullet OH + OH^- \tag{6.31}$$

$$\text{(c) } NO_3^- + H_2O_{(l)} + h\nu \rightarrow NO_2^\bullet + OH^- + {}^\bullet OH \tag{6.32}$$

The photolysis of nitrites is as follows:

$$NO_2^- + h\nu \rightarrow NO + {}^\bullet O^- \tag{6.33}$$

$$^\bullet O^- + H_2O_{(l)} \rightleftarrows {}^\bullet OH + OH^- \tag{6.31}$$

These $^\bullet OH$ radicals produce several environmentally important oxidation reactions. They can be scavenged primarily by dissolved organic matter, DOM (in waters with high dissolved organic carbon concentration, DOC), or by carbonate and hydrogen carbonate ions (in waters with high alkalinity). The bromide ion is their key scavenger in seawater. Nitrate photolysis is likely to provide a key pathway for the oxidation of different types of DOM.

c. Photolysis of Metal Complexes

The photochemistry of metal complexes is rather interesting, because there are several pathways for reaction upon excitation. For example, in a given transition metal complex that has d electrons, there are several $d \rightarrow d$ transitions allowed. Similarly, there exist charge-transfer transitions where the excited state permits the transfer of electronic charge from an occupied orbital in the ligand to an unoccupied orbital in the central metal ion, reducing it to a lower oxidation state (*ligand to metal charge transfer, LMCT*). The final products depend on whether the irradiation energy is aimed at the d–d bands ($h\nu_1$) or at the charge-transfer band ($h\nu_2$), as exemplified in the generalized scheme below, where M is a metal ion in the $(n + 1)$ oxidation state (unless otherwise specified), L′ is a neutral ligand, and L is a negatively charged ligand. $(L')^0$ denotes a neutral species.

(a) Ligand exchange:

$$[M(L)_5L']^{n+} + H_2O_{(l)} + h\nu_1 \rightarrow [M(L)_4(H_2O)L']^{n+} + L \tag{6.34}$$

(b) Photoredox reaction:

$$[M^{(n+1)+}(L)_5L']^{n+} + h\nu_2 \rightarrow [M^{n+}(L)_5]^{n+} + (L')^0 \quad (6.35)$$

A typical example is the photolysis of iron–carboxylato complexes (i.e., complexes with oxalate, aminopolycarboxylates, citrate, humic or fulvic acids) that can occur with high quantum yields. A simplified reaction mechanism (using oxalate as the ligand) is

$$[Fe(III)(C_2O_4)_3]^{3-} + h\nu \rightarrow Fe(II) + 2C_2O_4^{2-} + C_2O_4^{-\bullet} \quad (6.36)$$

$$C_2O_4^{-\bullet} \rightarrow CO_2^{-\bullet} + CO_2 \quad (6.37)$$

$$CO_2^{-\bullet} + Fe(III) \rightarrow Fe(II) + CO_2 \quad (6.38)$$

Note that in the $C_2O_4^{2-}$ reactant, C is in the +3 oxidation state, whereas in the $C_2O_4^-$ product it is +7/2. Thus, it underwent oxidation in order to reduce Fe(III) to Fe(II). This Fe(II) can (in the presence of H_2O_2) generate the potent $^\bullet$OH radicals. This is called the *Fenton reaction*, and when the Fe(II) is produced by the photolytic reduction of Fe(III), it is called a *photo-Fenton reaction* (see Section 10.1.1.2).

Some complexes (e.g., [Fe(III)EDTA]) can undergo total photolysis in a sunny day within hours, while others are only slightly affected (e.g., [Mn(II)EDTA], [Co(III)EDTA]), or not affected by light at all. The ability of [Fe(III)EDTA] to undergo photolysis is very fortunate because EDTA is a refractory compound, and thus the natural photolytic pathway provides a means for its destruction. (From these cases it can also be deduced that some metal complex–containing samples to be analyzed for environmental purposes must be isolated from light immediately after collection).

6.3.2 Natural Removal and Entrainment of Species in Aqueous Systems by Chemical and Physical Processes

There are several natural pathways for the removal and entrainment of inorganic and organic materials from water. Some examples follow.

6.3.2.1 Sorption onto Colloidal, Suspended, or Settled Sediments

We use here the term *sorption* as the retention of a compound on the surface of a solid particle that removes it from the aqueous medium. This phenomenon affects the composition of water by transferring the compound or ion from the aqueous medium to a solid (mainly a sediment in suspension or a colloid). Then, it may no longer be present in water, especially if the sediment settles. Sorption may be identified and associated with adsorption, surface precipitation, surface complexation, and/or ion exchange (or even absorption).

Sorption is a surface phenomenon determined by the surface charges and those of the ions surrounding it. One or more of the following mechanisms can be involved in the removal of species by sorption: (i) mechanical entrapment, (ii) absorption, (iii) physical sorption, or (iv) chemical sorption on the surface of the solid particle. Physical adsorption (which is weaker than its chemical counterpart) occurs through Van der Waals' forces and it is generally reversible and instantaneous. On the other hand, chemical adsorption or *chemisorption* occurs through the formation of chemical bonds at specific sites. This is closely related to ion exchange processes and complexation.

Surface functional groups in the suspended particles determine the type of process that will take place. In the case of inorganic colloidal particles (e.g., clays) the main functional groups are silanol (≡Si – OH) and aluminol (≡Al – OH), whereas in metal oxides or hydroxides the functional groups are (≡M – OH). These groups may become protonated or deprotonated, depending on the pH of the aqueous medium, by sorption of H^+ or OH^- ions as follows:

$$(a)\ \equiv M - OH + H^+ \rightarrow\ \equiv M - OH_2^+ \quad (6.39)$$

$$(b)\ \equiv M - OH \rightarrow\ \equiv M - O^- + H^+ \quad (6.40)$$

Then, they can function as surface-bound ligands (depending on pH) and adsorb or desorb charged species through the formation of surface complexes. The silanol groups generally dissociate to liberate H^+ (leaving a negative charge), whereas aluminol and iron oxide and hydroxide can dissociate to end up with either negative or positive charges (and also bind H^+).

Surface ionization and complexation models account for metal sorption reactions at these interphases, and are based upon the simple reaction:

$$\equiv\mathrm{M}-\mathrm{OH}+\mathrm{Me}^{n+} \rightarrow \equiv\mathrm{M}-\mathrm{OMe}^{(n-1)+}+\mathrm{H}^{+} \quad (6.41)$$

where $\equiv\mathrm{M}-\mathrm{OH}$ represents a singly protonated surface oxide site, Me^{n+} is a metal cation, and $\equiv\mathrm{M}-\mathrm{OMe}^{(n-1)+}$ is the resulting surface complex. An increase in pH and/or concentration of the adsorbent sites will increase cation sorption (by Le Chatelier's principle), whereas the presence of foreign anionic complexing ligands will create competition for the target metal ions and thus decrease their adsorption. In this reaction model, the adsorbates are cationic metal ions, but aquo or hydroxo metal–ligand complexes can be strongly bound by oxide surfaces as well. Other types of dissolved metal complexes can also adsorb to these sites, although less strongly than the above. Consistent with this rationale, a complex is called a *metal-like* complex if its adsorption increases with pH, whereas it is a *ligand-like* complex if it decreases.

When there is a water molecule between the ion or molecule and the functional group of the solid phase, the complexes that form are called *outer-sphere complexes* (see Section 3.1.4). Here, bonding is due to weak electrostatic interactions. This type of adsorption or complex formation is rapid and reversible, and it is affected by the ionic strength of the surrounding medium. On the other hand, when the ion or molecule forms a bond directly with the surface functional group, the resulting moiety is an *inner-sphere complex*, and stronger bonds are generally involved. This is a slower, typically irreversible process in which monodentate or polydentate species may participate. The process is slightly affected by the ionic strength of the medium. In this case, the adsorbed or complexed compound, called a *sorbate*, can undergo charge modification. The metal ions that bind to these oxide surfaces normally tend to form aquo or hydroxo complexes in solution. The adsorption of metal cations is therefore dependent on pH, on concentration, and on the type of adsorbents or solid particles.

Anions (including metal oxyanions such as chromate) can also be adsorbed, as can anionic ligands (such as phosphates and sulfates), and dissolved or suspended humic substances (such as fulvic acids). The ionic strength and pH influence the sorption of anions since they compete with the OH^- ions for the surface positive charges. Some anions—usually those related to the conjugates of monoprotic acids—adsorb more at a higher pH and reach a maximum value near the pK_a of the corresponding acid. On the other hand, conjugate anions of diprotic acids tend to sorb less with pH even near the pK_2 value, after which the decrease is more pronounced.

Particulate or dissolved humic substances tend to adsorb onto solid phases (generally clays), sometimes coating them completely. Even after adsorption, they still possess enough active sites to complex metallic ions or adsorb other organic substances. Here, the sorbed organic molecule (generally neutral) penetrates and almost "dissolves" in the porous structure of the adsorbed humic substance. Globular structures and coiling minimize the degree of hydrophobic-surface exposure to the aqueous medium. Other organic substances (e.g., organic acids and amino acids) can also bind directly to inorganic colloids or particles.

6.3.2.2 Ion Exchange in Sediments and in Aqueous Colloidal and Suspended Matter

Colloids and suspended matter in water typically have sorbed ions on their surface. When these charged particles (with electrostatically sorbed cations or anions) come in contact with water rich in dissolved solids or high in electrolytes, the ions in solution will substitute the weakly attached ions on the surface of the particle. The higher the charge and concentration of the counter ion in the aqueous medium, the higher the probability of displacing the ion originally attached. The process is normally instantaneous and reversible, and it takes place at a stoichiometric ratio that preserves electroneutrality. This means, for example, that a cation with a 3+ charge will use three (mono) negative sites. This also depends on how easily the counter ion diffuses towards the charged site.

When several types of counter ions are present, there will be an exchange preference for one ion over the other (i.e., the process is *selectivity-controlled*). Here, cations with the smallest hydrated radii are preferred for the exchange because of their greater charge density and stronger ability to produce polarization. For instance, Cu^{2+} is preferred over Li^+ for cation exchange owing to its smaller radius and greater charge density. (Interestingly, hydrated Li^+ is a very large ion with a radius of 3.40 Å).

Ion exchange is common in colloidal clays or in clay sediments that tend to flow and re-suspend with water movement. These minerals have uncoordinated oxygens that give the particle a negative charge when the minerals are exposed. When the octahedral layers of the clay particles are exposed, the hydroxyl groups dissociate and generate a negative charge that attracts positive ions.

The facts described above pave the way toward the concept of *point of zero charge*. This corresponds to the point where the net, total charge adsorbed at the surface of the particle (including all the cations and anions) is zero. The pH of the suspension that corresponds to the point of zero charge is known as the pH_{PZC}, or simply, *pzc*. At this pH, the charge balance on the surface of the colloid is zero. As a result, the pH of the solution defines the type of exchange that predominates in the particle:

(a) At $pH < pH_{PZC}$ the surface will contain excess protons and the particle will have an *anion exchange capacity* or *anion adsorption capacity (AAC)*.
(b) At $pH = pH_{PZC}$ the particle will be balanced with protons and hydroxyls so that the net charge becomes zero. There is no exchange capacity here.
(c) At $pH > pH_{PZC}$ there will be an excess of dissociated hydroxyl negative groups, and the particle will have a *cation exchange capacity (CEC)*.

For example, montmorillonite (a strong water-absorbent clay) has an average pH_{PZC} of 2.5, and for that reason the CEC is dominant at a $pH > 2.5$. Goethite (α-FeOOH) has a pH_{PZC} of 6–7, and therefore it can have an AAC at $pH < 6$ and a CEC at $pH > 7$. In the case of α-AlOOH, its pH_{PZC} is 9.1 and it displays a predominantly AAC in natural waters. Organic suspended particles (mainly humic substances) have pH_{PZC} values in the vicinity of 3, and thus in natural waters they are negatively charged particles with a high CEC. Natural pH values are rarely above 8.6.

Clays and particles of soil organic matter have negative charges and high CECs, as confirmed by the following values: 150–500 meq/100 g for organic matter and 3–150 meq/100 g for clay minerals (as kaolinite and smectite). On the other hand, aluminum and iron hydroxide colloids tend to be hydrophobic, with surface positive charges, and, consequently, they are predominantly anion adsorbers.

Ion exchange in colloids and sediments plays a critical role in the composition of water because it determines which ions will remain in solution and which will be adsorbed onto the surface of the particles. This is evident in the composition of seawater, where $[Na^+]$ predominates over $[K^+]$ since the hydrated radius of the latter is smaller (i.e., 2.76 vs 2.32 Å, respectively) and thus has more affinity for seawater colloids. Likewise, Pb^{2+} is preferentially adsorbed or retained over Cu^{2+} or Mg^{2+}.

Ion exchange also occurs in estuaries (i.e., where rivers discharge) rich in clay-suspended particles saturated with adsorbed Ca^{2+} ions. As river water mixes with the high salinity of seawater (rich in Na^+), ion exchange takes place and Ca^{2+} is liberated while Na^+, K^+, and Mg^{2+} are removed. Phosphates and Fe ions may also be removed. This is why the Na^+/Ca^{2+} proportion in estuaries is sometimes inverted with respect to that in the oceans.

Ion exchange is normally defined by a *distribution coefficient* or by a *selectivity coefficient* more than by an equilibrium exchange constant (see below). These coefficients relate the amount of the exchanged ions that stay in the colloidal solid matrix to that in the aqueous phase. In this context, a simplified example of an ion exchange reaction (e.g., H^+ for K^+) is

$$\text{Clay–Si}-O^-H^+ + K^+ \rightleftarrows \text{Clay–Si}-O^-K^+ + H^+ \tag{6.42}$$

The *distribution* coefficient in this case can be defined as

$$K_d = W_{\text{ion-clay}}/W_{\text{ion-solution}} \tag{6.43}$$

where $W_{\text{ion-clay}}$ is the mass of the target ion adsorbed or retained per unit mass of clay (or solid) at equilibrium, and $W_{\text{ion-solution}}$ is the mass of the ion in solution per unit mass of solution. If one assumes that the only exchangeable cations in the solution are K^+ and H^+, then a *selectivity* coefficient, K_{K-H} can be defined in terms of products/reactants as an "equilibrium constant" for equation 6.42:

$$\begin{aligned} K_{K\text{–}H} &= (X_{K\text{-clay}}[H^+])/(X_{H\text{-clay}}[K^+]) \\ &= (X_{K\text{-clay}}/(K^+])/(X_{H\text{-clay}}/(H^+]) \\ K_{K\text{–}H} &= (X_{K\text{-clay}}/X_{H\text{-clay}})([H^+]/[K^+]) \end{aligned} \tag{6.44}$$

where

$$X_i = \text{mass fraction of ion } i \text{ in the clay}$$

Using a definition similar to that in Section 2.1.2, these fractions are given by

$$X_{\text{H-clay}} = W_{\text{H-clay}}/(W_{\text{H-clay}} + W_{\text{K-clay}}) \quad (6.45)$$

and

$$X_{\text{K-clay}} = W_{\text{K-clay}}/(W_{\text{H-clay}} + W_{\text{K-clay}}) \quad (6.46)$$

If we now define $m_{\text{K-clay}}$ and $m_{\text{H-clay}}$ as the concentrations of adsorbed K^+ or H^+ per unit mass of clay (in meq/kg), respectively, we can equate their sum to the CEC of the solid sample under analysis (which can generally be obtained experimentally):

$$\text{CEC (in meq/kg)} = (m_{\text{H-clay}} + m_{\text{K-clay}}) \quad (6.47)$$

Then, in a similar fashion as in equation 6.44, one can write a selectivity coefficient in terms of concentrations as

$$K'_{\text{H-K}} = [m_{\text{K-clay}}/m_{\text{H-clay}}]([H^+]/[K^+]) \quad (6.48)$$

$$= [m_{\text{K-clay}}/(\text{CEC} - m_{\text{K-clay}})]([H^+]/[K^+]) \quad (6.49)$$

If the total cation concentration in solution (i.e., $[K^+] + [H^+]$) is given by C, then

$$K'_{\text{H-K}} = [m_{\text{K-clay}}/(\text{CEC} - m_{\text{K-clay}})]\{[H^+]/(C - [H^+])\} \quad (6.50)$$

Then, knowing the amount of K^+ and H^+ retained per unit mass of clay, the CEC, the C, and the pH of the solution, one can calculate this coefficient.

(For the case where a divalent cation is exchanged, the corresponding exponents are simply included in these equations).

6.3.2.3 *Precipitation Reactions and Co-precipitation*

Precipitation is the formation of a compound that exceeds its solubility limit in a given medium. Co-precipitation is the inclusion or trapping of an otherwise soluble compound when a precipitate is formed under the same conditions. Precipitation calculations, including equilibrium diagrams involving the solubility–precipitation of solids, are discussed in Section 5.3.

Precipitation is one of the reactions responsible for the removal of ions in water. This is especially important in seawater, where ions such as Ca^{2+}, Mg^{2+}, Fe^{2+}, Na^+, Cl^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, and SiO_4^{4-} precipitate and end up in the sediments. The main precipitation products are gypsum ($CaSO_4$), halite (NaCl), opal (SiO_2), and calcite ($CaCO_3$). Other important precipitation reactions include the formation of solid MnO_2 and $Fe(OH)_3$, generally due to oxidation reactions in the upper strata of the ocean. In the case of Fe^{3+}, precipitation can be reverted when reaching the anoxic zone at the bottom (i.e., under reducing conditions) that change insoluble $Fe(OH)_3$ back to soluble Fe^{2+}.

Pyrite formation (FeS_2) is related to biologically mediated reduction of sulfate to sulfide and of Fe^{3+} to Fe^{2+} in anoxic zones. In the case of phosphate, this can be removed through precipitation reactions with Ca^{2+} and Fe^{3+} (by formation of apatite or iron phosphate, respectively), by co-precipitation, or by formation of surface complexes with Fe or Mn oxides or hydroxides.

Another natural ion-removal scheme involves the biogenic formation of solid hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ as well as $CaCO_3$ and SiO_2 as exoskeletons, bones, or scales of aquatic flora and fauna that precipitate as sediments upon the death of the organisms.

6.3.2.4 *Solidification and Deposition Processes Due to Evaporation*

These processes occur by precipitation through evaporative concentration of a solute in the aqueous medium until its dissolution capacity is exceeded. Then, a solid is formed and deposited either as a sediment or on a nearby surface. These products are called *evaporites*. A typical example is the deposition and formation of calcium carbonate *stalactites* and *stalagmites*. Evaporation is a major process in arid areas and it influences the chemistry of surface waters. That is why in saline lakes, inland seas, or even in estuaries, evaporites of NaCl or NaCl/KCl and deposits of $CaSO_4$ and $CaCO_3$ are formed. Here, $CaSO_4$ generally precipitates first, and then NaCl.

6.3.2.5 *Colloidal and Sediment Transport into Surface Water*

Entrainment of suspended solids (made of solid chemical compounds or chemical colloids) may occur under turbulent or agitated flow of surface water. In this case, the theoretical aqueous equilibrium concentrations can be exceeded. As discussed in Section 6.3.1, colloids can be organic or inorganic in nature, and the interactions of the solid particles and adsorbed substances may modify the solute composition. In water-saturated porous media, colloid mobilization depends on their interaction with the pore walls. The resulting *net interaction potential* is the sum of the *electrostatic double layer force*, the *Van der Waals'* force, and the *short-range solvation* or *steric* forces. A large interaction potential means that the colloidal particles will not be released from the pore water and thus their transport will be prevented. In the same manner as colloids can aggregate or not, depending on the ionic strength of the solution (see Section 6.3.1), a decrease in the ionic strength of pore water brings about an increase in the repulsive magnitude of the electrostatic double layer force, and the colloid can then be released and transported away from the pore.

6.3.2.6 Volatilization of Organic and Inorganic Compounds

Volatilization of naturally formed gases (e.g., H_2S, CO_2, CH_4, NH_3) represents a removal process that modifies the composition of a water reservoir and the surrounding air. It depends on the Henry's law constants and on the partial pressures of the compounds, the ambient temperature and pressure, as well as on factors that may favor the mass-transfer process.

Another form of removal through the water–atmosphere interphase is aerosol formation in marine surface waters where salt spray tends to remove mainly NaCl, $NaSO_4$, and $MgSO_4$. These are generally known as *cyclic salts* due to their potential return to the sea through rain washout.

All the concepts and examples presented in this chapter refer to natural phenomena in the hydrosphere, and are basic for understanding the dynamics, quality, and characteristics of aqueous systems. They are also relevant for understanding what may happen to these natural systems that could alter, deviate, or intensify the natural processes when other types of substances or conditions are introduced by anthropogenic activities and pollution processes. These issues are further discussed in Chapter 8, where we will consider the impact of these activities on the surrounding systems and the resulting chemical processes.

Related Experiments in the Companion Book

1. Water characterization
2. Dissolved oxygen in water
3. Alkalinity and buffering capacity of water
4. Aqueous carbonate equilibria and water corrosiveness
5. The point of zero charge of oxides
6. Experimental transitions in *E* vs pH (or Pourbaix) diagrams
7. Air oxidation of metal ions
8. Photoassisted reduction of metal complexes
9. Anionic detergents and *o*-phosphates in water

Additional Related Experiments/Activites

Anderlick, B. "Water Analysis Experiment," *J. Chem. Educ.* **1972**, *49*, 749.

Barrett, Richard L. "CO_2-H_2O Equilibrium and the Principle of Le Chatelier," *J. Chem. Educ.* **1959**, *36*, A741.

Bauer, R.; Birk, J.; Sawyer, D. *Laboratory Inquiry in Chemistry*, 2nd ed; Brooks-Cole: Stamford, CT, 2005.

- Is the water hard or soft? (Experiment 7)

Boehnke, D. N.; Delumyea, R. D. *Laboratory Experiments in Environmental Chemistry*; Prentice-Hall: New York, 1999.

- The pH and buffer capacity of environmental waters (Experiment 3)
- Alkalinity of streams and lakes (Experiment 4)

Bowers, P. G.; Rubin, M. B.; Noyes, R. M.; Andueza, D. "Carbon Dioxide Dissolution as a Relaxation Process: A Kinetics Experiment for Physical Chemistry," *J. Chem. Educ.* **1997**, *74*, 1455–1458.

Buell, P.; Girard, J. *Laboratory Manual for Chemistry Fundamentals*, 2nd ed.; Jones and Bartlett: Boston, MA, 2002.

- Determination of the hardness of water (Experiment 12)
- Determination of chloride in seawater (Experiment 21)

Bush, P. "Solubility of Carbon Dioxide in Water," *Sci. Activit.* **1992**, *29*(3) 33–36.

Carvalho, K. M. "Water Quality: A Project-based Laboratory for Introductory Chemistry," 225th Am. Chem. Soc. National Meeting, New Orleans, LA, March 23–27, 2003. Chem. Ed. Division Paper # 44.

Clemson University. *Introductory Chemistry Lab Experiments in Environmental Chemistry*; Environmental Chemistry Library. National Science Foundation, 2002. http://www.ces.clemson.edu/ecl/labs/general/index.html

- Hardwater determination
- Changes in alkalinity and pH
- pH and buffer capacity
- Total suspended solids
- Total dissolved solids

Cornell University, School of Civil and Environmental Engineering, Hollister Hall, Ithaca, New York. "Measurement of Acid Neutralizing Capacity". pp. 49–60. http://Ceeserver.Cee.Cornell.Edu/Mw24/Archive/03/Cee453/Lab_Manual/Pdf/Gran.Pdf

Crosson, M.; Gibb, R. "Dissolved Oxygen and Chloride Determination in Water," *J. Chem. Educ.* **1992**, *69*, 830–832.

Dolan, E.; Zhang, Y.; Klarup, D. G. "The Distribution Coefficient of Atrazine with Illinois Soils: A Laboratory Exercise in Environmental Chemistry," *J. Chem. Educ.* **1998**, *75*, 1609–1610.

Dorman, S. C. "Using the Local Watershed as an Outdoor Laboratory: A Campus-Community Partnership", 225th Am. Chem. Soc. National Meeting, New Orleans, LA, March 23–27, 2003. Chem. Ed. Division Paper # 130.

Favaretto, L. "An Inexpensive Device for Collection of Samples of Water for Dissolved Oxygen Determination without Air Contact," *J. Chem. Educ.* **1990**, *67*, 509.

Ganong, B. R. "Hand-Held Conductivity Meter and Probe for Small Volumes and Field Work," *J. Chem. Educ.* **2000**, *77*, 1606–1608.

Greco, T. G.; Rickard, L. H.; Weiss, G. S. *Experiments in General Chemistry: Principles and Modern Applications*, 8th *ed.*; Prentice Hall: Upper Saddle River, N.J., 2002.

- Determination of water hardness (Experiment 26)

Halstead, J. A. "Rain, Lakes and Streams: Investigating Acidity and Buffering Capacity in the Environment," JCE Classroom Activity #4, *J. Chem. Ed.* **1997**, *74*, 1456A–1456B.

Harris, T. M. "Potentiometric Measurements in a Freshwater Aquarium," *J. Chem. Educ.* **1993**, *70*, 340–341.

Hughes, K. D. "Marine Microcosm—Using an Aquarium to Teach Undergraduate Analytical Chemistry", *Anal. Chem.* **1993**, *65*, 883A–889A.

Ibanez, J. G.; Miranda, C.; Topete, J.; García, E. "Metal Complexes and the Environment: Microscale Experiments with Iron-EDTA Chelates," *Chem. Educ.* **2000**, *5*, 226–230. http://journals.springerny.com/chedr/

Ibanez, J. G. "Redox Chemistry and the Aquatic Environment: Examples and Microscale Experiments," *Chem. Educ. Int. (IUPAC)* **2005**, *6*, 1–7.

Jackson, G. B. *Applied Water and Spentwater Chemistry. A Laboratory Manual*; Van Nostrand-Reinhold: New York, 1993.

- Alkalinity measurement (Experiment 13)
- Hardness measurement (Experiment 14)
- Calcium and magnesium measurement (Experiment 15)
- Total suspended solids measurement (Experiment 16)
- Calcium carbonate stability measurement (Experiment 17)
- Total residual chlorine measurement (Experiment 21)
- Chlorine demand measurement (Experiment 22)
- Dissolved oxygen measurement (Experiment 27)
- Oil and grease measurement (Experiment 33)
- Volatile acid to alkalinity ratio measurement (Experiment 34)

Johll, M. E.; Poister, D.; Ferguson, J. "Statistical Comparison of Multiple Methods for the Determination of Dissolved Oxygen Levels in Natural Waters," *Chem. Educ.* **2002**, 7, 1146–1148.

Juhl, L.; Yearsley, K.; Silva, A. J. "Interdisciplinary Project-Based Learning through an Environmental Water Quality Study," *J. Chem. Educ.* **1997**, *74*, 1431–1433.

Lambert, J. L.; Meloan, C. E. "A Simple Qualitative Analysis Scheme for Several Environmentally Important Elements," *J. Chem. Educ.* **1977**, *54*, 249–252.

Lewis, A.; Bumpus, J. A.; Truhlar, D. G.; Cramer, C. J. "Molecular Modeling of Environmentally Important Processes: Reduction Potentials," *J. Chem. Educ.* **2004**, *81*, 596–604.

Livneh, M. "Determination of the Hardness of Water by a Microscaled EDTA Titration," *J. Sci. Educ. (Rev. Educ. Cien., Colombia)*, **2005**, *6*(1), 51–52.

Lunsford, S. K.; Slattery, W. "An Interactive Environmental Science Course for Education Science Majors," *J. Chem. Educ.* **2006**, *83*, 233–236.

McCormick, P. G. "The Determination of Dissolved Oxygen by the Winker Method— A Student Laboratory Experiment," *J. Chem. Educ.* **1972**, *49*, 839–841.

McInnes, D. M.; Kampbell, D. "Bubble Stripping To Determine Hydrogen Concentrations in Ground Water: A Practical Application of Henry's Law," *J. Chem. Educ.* **2003**, *80*, 516–519.

Mihok, M.; Keiser, J. T.; Bortiatynski, J. M.; Mallouk, T. E. "An Environmentally-focused General Chemistry Laboratory," *J. Chem. Educ.* **2006**, *83*, 250. http://jchemed.chem.wisc.edu/Journal/Issues/2006/FebACS/ACSSub/ACSSupp/JCE2006p0250W.pdf

- Iron and alkalinity determination (Experiment 2)

Myers, R. L. "Identifying Bottled Water: A Problem-Solving Exercise in Chemical Identification," *J. Chem. Educ.* **1998**, *75*, 1585–1587.

Ortega, T.; Forja, J. M.; Gómez-Parra, A. "Teaching Estuarine Chemical Processes by Laboratory Simulation," *J. Chem. Educ.* **2001**, *78*, 771–775.

Pidello, A. "Environmental Redox Potential and Redox Capacity Concepts Using a Simple Polarographic Experiment," *J. Chem. Educ.* **2003**, *80*, 68–70.

Scheuer, Paul J. "Exploring the Ocean—Stating the Case for Chemistry," *J. Chem. Educ.* **1999**, *76*, 1075–1079.

Selco, J. I.; Roberts, J. L., Jr.; Wacks, D. B. "The Analysis of Seawater: A Laboratory-Centered Learning Project in General Chemistry," *J. Chem. Educ.* **2003**, *80*, 54–57.

Sanderson, P. L. "Environmental Chemistry in Action," *Educ. Chem.* **1987**, *24*(1) 16–18.

Sawyer, C. N.; McCarty, P. L.; Parkin, G. F. *Chemistry for Environmental Engineering*; McGraw-Hill International editions, Civil Engineering Series: New York, 1994.

- Acidity (Chapter 16)
- Alkalinity (Chapter 17)
- Hardness (Chapter 18)
- Chlorides (Chapter 20)
- Dissolved oxygen (Chapter 21)
- Nitrogen (Chapter 24)
- Solids (Chapter 25)
- Iron and manganese (Chapter 26)
- Sulfate (Chapter 28)

Shakhashiri, B. Z. *Chemical Demonstrations: A Handbook for Teachers of Chemistry*; Vol. 3, The University of Wisconsin Press: Madison, WI (USA), 1989.

- Acid neutralizing capacity of lake beds (page 125)

Stagg, W. R. "Dissolved Oxygen—A Relevant Experiment for the Introductory Laboratory," *J. Chem. Educ.* **1972**, *49*, 427–428.

Thistlethwayte, D.; Ellis, J.; Kanamori, S. "The Measurement of Dissolved Oxygen," *Educ. Chem.* **1974**, *11*(1) 23–24.

Tratnyek, P. G.; Reilkoff, T. E.; Lemon, A. W.; Scherer, M. M.; Balko, B. A.; Feik, L. M.; Henegar, B. D. "Visualizing Redox Chemistry: Probing Environmental Oxidation–Reduction Reactions with Indicator Dyes," *Chem. Educ.* **2001**, *6*(3) 172–179.

Urbansky, E. T.; Schock, M. R. "Understanding, Deriving, and Computing Buffer Capacity," *J. Chem. Educ.* **2000**, *77*, 1640–1644.

Walker, N.; Mintz, J. "Hydrolysis of the Carbonate Ion," *J. Chem. Educ.* **1970**, *47*, A119.

Williams, D. J.; Williams, M. C.; Foster, B. E.; Malone, J. C.; Milner, E. E.; Tartaglia, A. L.; Turner-Reed, A.; Koether, M. C. "Teaching Environmental Chemistry with Wetland Microcosms," *Chem. Educ.* **2003**, *8*, 312–314.

Whisnant, D. M.; McCormick, J. A. "BCTC for Windows: Abstract of Issue 9903W," *J. Chem. Educ.* **1999**, *76*, 719.

Wu, R. S. S. "Change of Forms of Cadmium in the Aquatic Environment," *J. Chem. Educ.* **1995**, *72*, 264–265.

References and Further Reading

Alloway, B. J.; Ayres, D. C. *Chemical Principles of Environmental Pollution*, 2nd ed.; Chapman & Hall: London, 1997.

Atkins, P. W.; Beran, J. A. *General Chemistry*, 2nd ed.; W. H. Freeman: New York, 1992. Chapter 21.

Barona, A.; Etxebarria, B. "Distribution and Extraction of Pb and Zn with Chelating Agents in Soils with Varying Pollution Level," American Institute of Chemical Engineers, 5th World Congress. Chem. Eng., Jul. 14–18, 1996. San Diego, CA., Vol. III, pp. 576–581.

Berner, E. A.; Berner, R. A. *The Global Water Cycle, Geochemistry and Environment*; Prentice Hall: Englewood Cliffs, USA, 1987.

Bolin, B.; Degens, E. T.; Kempe, S.; Ketner, P., Eds. *The Global Carbon Cycle*; Scope Report No. 13, Wiley: London, 1979. e-version by M. S. Swaminathan Research Foundation: Chennai, India. http://www.icsu-scope.org/

Bolin, B.; Cook, R. B., Eds. *The Major Biogeochemical Cycles and their Interactions*; Scope Report No. 21, Wiley: London, 1983. e-version by M. S. Swaminathan Research Foundation: Chennai, India. http://www.icsu-scope.org/

Butcher, S. S.; Charlson, Robert, J.; Orians, Gordon H.; Wolfe, Gordon V., Eds. *Global Biogeochemical Cycles*; Academic Press: London, 1992.

Brezonik, P. L.; Fulkerson-Brekken, J. F. "Nitrate-Induced Photolysis in Natural Waters: Controls on Concentrations of Hydroxyl Radical Photo-Intermediates by Natural Scavenging Agents", *Environ. Sci. Technol.* **1998**, *32*, 3004–3010.

Bunce, N. J. *Introduction to Environmental Chemistry*; Wuerz Publishing: Winnipeg, 1993.

Darthmouth University. http://www.dartmouthuniv.edu/chemlab/chem3–5/acid1/fulltext/chemistry.html

DGPCC/DRAMA. Annual Report, Acid Precipitations Program of the Metropolitan Zone, Mexico City; Environmental Secretariat, DDF: Mexico, 1996.

Egen, N.; Ford, P. C. "Hard Water, Water Softening, Ion Exchange," *J. Chem. Educ.* **1976**, *53*, 302–303.

Environment Canada. http://www.ec.gc.ca/water/images/nature/grdwtr/a5f3e.htm

Environmental Protection Agency, Response of Surface Water Chemistry to the Clean Air Act Ammendments of 1990 (EPA 620/R-03/001, Jan. 2003, p. 18). http://www.epa.gov/ord/htm/CAAA-2002-report-2col-rev-4.pdf

Hill, S. J. "Speciation of Trace Metals in the Environment," *Chem. Soc. Rev.* **1997**, *26*, 291–298.

Howard, A. G. *Aquatic Environmental Chemistry*; Oxford Science Publications, Oxford University Press: Oxford, 1998.

Kegley, S. E.; Andrews, J. *The Chemistry of Water*; University Science Books: Sausalito, CA, 1997.

Kieber, R. J.; Li, A.; Seaton, P. J. "Production of Nitrite from the Photodegradation of Dissolved Organic Matter in Natural Waters," *Environ. Sci. Technol.* **1999**, *37*, 993–998.

Krauskopf, K. B. *Introduction to Geochemistry*, 2nd ed.; McGraw Hill-Kogakusha: Tokyo, 1979.

Lenhart, J. J.; Saiers, J. E. "Colloid Mobilization in Water-Saturated Porous Media under Transient Chemical Conditions," *Environ. Sci. Technol.* **2003**, *37*, 2780–2787.

Lien, L.; Raddum, G. G.; Fjellheim, A.; Henriksen, A. "A Critical Limit for Acid Neutralizing Capacity in Norwegian Surface Waters, Based on New Analyses of Fish and Invertebrate Responses," *Sci. Tot. Environ.* **1996**, *26*, 173–193.

Lin, C.-F. "The Effects of Strongly Complexing Ligands on the Adsorptive Partitioning of Metal Ions," *Wat. Res.* **1992**, *26*, 397–407.

Livingston, D. A. *Chemical Composition of Rivers and Lakes*; U.S. Geol. Surv., Prof. Pap. 440 G: Washington, 1963.

Martell, A. E.; Hancock, R. D. *Metal Complexes in Aqueous Solutions*; Plenum Press: New York, 1996.

Martin, S. B.; Allen, H. E. "Recycling EDTA after Heavy Metals Extraction," *Chemtech* **1996**, *26*(4) 23–25.

Meybeck, M.; Chapman, D.; Helmer, R., Eds. *Global Freshwater Quality: A First Assessment*: Blackwell Reference: Oxford, 1989.

Mono Lake Committee. http://www.monolake.org/naturalhistory/stats.htm

National Environmental Technology Centre, *Acid Deposition Data Report*; AEA: London, 2002.

Nowack, B.; Lutzenkirchen, J.; Behra, P.; Sigg, L. "Modeling the Adsorption of Metal-EDTA Complexes onto Oxides," *Environ. Sci. Technol.* **1996**, *30*, 2397–2405.

O'Neill, P. *Environmental Chemistry*; Chapman and Hall: London, 1993. Chapter 8.

Peavy, H. S.; Rowe, D. R.; Tchobanoglous, G. *Environmental Engineering*; McGraw Hill: New York, 1985.

Rajeshwar, K.; Ibanez, J. G. *Environmental Electrochemistry*; Academic Press: San Diego, 1997, Chapter 6.

Robertson, A. P.; Leckie, J. O. "Acid/Base, Copper Binding, and Cu^{2+}/H^+ Exchange Properties of Goethite, an Experimental and Modeling Study," *Environ. Sci. Technol.* **1998**, *32* 2519–2530.

Sawyer, C. N.; McCarty, P. L.; Parkin, G. F. *Chemistry for Environmental Engineering*; McGraw-Hill International Editions, Civil Engineering Series: New York, 1994.

Schnitzer, M.; Khan, S. U., Eds. *Humic Substances in the Environment*; Marcel Dekker: New York, 1972.

Schnitzer, M.; Hansen, E. H. "Organo-metallic Interactions in Soils: 8. An Evaluation of Methods for the Determination of Stability Constants of Metal-Fulvic Acid Complexes," *Soil. Sci.* **1970**, *109*, 333–340.

Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; Wiley: New York, 1993.

Shiklomanov, I. A. *A World of Salt: Total Global Saltwater and Freshwater Estimates*; UNESCO (UNEP): Paris, 1999.

Sparks, D. L. *Environmental Soil Chemistry*; Academic Press: San Diego, 1995.

Spiro, T. G.; Stigliani, W. M. *Chemistry of the Environment*; Prentice Hall: Upper Saddle River, NJ, 1996.

Stumm, W.; Morgan, J. J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*; Wiley Interscience: New York, 1996.

Thomas, F.; Masion, A.; Bottero, J.; Roullier, J.; Genevrier, F.; Boudot, D. "Aluminum(III) Speciation with Acetate and Oxalate. A Potentiometric and ^{27}Al NMR Study," *Environ. Sci. Technol.* **1991**, *25*, 1553–1559.

Thomas, R.; Meybeck, M.; Beim, A. Chapter 7: Lakes, in *Water Quality Assessment: A Guide to Use of Biota, Sediments and Water in Environmental Monitoring*, 2nd ed.; Chapman, D., Ed., UNESCO/WHO/UNEP, Chapman Hall: London, 1992. http://www.who.int/docstore/water_sanitation_health/wqassess/ch12.htm

UNEP, Vital Water Graphics: An Overview of the State of the World's Fresh and Marine Waters, 2002. http://www.unep.ort/vitalwater/

U.S. Geological Survey, National Field Manual for the Collection of Water-Quality Data. Techniques of Water-Resources Investigations, TWRI Book 9. 2004. http://water.usgs.gov/owq/FieldManual/

Vaughan, P.; Blough, N. V. "Photochemical Formation of Hydroxyl Radical by Constituents of Natural Waters," *Environ. Sci. Technol.* **1998**, *32*, 2947–2953.

Wetzel, R. G. "Natural Photodegradation by UV-B of Dissolved Organic Matter of Different Decomposing Plant Sources to Readily Degradable Fatty Acids," *Verhand. Int. Verein. Limnol.* **2001**, *27*, 2063–2073.

Xue, Y.; Traina, S. J. "Oxidation Kinetics of Co(II)-EDTA in Aqueous and Semi-Aqueous Goethite Suspensions," *Environ. Sci. Technol.* **1996**, *30*, 1975–1981.

Yang, Z.; Zhang, J. "Chemical Speciation and Coordination Chemistry in Aquatic Environment", Preprints of Extended Abstracts, 217th Nat. Meet., Am. Chem. Soc. Anaheim, CA. Vol. 39 (1) March, 1999, p. 58–60.

Zepp, R. G.; Hoigne, J.; Bader, H. "Nitrate-Induced Photooxidation of Trace Organic Chemicals in Water", *Environ. Sci. Technol.* **1987**, *21*, 443–450.

7

Natural Biochemical Processes and Organisms in the Biosphere

Up to now, we have presented key chemical processes in our environment. Biochemical processes fashioned by different organisms, and the biogeochemical cycles of key elements and water, are also of paramount importance. We proceed now to discuss them.

7.1 Classification of Living Organisms

There is no simple definition for life. It may be characterized by a list of properties shared by all living organisms (with the exception of viruses) that distinguish them from non-living matter: movement, responsiveness, growth, feeding, reproduction, energy release, and excretion. Thus, a living organism is a self-reproducing system capable of growing and maintaining its integrity by the expenditure of energy. In addition, all living organisms share the same basic unit structure termed *the cell.*

There is an age-old interest in understanding the relationships that exist among living organisms and establishing their classification according to different categories. In fact, Aristotle had the key idea that, in order to classify in a formal and reproducible way, it was necessary to choose among different criteria. Thus, he divided animals not, for example, according to their number of legs, but as oviparous (those that lay eggs) and viviparous (the mammals).

The main representative of the classic period of taxonomy, the discipline that classifies and identifies all living creatures, was Carolus Linnaeus (Linneo) (1707–1778), who divided living creatures in two kingdoms: animal and vegetal, or the *Animalia* and the *Plantae.* He also proposed a binomial system for the nomenclature of all organisms: one generic (genus) and one specific (species), which is still in use today. He proposed a hierarchic system of classification formed by six ranks, each one nestled in the higher level: species, genus, order, class, and kingdom.

In the 18th century there was no alternative but to use a strictly morphological approach, so that the more structural traits shared by different organisms (i.e., the number and placement of limbs, the shapes of leaves, or internal organs), the closer their taxonomic relationship.

Two major factors have altered the basis on which taxonomies are constructed and their uses established. The first was Charles Darwin's theory of evolution. The second was the advent of new techniques for studying the physiology, embryology, and biochemistry of living creatures.

Evolutionary thought and theory since the time of Darwin have created a new function for taxonomic classification: to provide a framework for the study of evolutionary relationships. The overwhelming evidence we have that all organisms on Earth are related by common descent from some of the first cells, has led to different methods for tracing the family trees or phylogenetic trees of living and fossil organisms.

The discipline that attempts to understand the evolutionary interrelationships of living things, trying to interpret the way in which life has diversified and changed over time is *systematics*, while *taxonomy* is primarily the creation of names and groups.

In the 19th century, evidence began to accumulate showing that the classification in the animal and plant kingdoms was inadequate to express the diversity of life. The development of the electron microscope in the 1950s permitted detailed examination of the cell structure. These studies revealed a fundamental dichotomy, as it became evident that two basic cell types exist: the *eukaryotic* cell, which contains a nucleus and other internal organelles surrounded by membranes, and the *prokaryotic* cell, which has no internal membranes, and thus no nucleus. Such differentiation led to various classification schemes, and three, four, or more kingdoms were proposed. The scheme most widely used divided all living organisms into five kingdoms, as established by Whittaker in 1963: *Monera, Protoctists, Fungi, Plantae*, and *Animalia.* This classification coexists with the scheme mentioned above that separates life into two main divisions: the Prokaryotae (bacteria) and the Eukaryotae (animals, plants, fungi, and protists). The basis for this taxonomy is shown in Table 7.1 and Figure 7.1.

According to most theories on the origin of life, prokaryotes were the first living inhabitants of the Earth. Several theories explain the evolution of modern eukaryotic microbial cells. One of the most interesting constructs states that organelles and higher life forms evolved by serial symbiosis with genetically distinct cell lines uniting to form entirely new organisms.

Modern taxonomy allows the construction of various types of phylogenetic trees and the relatedness among organisms. Ideally, forms collected into one *taxon* (i.e., a category in a system of taxonomy)—whether a species, a family, a phylum, a division, or others—can be considered as evolved from one ancestral species. All organisms that have evolved in this way are *monophylectic.* A group of monophylectic organisms is a *clade*, and the study of how closely related groups branched and separated from one another is called *cladistics.*

Traditionally, phylogenetic trees were constructed relying on morphology and on the fossil records. Nowadays, however, they are constructed from comparisons of DNA or protein sequences in living organisms. Because of the antiquity of

TABLE 7.1. General organism classification

Type of cell	Other general characteristics	Type of organism	Kingdom
Akaryotic	No cellular organization	virus	
Prokaryotic	Unicellular, filamentous, colonial or mycelial Little or no differentiation Anaerobic, aerobic, facultatively-anaerobic, microaerophilic or aerotolerant Asexual reproduction Cell walls (with some exceptions)	bacteria and archaea	*Monera*
Eukaryotic	Unicellular More than a single chromosome per cell Heterotrophic or photoautotrophic nutrition Asexual or sexual reproduction	protists	*Protoctist*
	Multicellular, filamentous (mycelial) composed of hyphae, or unicellular (yeasts) Propagation by spores Chitinous walls Absorptive nutrition	fungi	*Fungi*
	Multicellular Extensive differentiation Photoautotrophic nutrition	higher plants	*Plantae*
	Multicellular Extensive differentiation Sexual reproduction Heterotrophic nutrition (ingestive or absorptive)	animals	*Animalia*

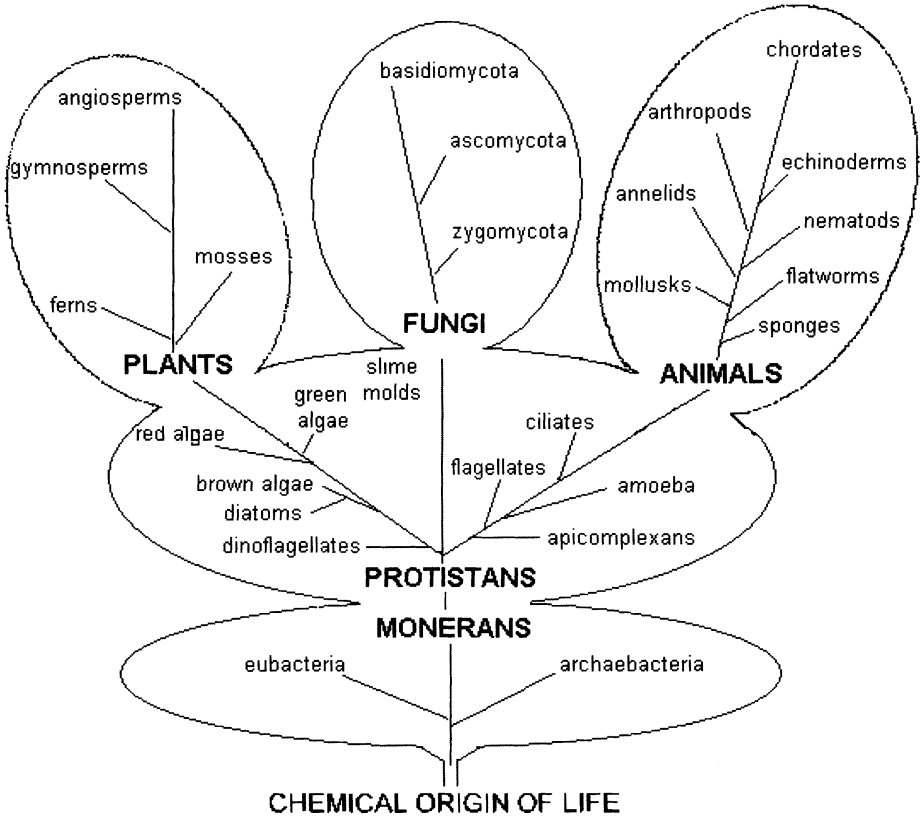


FIGURE 7.1. Graphical organism classification. (Source: Talaro, 1999).

the protein-synthesizing process, ribosomal RNAs appear to be excellent molecules for discerning evolutionary relationships among organisms. Use of 16S and 23S RNA as phylogenetic tools was pioneered in the early 1970s by Carl Woese. At present, a number of groups throughout the world work favorably with it. Molecular phylogeny, as this approach has been called, has greatly changed our evolutionary thinking about living organisms.

The main conclusion from ribosomal RNA phylogeny is that life on Earth is based on three main lines of cellular descent, all derived from a universal ancestor. See Figure 7.2.

As prokaryotes are far more diverse than suspected, the *Prokaryotae* are now divided in two groups: the *Bacteria* and the *Archaea*, which are as different from each other as either one is from the *Eukaryota*. In addition, a new taxon called a *domain* has been proposed above the kingdom level to emphasize the importance of the tripartite division of the living world: *Bacteria*, *Archaea*, and *Eukarya*. None of these is an ancestral group of the others, and each shares certain features with the others as well as having unique characteristics of its own.

As the tree shows, the true relatives of the archaea are not the bacteria but the eukaryotes. However, because the archaea branch-off closest to the root of the tree, the suggestion is that they are the most primitive of the three kingdoms of organisms whereas the eukaryotes are the least primitive (or the most derived). Placement of the archaea closest to the universal ancestor is supported by the fact that many archaea inhabit extreme environments involving high temperature, low pH, high salinity, and so on. Thus, archaea may well be evolutionary relics of the Earth's earliest forms of life.

Although the primary domains—Bacteria, Archaea, and Eukarya—were originally classified on the basis of comparative ribosomal RNA sequencing, subsequent studies have shown that each kingdom can also be defined on the basis of other

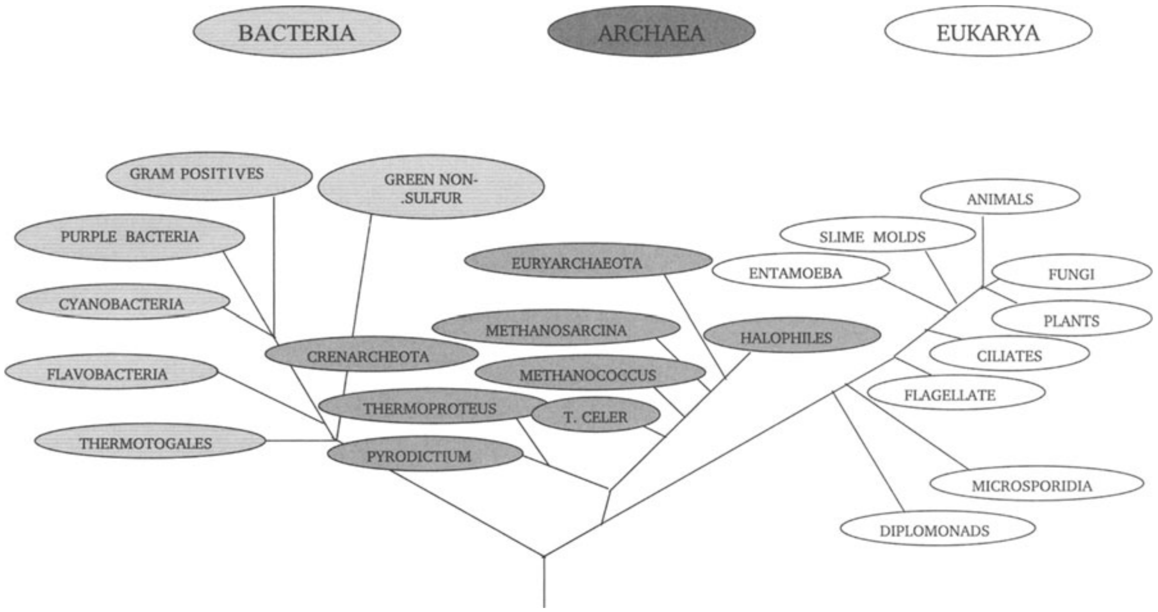


FIGURE 7.2. Lines of cellular descent. (Source: Levine, 1994).

phenotypic properties. Some of these properties are shown in Table 7.2.

7.2 Nutritional Classification of Organisms

Organisms live in nature forming complex webs of interactions among themselves and with the environment in which they flourish.

All organisms require energy to stay alive and grow. Organisms are divided into two major categories, based on the nature of their energy source: *phototrophs* and *chemotrophs. Phototrophs* capture the radiant energy of sunlight and transform it into chemical energy that is stored in the bonds of carbohydrates and other molecules. Green plants, algae, cyanobacteria, and photosynthetic green and purple bacteria are examples of phototrophs.

Most organisms, however, are unable to use radiant forms of energy and rely instead on the oxidation of chemical compounds as a source of energy. These organisms (called chemotrophs) are divided in two groups on the basis of the type of

TABLE 7.2. Phenotypic properties of the different domains of organisms

Characteristic	Eubacteria	Archaebacteria	Eukaryotes
Membrane-bound nucleus	absent	absent	present
Membrane lipids. Linkage to glycerol	ester-linked	ether-linked	ester-linked
Muramic acid in the cell wall	present	absent	absent
Introns in tRNA genes	no	yes	yes
Initiator tRNA	formylmethionine	methionine	methionine
Sensitivity to chloramphenicol, streptomycin and kanamycin	yes	no	no
Ribosomes	70S	70S	80S

chemical compounds they use: *chemorganotrophs* and *chemolithotrophs.*

Chemorganotrophs obtain their energy from the oxidation of organic compounds. Most bacteria are chemorganotrophs, and they use compounds such as carbohydrates, organic acids, and proteins as energy sources.

Chemolithotrophs obtain their energy from the oxidation of inorganic compounds such as hydrogen sulfide (H_2S), hydrogen gas (H_2), nitrite (NO_2^-), ammonia (NH_3), and ferrous iron (Fe^{2+}). Chemolithotrophy is restricted to bacteria and is not found in higher forms of life. Chemolithotrophic bacteria are widespread in soil and water, and they benefit from the inorganic energy sources available in these habitats.

The carbon required by living organisms is an important constituent of cellular structure and metabolic compounds. This element is present in the environment in many forms. It may appear in simple form as gaseous carbon dioxide or as more complex organic compounds. Microorganisms are remarkably diverse in their carbon requirements and they are divided into two groups: *autotrophs* and *heterotrophs*, based on their carbon source.

Autotrophic microorganisms synthesize organic substances from carbon dioxide through a process known as *carbon dioxide fixation.* They are important in nature because carbon dioxide fixation works as a precursor for the organic substrates that form the basis of the food chain for other organisms. Autotrophic bacteria include those that obtain their energy from light (*photoautotrophs*) and those that obtain it from the oxidation of chemical bonds (*chemoautotrophs*).

Most microorganisms are unable to use carbon dioxide as their main carbon source, and thus they require preformed organic compounds instead. These microorganisms are called *heterotrophs. Chemoheterotrophs* obtain the energy they need by oxidizing chemical compounds, wherefrom they require organic forms of carbon. Heterotrophic bacteria vary considerably in their requirements for organic substrates. Some (as the methane-oxidizing bacteria of the *Methylomonadaceae* family) use methane and other one-carbon compounds as their sole source of energy and carbon; they are called *methylotrophs.* Still other bacteria use a wide variety of organic substrates as energy and carbon sources; for example, several versatile strains of *Pseudomonas* are capable of using more than 100 different types of organic compounds. Because of this capacity, pseudomonas is widely distributed in water and soil. A summary of modes of nutrition is given in Table 7.3.

Oxygen is a universal component of cells that is always provided in large amounts by the major nutrient: water. However, many organisms also require molecular oxygen (O_2). These are organisms that are dependent on aerobic respiration for the fulfillment of their energy needs, and for which molecular oxygen works as a terminal oxidizing agent. Such organisms are termed *obligate aerobic.*

At the other physiological extreme are those microorganisms that obtain energy by means of reactions that do not involve molecular oxygen. Indeed, for many of these physiological groups, molecular oxygen is a toxic substance that either kills them or inhibits their growth. Such organisms are *obligate anaerobic.*

Some microorganisms are *facultative anaerobes*, able to grow either in the presence or absence of molecular oxygen. In metabolic terms, facultative anaerobes fall into two subgroups. Some (as the lactic acid bacteria) have an exclusively fermentative energy-yielding metabolism but are relatively insensitive to the presence of dioxygen; such organisms are most accurately termed *aerotolerant anaerobes.* Others (as many yeasts and enteric bacteria) can shift from a respiratory to a fermentative metabolism. Such facultative anaerobes use O_2 as a terminal oxidizing agent when it is available, but they can also obtain energy in its absence by fermentative reactions.

Some obligate aerobes grow best under oxygen partial pressures considerably below its pressure in air (0.2 atm); they are called *microaerophilic.* This is probably due to some of their enzymes, which are inactivated under strong oxidizing conditions; such obligate anaerobes can thus be maintained in a functional state only at low O_2 partial pressures. Many bacteria that obtain energy from the oxidation of molecular hydrogen show this behavior, and *hydrogenase*—the enzyme involved in hydrogen utilization—is readily inactivated by dioxygen.

TABLE 7.3. Modes of nutrition of organisms

Energy source	Electron source	Carbon source	Organisms and their hydrogen or electron donors
Photo- (light)	**Litho-** (inorganic and C_1 compounds)	**Auto-** (CO_2)	**Prokaryotes** Chlorobiaceae, H_2S, S Chromatiaceae, H_2S, S Rhodospirillaceae, H_2 Cyanobacteria, H_2O **Protista** (algae), H_2O
	Organo- (organic compounds)	**Hetero-**	**Prokaryotes** Chromatiaceae Chloroflexaceae Heliobacteriaceae
Chemo- (chemical compounds)	**Litho-** (inorganic and C_1 compounds)	**Auto-** (CO_2)	**Prokaryotes** Methanogens, H_2 Hydrogen oxidizers, H_2 Methylotrophs, CH_4, -CHOH Ammonia, nitrite oxidizers, NH_3, NO_2^-
		Hetero-	**Prokaryotes** Sulfur bacteria, S Manganese oxidizers, Mn^{2+} Iron bacteria, Fe^{2+} Sulfide oxidizers Sulfate reducers
	Organo- (organic compounds)	**Auto-** (CO_2)	**Prokaryotes** Clostridia
		Hetero-	**Prokaryotes** Nitrate, sulfate, oxygen and phosphate as terminal electron acceptors **Protista** **Fungi** **Plants** **Animals**

Source: Margulis, 2000.

7.3 Basic Aspects of Ecology

The interactions among organisms and the environment determine their distribution and abundance in nature. Such interactions necessarily begin with a constant source of energy—predominantly the flow and harvesting of life-supporting solar energy through photosynthesis or food gathering. These interactions extend to chains or forms of dependence among particular organisms, and ultimately to complex networks that weave together communities of organisms with the physical and chemical constituents of their environment.

The most complex level of biological organization is the ecological system or *ecosystem*, which is generally defined as a community of organisms living in a particular environment (the biotic component), along with the physical elements in that environment (abiotic component) with which they interact. Ecosystems are dynamic and incredibly complicated. Nowhere is this better observed than in the largest ecosystem: the Earth itself or, more precisely, its life-supporting soils, seas, and atmosphere as well as all the organisms in them, collectively called the *biosphere.* The term ecosystem can also be applied to much smaller environments which have natural boundaries that make them more or less self-contained. Examples include a meadow within a forest, a beach with water on one side and grassy dunes on the other, or an island surrounded by ocean. In every one of these cases, however, the boundaries are not sharp, nor are the ecosystems truly self-contained because

- energy must enter into them
- gases, nutrients, and water cycle in and out
- organisms come and go in space and time

These blurred boundaries reflect the fact that every small ecosystem exists within larger ecosystems. Each ecosystem blends into the next through a transitional zone called *ecotone*, which contains many of the species and characteristics of the two adjacent systems, plus unique species adapted to the special conditions of the interphase.

The biosphere has many parts and subparts, as deciduous forest and rain forest, grassland and dessert, seacoast and ocean floor, which provide a myriad of *habitats* or actual places where organisms live. The Earth's major ecosystems are called *biomes*, which have characteristic types of organisms. Some useful definitions are listed in Table 7.4.

7.3.1 The Habitats of Life: Air, Land, and Water

Climatic differences associated with the various biomes largely determine where particular types of organisms may live. At a more fundamental level, however, the three very different states of matter that make up habitats (solid, liquid, and gas) impose constraints on organisms and affect their way of living.

7.3.1.1 Atmosphere

Gaseous constituents in the air provide important chemical raw materials for life. Carbon dioxide is, of course, the carbon source for photosynthesis. Nitrogen, reduced by nitrogen-fixing organisms, is a necessary component of proteins and nucleic acids. The amount of water vapor in the air (i.e., the relative humidity) largely determines rates of evaporation from the skin of a frog, through the stomata of a plant, and so on. Hence, organisms that live in habitats with low relative humidity must adapt for survival. Finally, although we think of rain as beneficial for plants, it is also true that raindrops may strip the waxy covering layer from leaves, rendering them vulnerable to pollutants, pathogens, and chemicals. Rain also leaches nutrients from leaves and decreases plant productivity as a result. But at the same time, raindrops may contain dissolved phosphate, potassium, calcium, and other essential plant nutrients. Thus, with the potential harm comes an even greater good.

7.3.1.2 Land

Many plants and most animals acquire water and non-gaseous mineral nutrients directly or indirectly from soil. Without living organisms, the material we know as soil would not exist, for it is a product of the interplay of organisms and the Earth's crust. Plant roots, burrowing mammals, earthworms, and fungal hyphae inhabit the soil and are found amid soil particles, where water and air also occur.

Soil chemistry and structure determine the amount and availability of minerals and water to organisms. For instance, soil pH determines whether Ca^{2+}, $PO_4{}^{3-}$, and other essential ions are bound tightly to its particles or are free to be absorbed by organisms, or else leached away in water runoff. Likewise, plants tend to adapt to a specific soil pH. Soil is a restrictive environment for most animals, because relatively little food and oxygen are available, and movement through densely packed dirt, rocks, sand, and organic debris is difficult. On the

TABLE 7.4. Important definitions related to the biosphere

Biosphere
The assemblage of regions of the Earth that support life, including the lower atmosphere, the Earth's surface and aquatic environments. The term may also define a system rich in feedback loops that link life with non-living aspects of the environment.

Biomes
Biomes are a group of closely related ecosystems (see below). Terrestrial biomes include tundras, taigas, temperate forests, deserts, grasslands, and tropical rain forests. Major aquatic biomes are freshwater swamps, marshes and bogs, lakes and rivers, estuaries, inter-tidal zones, coastal oceans and open oceans.

Ecosystems
A sizable interacting system composed of living organisms and their physical environment. An ecosystem is a grouping of various species of plants, animals and microbes interacting with each other and with their environment.

Biotic factors
Organisms and their products (secretions, wastes, and remains).

Abiotic factors
They include rainfall (amount and distribution over the year), temperature (extremes of heat and cold as well as their average), light, water, wind, chemical nutrients, pH, salinity, and fires. The climate for a given region involves its temperature and precipitation. The degree (high or low) to which each of these factors is or is not present profoundly affects the ability of organisms to survive. The difference in response to environmental factors determines which species may (or may not) occupy a given region. In turn, the organisms that do or do not survive determine the nature of a given ecosystem. Each species has an optimum range, a zone of stress, and tolerance limits with respect to every abiotic factor.

Population
A population consists of all the members of a species living in a given area at the same time. It is an interbreeding reproducing group.

Habitat
Location within an ecosystem where a population actually lives and thrives. The habitat must supply the needs of organisms, such as food, water, temperature, oxygen, and minerals. If the population's needs are not met, it will move to a better habitat. Several populations may share a habitat, but competition may be small or non-existent because different populations have different *niches*.

Community
A coherent assembly of populations that inhabit the same habitat and interact with each other. Each successful population within a community plays a functional role that contributes to the maintenance of that community. Populations within a community that use the same resources—the *guild structure* of the community—often exhibit intense competition. The species assemblage that successfully inhabits a delineated volume of resources is called a *unit community*. Populations in a unit community tend to interact with each other and not with populations in other unit communities.

Niche
Each population that functions as a member of the community in a given habitat has a specialized functional role called a niche. An ecological niche is a functional description of the role that a species plays in a community—how it obtains food, what relationship it has with other species and the services it provides in its biological community.

Some species are specialists and occupy a very narrow niche; others are generalists that eat a wide variety of food and live in a broad range of habitats.

other hand, however, burrowing animals that have adapted to underground life are more difficult for predators to find, and although the soil surface may be subject to extreme temperatures, creatures living even a few centimeters beneath it are relatively well insulated from both heat and cold.

7.3.1.3 Water

In contrast to terrestrial organisms—whose life support comes from both air and land—aquatic life forms derive food, water, gases, support, protection from temperature extremes, and other basic needs from the surrounding water. Some waters contain nutrients and provide around 15% or less of the amount of oxygen present in air. The density of water is between that of air and soil, and buoys up the bodies of plants and animals so effectively that less massive support structures are needed. Like deep soil, water moderates temperatures because of its large capacity to absorb and hold heat; thus, the temperature extremes occurring in the air are not encountered in oceans and lakes. Very deep waters may be cold—in fact near freezing—and yet their unchangeability has allowed organisms to evolve enzymes that function very rapidly at such temperatures. Lastly, water itself—a critical requirement for life—is available in unlimited supply.

Although there is animal life even in the inky and ice-cold depths of great ocean basins, plants can survive only in the top layer of water known as the *photic zone*, where enough light is present for photosynthesis. Because water both reflects and absorbs light, even the cleanest ocean water has a photic zone of only about 100 meters deep. Most animals living deeper are either carnivores that eat smaller animals that consume phytoplankton in the photic zone, or scavengers that depend on a steady supply of dead and dying plant and animal bodies drifting down from the above.

Interestingly, true miniature ecosystems that do not rely on energy arriving from the photic zone exist in deep ocean abysses. Communities of giant tubeworms, huge clams, crabs, a few fish, and other animals cluster around deep-sea vents or perforations in the sea floor where superheated mineral-laden water pours out. The ultimate source of food that supports these vent communities is the population of chemolithotrophic bacteria that oxidize hydrogen sulfide or other compounds spewing from the vents in order to harvest energy to build organic materials. These sulfur bacteria live symbiotically in the tissues of tubeworms and in clams' gills, while crabs consume the producers directly.

Thus, each environment supports a more-or-less unique grouping of organisms interacting with each other and with their surroundings in a way that perpetuates or sustains the entire group. In other words, an ecosystem is an environment plus the species it supports. Every ecosystem is interconnected with others through ecotones and through some species that cross from one system to another. Each species and ecosystem is kept within certain bounds by limiting factors:

(a) biotic and abiotic conditions that each species cannot tolerate
(b) competition with other species
(c) one or more physical barriers.

7.3.2 Trophic Levels

The biotic structure is similar in all ecosystems and includes three basic categories of organism-feeding relationships that interact forming a *food web:*

- Producers
- Consumers
- Detritus feeders and decomposers

Producers are photoautotrophic organisms such as green plants and bacteria that employ photosynthesis to produce glucose and that release dioxygen as a by-product. Plants are able to manufacture all the additional complex molecules that make up their structure from glucose and mineral nutrients such as nitrogen, phosphorus, and sulfur that they absorb from the soil or from water. As this conversion from inorganic to organic molecules occurs, part of the energy from light is stored in the organic compounds as chemical energy.

All other organisms, which are heterotrophs, must consume organic material made by autotrophs in order to obtain energy and nutrients. In this way they may eat plants (*herbivores*) or animals (*carnivores*), or decompose the remains of other organisms and their waste products (*decomposers*). Herbivores are primary consumers, carnivores are secondary consumers, or they may be tertiary consumers if they eat other consumers.

Decomposers, such as many fungi and bacteria, obtain energy by breaking down complex molecules in tissues of dead plants and animals. These decaying organisms are essential for the health of all ecosystems because they cycle important nutrients.

Despite their complexity, food webs basically follow a series of steps or levels—from producers to primary consumers, to secondary consumers, and so on. These feeding levels are called *trophic levels*. All producers belong to the first trophic level; all primary consumers belong to the second trophic level, and so on. All feeding relationships can be visualized as a flow of nutrients and energy through a series of trophic levels. There are no more than three or four discernible trophic levels in any ecosystem.

For instance, a typical food chain in a field ecosystem might be

grass → zebra → lion

The real world, of course, is more complicated than a simple food chain. While many organisms do specialize in their diets, other organisms do not. Hawks do not limit their diet to snakes, snakes eat things other than mice, mice eat grass as well as grasshoppers, and so on. A more realistic depiction of who

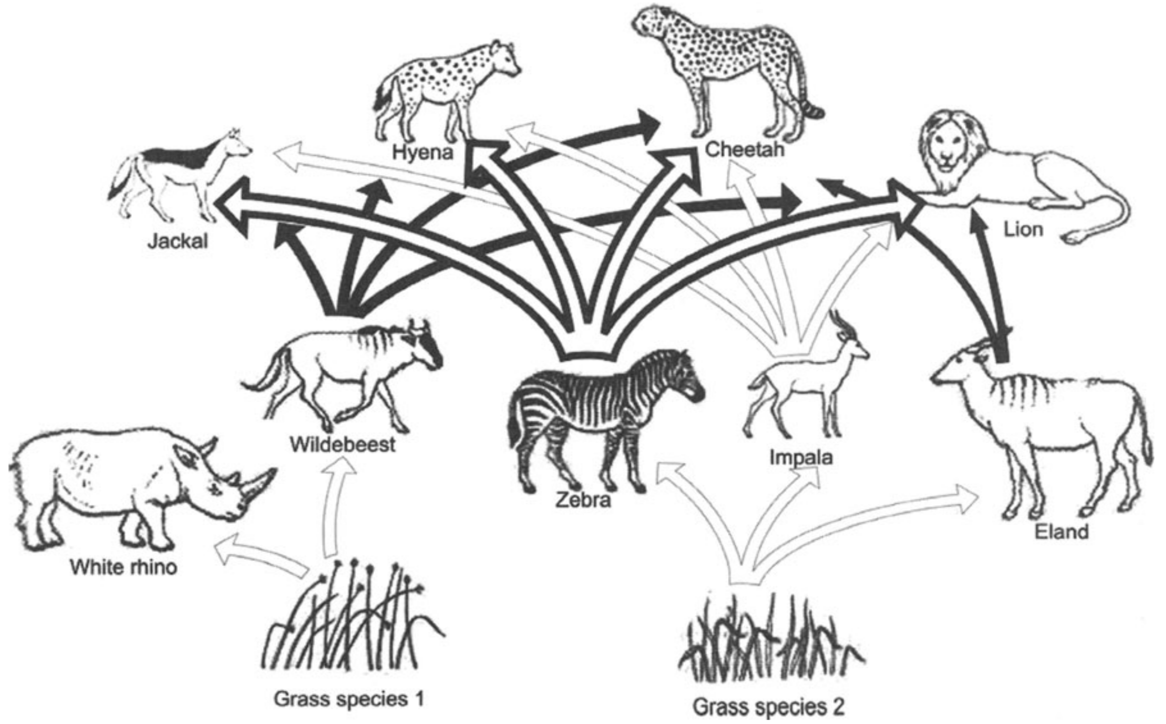


FIGURE 7.3. Sample food web.

eats whom is called a food web. An example is shown in Figure 7.3.

In food chains and webs, energy flows through trophic levels with smaller amounts of energy making it to the next level (approximately 10 %). Eventually all the energy is lost, much of it as heat.

7.3.3 Non-feeding Relations Among Species

The overall structure of ecosystems is dominated by feeding relationships. However, different populations may interact in a way that one or both of them may benefit from the interaction (*cooperation*), or one or both may be negatively affected (*competition*).

Cooperation

The types of positive interactions are:

- **Commensalism**
  Commensalism is a relationship in which one member clearly benefits and the other apparently is neither benefited nor harmed. It often results when the unaffected population, in the course of its normal growth and metabolism, modifies the habitat in such a way that another population benefits because the modified habitat is more suitable for its needs. For example, an epiphyte growing on a tree gets an increased supply of light while the tree is not affected.
- **Synergism**
  Both populations benefit from the relationship, but the relationship is not an obligatory one, as both populations are capable of surviving in their natural environment on their own. For example, there are synergistic relationships among bacterial populations involved in the cycling of nitrogen.
- **Mutualism**
  Mutualism is an obligatory relationship between two populations that benefits both. A mutualistic relationship requires close physical proximity; it is highly specific, as one member cannot be replaced by another related species. A typical example is that of flowers and insects. Insects benefit by obtaining nectar from the flowers, and the plants benefit by being pollinated in the process. In some cases, the mutualistic relationship has become so close that the species involved are no longer

capable of living alone. For example, lichens comprise two organisms, a fungus and an algae; the fungus provides protection for the algae, enabling it to survive in dry habitats where it cannot live by itself, and the algae (which is a producer) provides food for the fungus (which is a heterotroph).

- **Symbiosis**
  Symbiosis refers to the intimate association between members of different species. It does not specify a mutual benefit or harm. Therefore, symbiotic relationships may include mutualism, commensalism, or parasitism. Symbiotic relationships often entail some degree of coevolution of the partners, shaping in part their structural and behavioral characteristics.

Competition

Competition occurs when two populations utilize the same resources, whether space or a limiting nutrient. Competition tends to bring about ecological separation of closely related populations. This is known as the *competitive exclusion principle*, which states that two species will not occupy the same niche and compete for exactly the same resources in the same habitat for very long. Eventually, one group will gain a larger share of resources while the other will either migrate to a new area, become extinct, or change its behavior or physiology in ways that minimize competition.

The types of competition are:

- **Amensalism**
  When one population produces a substance that is inhibitory to another population, the relationship is called amensalism. Once an organism establishes itself surviving in the habitat, it may prevent other populations from surviving in that habitat.
- **Parasitism**
  In a relationship of parasitism the population that benefits, the parasite, normally derives its nutritional requirements from the population that is harmed, the host. The host–parasite relationship is characterized by a relatively long period of contact, which may be directly physical or metabolic. Normally, the relation is as specific as for example the viruses, which are obligate intracellular parasites of bacterial, fungal, algal, and protozoan populations.
- **Predation**
  A predator in an ecological sense is an organism that feeds directly upon another living organism, the prey. Predation is a potent and complex influence on the population balance of communities and a mayor factor in evolution and adaptation.

  Many species of plants and animals have toxic chemicals, body armor, and other ingenious defensive adaptations to protect themselves from competitors or predators.

Both positive and negative interactions may occur even within a single population. Such interactions are population-dependent. In general, positive interactions increase the growth rate of a population, whereas negative interactions have the opposite effect. With increasing population density, positive interactions theoretically increase the growth rate to some asymptotic limit. In contrast, negative interactions decrease growth rate as the population density increases.

Commonly, positive interactions predominate at low population densities and negative ones at high population densities. As a result, there is an optimal population density for maximal growth rate.

7.3.4 Sustainability of Ecosystems

Ecosystems change as conditions are altered. The one thing that enables ecosystems to sustain a given composition of species over long periods of time is the dynamic balance involving all the relationships within the system. Each species in an ecosystem exists as a population. An ecosystem remains stable over a long period of time as the population of each species remains more or less constant in size and geographic distribution. This means that reproductive rates are equaled by death rates and thus a balance is achieved.

There are several laws for the sustainability of ecosystems:

- They use sunlight as their primary energy source (except in certain deep ocean or underground habitats).
- The size of consumer population is maintained in such a way that overgrazing does not occur.
- Biodiversity is maintained, so that the ecosystem can adjust and adapt to various changes.
- Ecosystems vary greatly in the efficiency with which they retain specific materials such as essential nutrient elements. Habitats capable of retaining nutrients can sustain high rates of productivity.

7.4 Biogeochemical Cycles

In addition to obtaining energy from food, organisms must obtain the necessary nutrients to construct body tissues. For proper growth, most organisms require the following elements or essential nutrients (*biogenetic elements*):

Essential nutrients: C, H, O, N, S, P
Minor elements: Mg, K, Na, halogens
Trace elements: B, Co, Cu, Mo, Ni, Se, Sn, V, Zn

Interestingly, although energy and nutrients are passed on from one organism to another within the same complex molecules, their paths through ecosystems are quite different. Energy flows through ecosystems by steadily arriving from the Sun, then passing from one trophic level to the next, and dissipating into the environment as heat. On the other hand, elements are neither produced nor destroyed; they are transferred from one organism to another in closed loops called *nutrient cycles.* Because most of these cycles involve the passage of elements through living organisms and the atmosphere, hydrosphere, and lithosphere, they are often called *biogeochemical cycles.*

Those elements that are essential components of living organisms are normally subject to biogeochemical cycling. The major elemental components of living organisms are cycled most intensely whereas minor elements are cycled less intensely. In terms of biogeochemical cycling, the various chemical forms of a particular element constitute the so-called *pools* or *reservoirs.* When examining the biogeochemical cycling of an individual element, one should consider its global reservoirs and their size, and whether or not they are actively cycled.

7.4.1 Water Cycle

In the water cycle energy is supplied by the Sun, which drives evaporation from ocean surfaces or from treetops. The Sun also provides the energy that drives the weather systems and moves the water vapor (clouds) from one place to another. Precipitation occurs when water condenses from a gaseous state in the atmosphere and falls to earth. Evaporation is the reverse process in which liquid water becomes gaseous. Once water condenses, gravity takes over and the water is pulled to the ground. Gravity continues to operate, either pulling the water underground (groundwater) or across the surface (runoff). In either event, gravity continues to pull water lower and lower until it reaches the oceans or lakes. Frozen water may be trapped in cooler regions of the Earth (the poles, glaciers on mountaintops, etc.) as snow or ice, and may remain as such for very long periods of time. Lakes, ponds, and wetlands form where water is temporarily trapped. The oceans are salty because any weathering of minerals that occurs as the water runs to the ocean will add to the mineral content of the water, but water cannot leave the oceans except by evaporation, and evaporation leaves the minerals behind. Thus, rainfall and snowfall are comprised of relatively clean water, with the exception of pollutants (such as acids) picked up as the water falls through the atmosphere. Organisms play an important role in the water cycle. Most organisms contain a significant amount of water (up to 90% of their body weight). This water is not held for any appreciable length of time and moves out of the organism rather quickly in most cases. Animals and plants lose water through evaporation from the body surface, and through evaporation from the gas exchange structures (such as lungs). In plants, water is drawn in at the roots and moves to the gas exchange organs, the leaves, where it evaporates quickly. This special case is called *transpiration* because it is responsible for so much of the water that enters the atmosphere. In both plants and animals, respiration and photosynthesis participate in the water cycle.

7.4.2 Hydrogen Cycle

The largest global hydrogen reservoir is water, which is actively cycled by photosynthesis and respiration, although they do not normally result in H_2 evolution or consumption. Instead, reduction of CO_2 occurs with electrons coming directly from H_2S, from other low-molecular weight organic compounds (by *anoxyphotobacteria*), or from H_2O (by the other photosynthetic organisms). In respiration, electrons from reduced organic compounds pass along the respiratory chain and ultimately reduce dioxygen to water.

Free gaseous H_2 is biologically produced during anaerobic fermentations and also as a side product of photosynthesis coupled with nitrogen fixation by cyanobacteria and by *Rhizobium* legume associations. Most of the H_2 produced is utilized anaerobically to reduce NO_3^-, SO_4^{2-}, Fe(III), and Mn(IV) or

ΔG^0, K_{eq}, and E^0 in biochemistry

As discussed in Section 2.3, when a reacting system is not at equilibrium, the tendency to move toward equilibrium represents a driving force, the magnitude of which can be expressed as the free-energy change for the reaction ΔG. Under standard conditions (298 K = 25°C), when reactants and products are initially present at 1 M concentrations or, for gases, at partial pressures of 101.3 kPa or 1 atm, the force driving the system toward equilibrium is defined as the standard free-energy change, ΔG^0. By this definition, the standard state for reactions that involve hydrogen ions is $[H^+] = 1$ M, or pH 0. Most biochemical reactions occur in well-buffered aqueous solutions near pH 7; both the pH and the concentration of water (55.5 M) are essentially constant.

For convenience of calculations, biochemists therefore define a different standard state, in which the concentration of H^+ is 10^{-7} M (pH 7) and the water is 55.5 M. Physical constants based on the biochemical standard state are called *standard transformed constants* and are written as $\Delta G^{0'}$ or K'_{eq} to distinguish them from the untransformed constants used by chemists and physicists. By convention, when H_2O or H^+ are reactants or products, their concentrations are not included, but are incorporated into the constants $\Delta G^{0'}$ and K'_{eq}.

As in the definition of $\Delta G^{0'}$, biochemists define the standard sate of oxidation–reduction reactions as pH = 7 and express reduction potentials as $E^{0'}$, the *standard reduction potential at pH = 7.* Values of $E^{0'}$ represent the potential difference when the conjugate redox pair, at 1 M concentrations and pH = 7, is connected with the standard (pH = 0) hydrogen electrode. When the conjugate pair $2H^+/H_2$ at pH 7 is connected with the standard hydrogen electrode (pH = 0), electrons tend to flow from the pH = 7 to the standard (pH = 0) cell; the measured for the $2H^+/H_2$ pair is −0.414 V (Table 7.5).

The energy made available by spontaneous electron flow of a reaction (the free-energy change for the oxidation–reduction reaction) is:

$$\Delta G^{0'} = -nF\Delta E^{0'}$$

where n represents the number of electrons transferred in the reaction and F is the Faraday constant (96.496 kJ/V mole of electrons).

to generate CH_4. When H_2 rises through oxygenated soils or sediments, it is oxidatively metabolized to H_2O, and only a small part is likely to escape to the atmosphere.

The aerobic utilization of H_2 is performed by facultatively chemolithotrophic hydrogen bacteria according to the following reaction:

$$6H_{2(g)} + 2O_{2(g)} + CO_{2(g)} \rightarrow [CH_2O] + 5H_2O_{(l)} \qquad (7.1)$$

The formula in brackets represents cell material. The most efficient hydrogen-consuming bacteria belong to the genus *Alkaligens.*

A significant aspect of hydrogen cycling is the interspecies hydrogen transfer among microorganisms with different metabolic capabilities that complement each other in terms of nutritional factors (a phenomenon called *syntrophism*). Examples include the fermentative and methanogenic component of *Methanobacillus omelianskii* association, as well as the transfer between methanogens and sulfate reducers.

7.4.3 Carbon Cycle

The most actively cycled reservoir of carbon is atmospheric CO_2 (it constitutes 0.034% of the atmosphere). Carbon dioxide dissolves readily in water and is in direct equilibrium with dissolved inorganic forms of carbon (H_2CO_3, HCO_3^-, and CO_3^{2-}, see Section 6.2.1.3). Once there, it may precipitate as solid calcium carbonate (limestone). Corals and algae encourage this reaction and build up limestone reefs in the process, but a much larger portion in the deep sea equilibrates only at the slow rate of

TABLE 7.5. Standard reduction potentials of some biologically important half-reactions (25°C, pH = 7)

Half-reaction	$E^{0'}$ (V)
$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftarrows H_2O$	0.816
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	0.771
$NO_3^- + 2H^+ + 2e^- \rightleftarrows NO_2^- + H_2O$	0.421
$S + 2H^+ + 2e^- \rightleftarrows H_2S$	−0.243
$2H^+ + 2e^- \rightleftarrows H_2$ (at pH 7)	−0.414

Example 7.1 Determine the oxidizing and reducing agents in reaction (7.1).

Answer

Analyzing the change in oxidation numbers:

$\overset{0}{H_2} \rightarrow \overset{+1}{H_2O} + [\overset{+1}{CH_2O}]$ hydrogen loses electrons; therefore, it is a reducing agent.

$\overset{0}{O_2} \rightarrow \overset{-2}{H_2O}$ oxygen gains electrons; it is an oxidizing agent.

$\overset{+4}{CO_2} \rightarrow [\overset{0}{CH_2O}]$ carbon gains electrons; it is an oxidizing agent.

vertical seawater circulation. The carbon in limestone or other sediments can only be released to the atmosphere when they are subducted and brought to volcanoes, or when they are pushed to the surface and slowly weathered away.

From a biological perspective, the key events of this cycle are the complementary reactions of respiration and photosynthesis. *Respiration* takes carbohydrates and oxygen and combines them to produce carbon dioxide, water, and energy. *Photosynthesis* takes carbon dioxide and water and produces carbohydrates and oxygen. The outputs of respiration are the inputs of photosynthesis, and the outputs of photosynthesis are the inputs of respiration, as shown in Figure 7.4.

If glucose is used as the substrate for respiration, the reaction is the following:

$$C_6H_{12}O_6 + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)} \qquad \Delta G^{0'} = -2834\,\text{kJ/mol} \qquad (7.2)$$

The reactions are also complementary in the way they deal with energy. Photosynthesis takes energy from the Sun and stores it in the carbon–carbon bonds of carbohydrates; respiration releases that energy. Both, plants and animals accomplish respiration, but only plants (and other producers) can accomplish photosynthesis.

Then, plants take up carbon dioxide and convert it into carbohydrates. This carbon in the plants has three possible fates: it can be liberated to the atmosphere by the plant through respiration; it can be eaten by an animal; or it can be present in the plant when the plant dies. Animals obtain all their carbon in their food ultimately from plants (autotrophs). In the animal, the carbon also has the same three possible fates. Carbon from plants or animals that is released to the atmosphere through respiration will either be taken up by a plant in photosynthesis or dissolved in the oceans. Dead organic matter such as humus and organic sediments is also actively cycled carbon and two things can happen: it can be respired by decomposers (and released to the atmosphere) or it can be buried intact and ultimately form coal, oil, or natural gas (fossil fuels). See Figure 7.5.

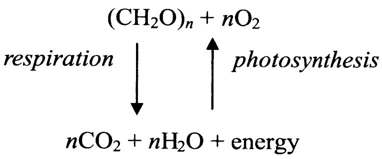


FIGURE 7.4. The respiration–photosynthesis cycle.

The natural rates of carbon cycling in oceans and land are nearly in a steady state; that is, the rates of movement of carbon between the atmosphere and trees, or between algae and the inorganic carbon dissolved in the ocean do not change measurably from year to year and tend to balance each other. However, human activities have recently introduced changes that will be addressed in Chapter 8.

7.4.4 Oxygen Cycle

The carbon cycle also describes the oxygen cycle, because these atoms are often combined. Oxygen is present in carbon dioxide, in carbohydrates, in water, and as a molecule of two oxygen atoms. Oxygen is released to the atmosphere by autotrophs during photosynthesis and taken up by both autotrophs and heterotrophs during respiration. In fact, all of the oxygen in the atmosphere is *biogenic*; that is, it was released from water through photosynthesis by autotrophs. It took about 2 billion years for autotrophs (mostly cyanobacteria) to raise the oxygen content of the atmosphere to the 21% that it is today; this

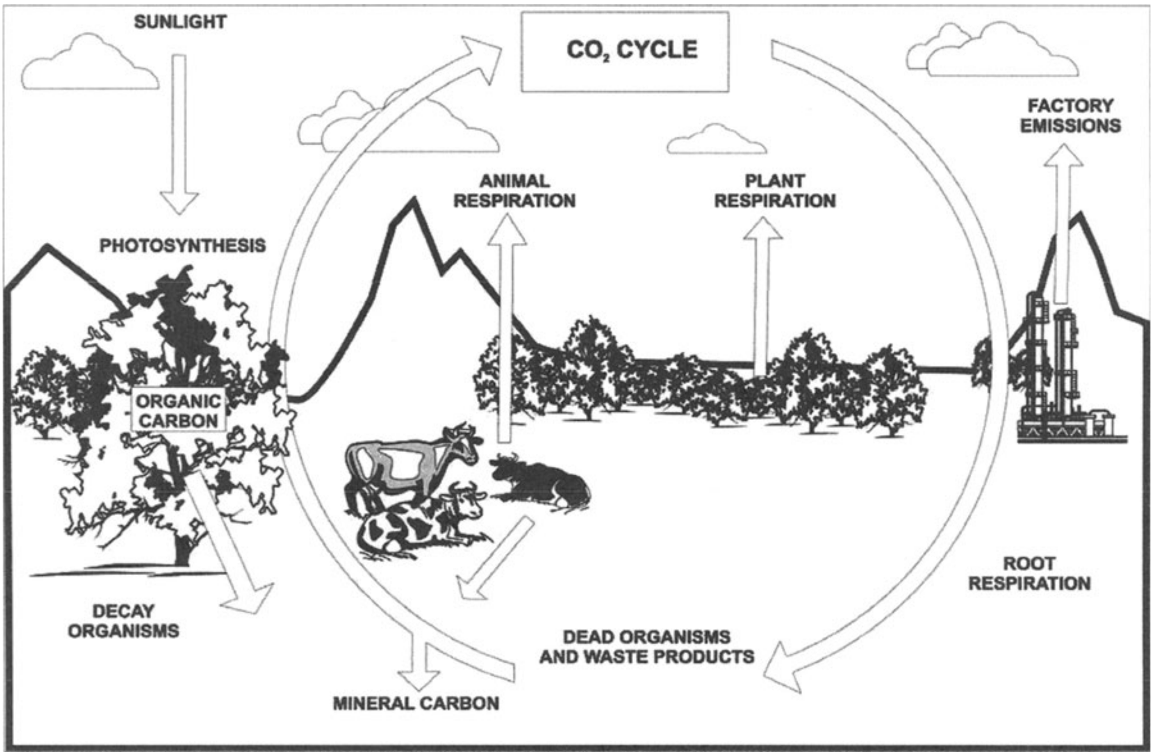


FIGURE 7.5. The carbon cycle.

Example 7.2 (a) Write the reduction and oxidation half-reactions that take place in the respiration process:

$$C_6H_{12}O_6 + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)}$$

(b) Determine the number of electrons transferred in this reaction.

Answer

Analyzing the change in oxidation numbers, carbon changes from

$$\begin{array}{cc} 0 \rightarrow & +4 \\ C_6H_{12}O_6 \rightarrow & CO_2 \end{array}$$

this is the **oxidation half-reaction**, which can be balanced in acid media:

$$6H_2O + C_6H_{12}O_6 \rightarrow 6CO_2 + 24H^+ + 24e^-$$

The reduction half-reaction is:

$$O_2 \rightarrow H_2O$$

as oxygen changes from 0 to −2.

The **reduction half-reaction** is balanced as:

$$4e^- + 4H^+ + O_2 \rightarrow 2H_2O$$

In order to balance the number of electrons, this reaction is multiplied by 6 and:

$$24e^- + 24H^+ + 6O_2 \rightarrow 12H_2O$$

Adding the half-reactions:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

(b) The number of electrons transferred is 24.

This is a global reaction. Electrons are transferred in pairs or individually in a series of reactions called *metabolic pathways.* In the case of respiration, the metabolic pathways are glycolysis, the citric acid cycle, electron transfer, and oxidative phosphorylation.

opened the door for complex organisms such as multicellular animals, which need a lot of oxygen.

The amount of oxygen combined with Fe and Mn, together with that in dissolved and sedimentary sulfates, exceeds the oxygen in the atmosphere several times over. These mineral reservoirs of oxygen (including the carbonates) participate to some extent in the oxygen cycle, but because of their large combined mass, their turnover rate is negligible. Atmospheric and dissolved oxygen in CO_2 and H_2O are the predominant actively cycled oxygen reservoirs. Oxygen in living and dead organic matter and nitrates constitute relatively small (but actively cycled) reservoirs.

The presence or absence of molecular oxygen in a given habitat is crucial in determining the type of metabolic activities that can occur there. Oxygen is inhibitory to strict anaerobes. Facultative anaerobes can gain more energy from organic substrates by using oxygen as the terminal electron acceptor than by fermentative metabolism.

Oxygen serves as the terminal electron acceptor not only in degradation of organic matter, but also in the oxidation of reduced inorganic chemicals used as energy sources by chemolithotrophs. The exhaustion of oxygen in an environment initiates the reduction of nitrate, sulfate, ferric iron, and oxidized manganese species. If such electron acceptors are unavailable or become exhausted, fermentative metabolism and methanogenesis (involving CO_2 reduction) become the only options.

Biogenic elements other than carbon, hydrogen, and oxygen are often referred to as *mineral nutrients*. They include nitrogen, sulfur, and phosphorus, and are usually taken up by autotrophs and phototrophic heterotrophs in the form of mineral salts. Biogenic elements such as nitrogen, sulfur, iron, and manganese exist in the ecosphere in several stable oxidation states and tend to be cycled in complex redox processes. Elements such as phosphorus, calcium, and silicon exist in compounds in only one stable oxidation state; they have relatively simple cycles comprising dissolution and incorporation into organic matter, balanced by mineralization and sedimentation.

7.4.5 Nitrogen Cycle

Nitrogen occurs in numerous oxidation states ranging from -3 (as in ammonia) to $+5$ (as in nitrate). It is a constituent of amino acids, nucleic acids, amino sugars, and their polymers. A large and slowly cycled nitrogen reservoir (approximately 3.8×10^{15} tons) is the N_2 gas contained in the atmosphere. The inorganic nitrogen ions (e.g., ammonium, nitrite and nitrate) occur as highly water-soluble salts and consequently spread in dilute aqueous media throughout the ecosystems. Living and dead organic matter also provide relatively small, actively cycled nitrogen reservoirs.

The biogeochemical nitrogen cycle strongly depends on microbial activity. The various transformations on nitrogen bring about the circulation of nitrogen from the atmosphere through terrestrial and aquatic habitats. These movements through the biosphere largely determine the ecological productivity of the different habitats. See Figure 7.6.

Key processes in the nitrogen cycle include:

(a) fixation
(b) ammonification
(c) nitrification
(d) nitrate reduction/denitrification.

7.4.5.1 *Fixation*

Nitrogen gas can be naturally taken from the atmosphere (i.e., fixed) in two basic ways. First, lightning provides enough energy to reduce nitrogen and generate nitrate. The second way is biological fixation of molecular nitrogen, which is carried out by several types of bacteria: free-living soil bacterial genera, bacteria that form symbiotic, mutualistic associations with the roots of bean plants and other legumes (rhizobial bacteria), and photosynthetic cyanobacteria (blue-green algae), which are found most commonly in water. All of these fix nitrogen, according to the following reaction:

$$N_{2(g)} + 8H^+ + 8e^- \rightarrow 2NH_{3(g)} + H_{2(g)} \qquad \Delta G^{0'} = +630 \text{ kJ/mol} \tag{7.3}$$

Nitrogenase is the complex enzyme responsible for nitrogen fixation. This process requires not only nitrogenase but also energy. The energy for carrying out these processes may be obtained from the conversion of light energy by photoautotrophs (such as cyanobacteria) or by respiration of heterotrophs (such as *Azobacter*). In the latter case, nitrogen fixation is limited by the availability of organic substrates.

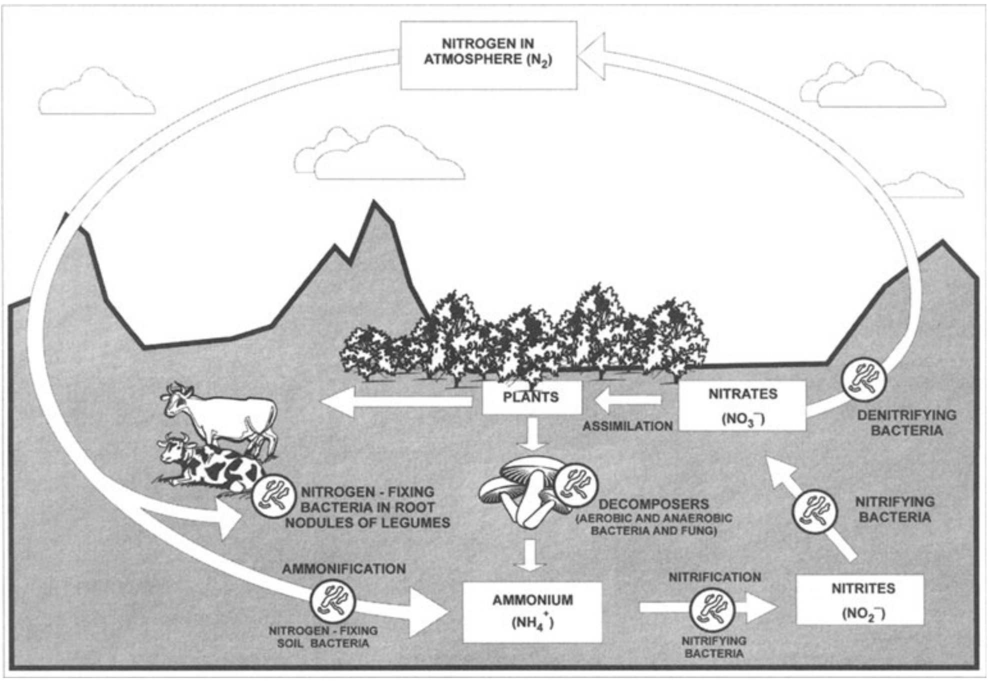


FIGURE 7.6. The nitrogen cycle.

In terrestrial habitats the symbiotic fixation of nitrogen by *Rhizobia* accounts for the largest contribution of combined nitrogen. For example, *Rhizobia* associated with an alfalfa field may fix up to 300 kg N/ha/year, compared with a rate of 0.5–2.5 kg N/ha/year for free-living *Azotobacter* species.

In aquatic habitats, cyanobacteria are the principal nitrogen fixers. Rates of nitrogen fixation by cyanobacteria are generally one or two orders of magnitude higher than those by free-living, nonphotosynthetic soil bacteria. Under favorable conditions, cyanobacteria may fix up to 1600 kg of N/ha/year in a rice paddy.

Nitrogen fixation also occurs within the digestive tracts of some animals (as termites). The fixation of nitrogen in organisms that primarily consume nitrogen-free cellulose is especially important for the formation of proteins. Ammonia is assimilated into amino acids that are then polymerized into proteins.

7.4.5.2 *Ammonification*

This is a process in which organic nitrogen is converted into ammonia. Nitrogen in living and dead organic matter occurs predominantly in the reduced amino form. A typical ammonification reaction is

$$NH_2\text{–}CO\text{–}NH_2 + H_2O_{(l)} \rightarrow 2NH_{3(g)} + CO_{2(g)} \tag{7.4}$$

Some of the ammonia thus produced is released from alkaline environments to the atmosphere, where it is relatively inaccessible to biological systems. This form of nitrogen (and others in the atmosphere) is subject to chemical and photochemical transformations, after which they can be returned to the litho- and hydrosphere through water deposition.

Numerous plants and microorganisms can assimilate ammonium ions by incorporating them into amino acids and other nitrogen-containing biochemicals. Animals acquire all of their amino acids when they eat plants (or other animals). When plants or animals die (or release waste), the nitrogen is returned to the soil. The usual forms of nitrogen returned to the soil in animal wastes or in the output of the decomposers are ammonia, urea, or uric acid.

7.4.5.3 *Nitrification*

In nitrification, ammonia or ammonium ions are oxidized to nitrite ions and then to nitrate ions:

$$NH_4{}^+ + 1.5O_{2(g)} \rightarrow NO_2{}^- + 2H^+ + H_2O_{(l)} \quad \Delta G^{0'} = -277.2 \text{ kJ/mol} \tag{7.5}$$

$$NO_2{}^- + {}^1/_2O_{2(g)} \rightarrow NO_3{}^- \quad \Delta G^{0'} = -71.4 \text{ kJ/mol} \tag{7.6}$$

Nitrification seems limited to a number of autotrophic bacteria. The dominant genus that is capable of oxidizing ammonia to nitrite in soils is *Nitrosomonas*, and the dominant genus capable of oxidizing nitrite to nitrate is *Nitrobacter.* Normally, the two processes are closely connected and nitrite accumulation does not occur. Nitrifying bacteria are chemolithotrophs that utilize the energy derived from nitrification to assimilate CO_2.

Nitrification is especially important in soils because the transformation of ammonium into nitrite and nitrate ions results in their charge switching from positive to negative. As discussed in Chapter 5, positively charged ions tend to be bound by negatively charged clay particles in soil, but negatively charged ions freely migrate in the soil water. This mobilization process results in a net nitrogen transfer within soil habitats. Most plants can take up nitrate and convert it to amino acids. Nitrite and nitrate can readily leach from the soil column into groundwater, which represents a loss of fixed forms of nitrogen from the soil that plants utilize for biomass production.

7.4.5.4 *Nitrate Reduction and Denitrification*

A heterogeneous group of microorganisms, including many bacterial, fungal, and algal species, are capable of assimilatory nitrate reduction, a process that reduces nitrate and nitrite to ammonia, which can be subsequently incorporated into amino acids.

Denitrifying nitrate reducers such as *Paracoccus denitrificans, Thiobacillus denitrificans*, and various *pseudomonads* follow a more complete reduction pathway, converting nitrate through nitrite to nitric oxide, nitrous oxide and lastly to molecular nitrogen:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \tag{7.7}$$

Primary denitrifying genera in soils are *Pseudomonas* and *Alkaligens.* Simultaneous with denitrification is organic matter oxidation. The utilization of glucose through nitrate reduction by *Pseudomonas denitrificans* can be written as

$$(5/6)C_6H_{12}O_6 + 4NO_3^- + 4H^+ \rightarrow 5CO_{2(g)} + 7H_2O_{(l)} + 2N_{2(g)} \tag{7.8}$$

Denitrification typically occurs under strictly anaerobic conditions or under low-oxygen partial pressures.

Example 7.3

(a) Establish the half-reactions in equation 7.5

(b) Determine the number of electrons transferred

(c) Determine $\Delta E^{0'}$ of the reaction.

(d) Based on information on Table 7.5, determine $E^{0'}$ for the oxidation of NH_4^+

$$NH_4^+ + 1.5O_{2(g)} \rightarrow NO_2^- + 2H^+ + H_2O_{(l)} \qquad \Delta G^{0'} = -277.2 \text{ kJ/mol}$$

Answer

(a) $2H_2O + NH_4^+ \rightarrow NO_2^- + 8H^+ + 6e^-$

$6e^- + 6H^+ + 1.5O_2 \rightarrow 3H_2O$

(b) $6e^-$

(c) $\Delta G^{0'} = -nF\Delta E^{0'}$

$\Delta E^{0'} = -\Delta G^{0'}/nF$

$\Delta E^{0'} = -277.2 \text{ kJ/mol}/(-6)(96.496 \text{ kJ/V mol})$

$\Delta E^{0'} = 0.478\text{V}$

(d) According to Table 7.5:

${}^1/_2O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad E^{0'} = 0.816\text{ V}$

$\Delta E^{0'} = E^{0'}_{\text{ox}} - E^{0'}_{\text{red}}$

$E^{0'}_{\text{ox}} = \Delta E^{0'} + E^{0'}_{\text{red}}$

$E^{0'}_{\text{ox}} = 0.478 + 0.816 = 1.294\text{ V}$

Example 7.4 Determine the oxidation number of nitrogen in each species of the sequence 7.7.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Answer

$+5 \rightarrow +4 \rightarrow +2 \rightarrow +1 \rightarrow 0$

Because different environmental conditions favor specific nitrogen-cycling processes, there is a spatial zoning of cycles. Nitrogen fixation occurs both in surface and in subsurface habitats, whereas nitrification exclusively occurs in aerobic habitats, and denitrification predominates in waterlogged soils and anaerobic aquatic sediments. The cycling of nitrogen within a given habitat also exhibits seasonal fluctuations because cyanobacteria bloom during spring and fall, and consequently the rates of nitrogen fixation in aquatic habitats increase.

7.4.6 Sulfur Cycle

Sulfur, a reactive element with stable oxidation states ranging from −2 to +6, is among the 10 most abundant elements in the Earth's crust. In living organisms, sulfur occurs mainly as sulfhydryl groups in amino acids and their polymers. At an approximate average concentration of 520 ppm, it rarely becomes a limiting nutrient.

In its fully oxidized state, sulfur exists as sulfate. Sulfate is the second most abundant anion in seawater, and the SO_4^{2-} in marine environments represents a large, slowly cycled sulfur reservoir.

Living and dead organic matter compose a smaller, more rapidly cycled sulfur reservoir. Largely inert sulfur reservoirs include metal sulfides in rocks, elemental sulfur deposits, and fossil fuels.

In soil, 90% of the sulfur present is organic: 50% is C–O–S linkages (sulfate esters), 20% is S-amino acids, and 20% as a wide range of different sulfur compounds. See Figure 7.7.

7.4.6.1 Sulfur Mineralization

Organosulfur decomposition in soils and sediments yields mercaptans and H_2S. Analogous to ammonification, this process is referred to as *desulfurization.*

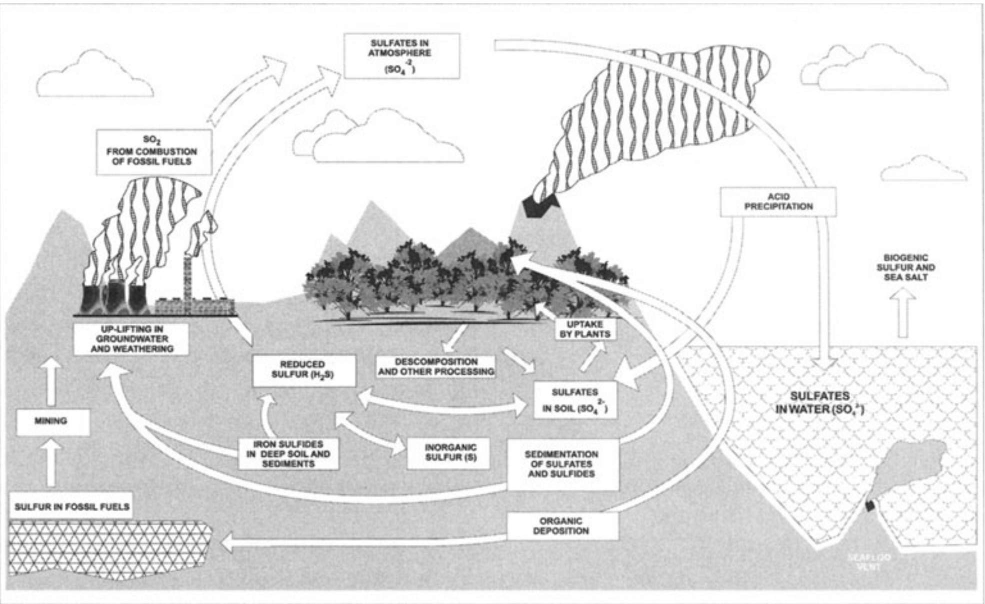


FIGURE 7.7. The sulfur cycle.

$HS\text{-}CH_2\text{-}CHNH_2\text{-}CO_2H$ (cysteine)

↓

$NH_3 + HS\text{-}CH_2\text{-}CO\text{-}CO_2H$ (β-mercaptopyruvic acid)

↓

$H_2S + CH_3\text{-}CO\text{-}CO_2H$ (pyruvic acid)

FIGURE 7.8. The degradation of cysteine.

So, as with nitrogen, these organic sulfur compounds are returned to the land or water after the plants die or are consumed by animals. As an example, consider the degradation of cysteine shown in Figure 7.8.

The H_2S and NH_3 are released into the atmosphere, contributing to the characteristic smell associated with putrefaction.

In the marine environment, a major decomposition product of organosulfur is dimethylsulfide (DMS). This product originates from dimethylsulfoniopropionate, a major metabolite of marine algae that may have a role in osmoregulation. The volatile DMS escapes from the oceans; according to some estimates, 90% of the total sulfur flux from the marine environment to the atmosphere occurs in the form of DMS. Another major product is H_2S. Once they escape to the atmosphere, DMS, H_2S and mercaptans are subject to photooxidative reactions that ultimately yield sulfates. H_2S also reacts directly with O_2 in the atmosphere.

If H_2S does not escape into the atmosphere, it may be subject to microbial oxidation under aerobic conditions. Alternatively, it may undergo phototrophic oxidation under anaerobic conditions, where sulfate as well as elemental sulfur may serve as electron acceptors while organic substrates are oxidized.

7.4.6.2 Oxidation of Sulfide and of Elemental Sulfur

In the presence of oxygen, reduced sulfur compounds can support chemolithotrophic microbial metabolism. Some examples are given below.

Beggiatoa, Thioploca, Thiothrix, and the thermophilic *Thermothrix* are filamentous, microaerophilic bacteria capable of oxidizing H_2S according to the equation:

$$H_2S_{(g)} + {}^1\!/_2O_{2(g)} \rightarrow S_{(s)} + H_2O_{(l)} \qquad \Delta G^{0'} = -210.4 \text{ kJ/mol} \tag{7.9}$$

Other *Thiobacillus* produce sulfate from the oxidation of elemental sulfur and other inorganic sulfur compounds:

$$S_{(s)} + 1.5O_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_4 \qquad \Delta G^{0'} = -629.2 \text{ kJ/mol} \tag{7.10}$$

Thiobacillus are acidophilic (they grow well at pH 2–3). They are obligate chemolithotrophs that obtain their energy exclusively from the oxidation of inorganic sulfur, and their carbon from the reduction of carbon dioxide. Most *Thiobacillus* are obligate aerobes, requiring O_2 for the oxidation of the inorganic sulfur compounds.

Thiobacillus denitrificans, however, can utilize nitrate ions as terminal electron acceptors in the oxidation of inorganic sulfur compounds:

$$5S_{(s)} + 6NO_3^- + 2H_2O_{(l)} \rightarrow 5SO_4^{2-} + 3N_{2(g)} + 4H^+ \tag{7.11}$$

Sulfur oxidation produces substantial amounts of H_2SO_4. The resulting acidification can lead to solubilization of phosphorus and other mineral nutrients in soils with a generally beneficial effect on both microorganisms and plants.

Hydrogen sulfide is also subject to phototrophic oxidation in anaerobic environments. The photosynthetic sulfur bacteria *Chromatiaceae, Ectothiorhodospiraceae*, and *Chlorobiaceae* can photoreduce CO_2 while oxidizing H_2S to S, in a striking analogy with the photosynthesis of eukaryotes:

$$CO_{2(g)} + H_2S_{(g)} \rightarrow \text{carbohydrate} + S_{(s)} \tag{7.12}$$

The chemoautotrophic fixation of CO_2 connected with this activity, only minimally contributes to the carbon cycling in most ecosystems. Notable exceptions to this include the deep-sea hydrothermal vent ecosystems, where the whole vent community is supported by the chemoautotrophic oxidation of reduced sulfur, primarily by *Beggiatoa, Thiomicropira*, and other sulfur oxidizers. In environments other than these, the generation of reduced minerals used in chemolithotrophic production is directly tied to the oxidation of photosynthetically produced organic matter. Therefore, sustainable primary production without solar energy input is unthinkable even in the case of chemolithotrophs.

7.4.6.3 Dissimilatory Sulfate or Sulfur Reduction

The sulfur- and sulfate-reducing microorganisms represent a large and diverse group that is strictly anaerobic. Most are eubacteria, but several archaea that reduce sulfur have also been described.

The analogy between H_2O and H_2S in oxygenic and anaerobic phototrophy, respectively, was pointed out above. Interestingly, elemental sulfur can be used in respiratory processes. *Desulfuromonas acetoxidans* grow on acetate, anaerobically reducing stoichiometric amounts of S to H_2S:

$$CH_3COOH + 2H_2O_{(l)} + 4S_{(s)} \rightarrow 2CO_{2(g)} + 4H_2S_{(g)} \quad \Delta G^{0'} = -23.9 \text{ kJ/mol} \tag{7.13}$$

They occur in anaerobic sediments rich in sulfide and elemental sulfur, and live syntrophically with the phototrophic green sulfur bacteria (*Chlorobiaceae*) that photooxidize H_2S to S and excrete sulfur extracellularly. *Desulfuromonas* regenerate H_2S by sulfur respiration, using, at least in part, organic matter leaked by *Chlorobium* cells.

From submarine hydrothermal vent environments, extremely thermophilic anaerobic archaea are capable of sulfur respiration with hydrogen gas:

$$H_{2(g)} + S_{(s)} \rightarrow H_2S_{(g)} \tag{7.14}$$

When obligate anaerobic bacteria carry out dissimilatory sulfate reduction, they are referred to as *sulfate reducers* or *sulfidogens.* The traditional sulfate-reducing genera are *Desulfovibrio* and *Desulfotomaculum.* Sulfate reduction results in the production of hydrogen sulfide:

$$4H_{2(g)} + SO_4^{2-} \rightarrow H_2S_{(g)} + 2H_2O_{(l)} + 2OH^- \tag{7.15}$$

Typical habitats are anoxic sediments or bottom waters of freshwater, marine, or hypersaline aquatic environments; thermophilic species occur in hot springs and submarine hydrothermal vents.

In soils that become deficient in oxygen, usually as a result of flooding, the sulfide level will increase to relatively high concentrations. The formation of sulfide by sulfate reduction in nature is enhanced in warm, wet, or waterlogged soils with a pH above 6.0. Sulfide accumulation may be particularly pronounced in sulfate-rich saline areas in which plant excretions (release of carbon compounds) serve as the oxidizable carbon source, in addition to the hydrogen. Thus, like denitrification, an oxidizable carbon source serves as the electron donor, while the sulfate serves as the electron acceptor.

Only a few compounds can serve as electron donors for sulfate reduction. The most common are pyruvate, lactate, and molecular hydrogen. Sulfate reduction is inhibited by oxygen, nitrate, or ferric ions and its rate is carbon-limited. Some bacteria are facultative chemolithotrophs as they can mixotrophically grow on acetate, CO_2, and H_2.

The production of even small amounts of hydrogen sulfide by sulfate reducers can have a marked effect on populations within a habitat. Since it is extremely toxic to aerobic organisms because of its affinity for Fe in the cytochrome systems, hydrogen sulfide can kill for example nematodes and plants.

7.4.6.4 Assimilatory Sulfate Reduction or Sulfur Immobilization

In contrast to the specialized dissimilatory sulfate reducers, many organisms (humans as well) are capable of assimilatory sulfate reduction. This process, which requires chemical energy in the form of ATP and a series of transfer reactions, can occur anaerobically and aerobically. It produces low concentrations of hydrogen sulfide that are immediately incorporated into organic compounds. Many microbes, plants, and animals have such a metabolic ability.

7.4.7 Phosphorus Cycle

Phosphorus is essential to all living systems. Within biological systems the most abundant forms of phosphorus are phosphate diester bonds, which form the links within nucleic molecules. Phosphate is an indispensable portion of the ATP molecule. The hydrolysis of phosphate from ATP to ADP forms the basis of most energy transfer reactions within biological systems. Phospholipids and sugar phosphates are constituents of all living cells.

However, phosphorus is not abundant in the biosphere and it often limits microbial growth. The availability of this element is restricted by its tendency to precipitate in the presence of several polyvalent metal ions at neutral to alkaline pH. Large, slowly cycled phosphate reservoirs occur in marine and other aquatic sediments, whereas small, actively cycled reservoirs comprise dissolved phosphate in soils and waters, as well as phosphate in living and dead organic matter. A largely inert reservoir is phosphate rock, such as apatite, $Ca_5(PO_4)_3(OH, F, Cl)$.

The microbial cycling of phosphorus does not alter its oxidation state. Most phosphorus transformations mediated by microorganisms can be viewed as inorganic to organic phosphate transfers or as transfers of phosphate from insoluble, immobilized forms to soluble or mobile compounds. Various microorganisms have evolved transport systems for the regulated acquisition of phosphate from the environment.

As phosphates are combined with calcium in many habitats, this renders them insoluble and thus makes them unavailable to plants and many microorganisms. Some heterotrophic microorganisms can solubilize phosphates from such sources. The mechanism for phosphate solubilization normally takes place through the production of organic acids. Some chemolithotrophic microorganisms such as *Nitrosomonas* and *Thiobacillus* mobilize inorganic phosphates by producing nitrous and sulfuric acids, respectively. Phosphate also exists within soils as the insoluble iron, magnesium, or aluminum salts.

Solubilization of insoluble ferric phosphates may occur when microorganisms reduce ferric ions to ferrous ions under anaerobic conditions.

Plants and microorganisms can take up soluble forms of inorganic phosphates readily and assimilate them into organic phosphates. Heterotrophs (animals) obtain their phosphorous from the plants they eat, although one type of heterotroph, the fungi, excels at taking up phosphorous and may form mutualistic symbiotic relationships with plant roots. These relationships are called *mycorrhizae*; the plant gets phosphate from the fungus and gives the fungus sugars in return. Animals may also use phosphorous as a component of bones, teeth, and shells. When animals or plants die (or when animals defecate), the phosphate may be returned to the soil or water by the decomposers. There, it can be taken up by another plant and used again.

This cycle will occur over and over until at last the phosphorous is lost at the bottom of the deepest parts of the ocean, where it becomes part of the sedimentary rocks forming there. Ultimately, phosphorous will be released if the rock is brought to the surface and weathered. Marine birds play a unique role in the phosphorous cycle, as they take phosphorous-containing fish out of the ocean and return to land, where they defecate. Their guano contains high levels of phosphorous and in this way marine birds return phosphorous from the ocean to the land. See Figure 7.9.

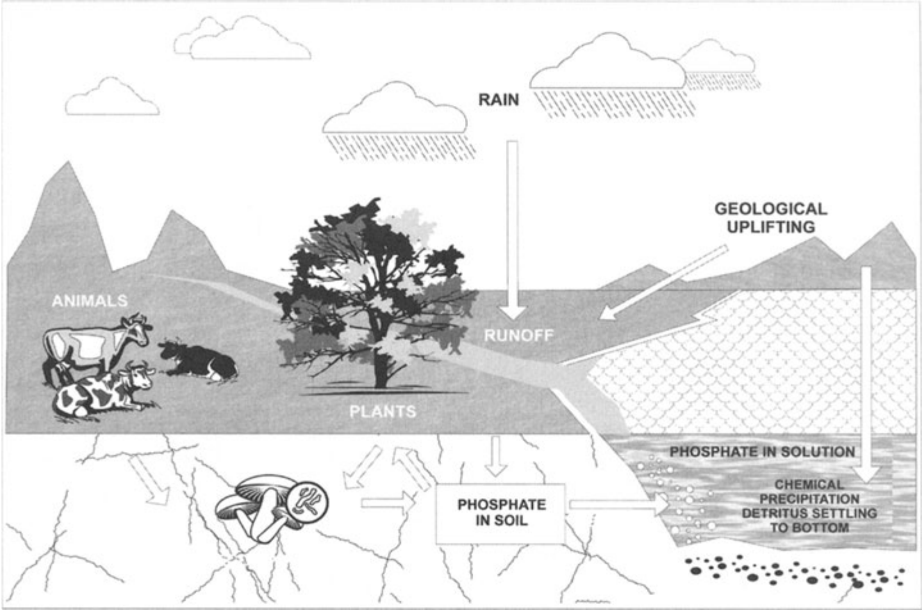


FIGURE 7.9. The phosphorous cycle.

7.4.8 Iron Cycle

Even though iron is the fourth most abundant element in the Earth's crust, only a small portion is available for biogeochemical cycling which consists largely of oxidation–reduction reactions of ferric to ferrous ions and vice versa. These reactions are important in organic and inorganic iron-containing compounds.

As discussed in Chapter 5, ferric and ferrous ions have very different solubility properties. Ferric ions precipitate in neutral to alkaline environments as ferric hydroxide, and under anaerobic conditions they may be reduced to the more soluble ferrous form. However, under certain anaerobic conditions enough H_2S may be present so as to precipitate iron as ferrous sulfide.

In organic compounds, iron is often attached to organic ligands by chelation and, thereby, it can undergo oxidation–reduction transformations that are utilized in electron-transport processes. Cytochromes in electron-transport chains contain chelated iron that undergoes such redox transformations.

Virtually all microorganisms—with the exception of certain lactobacilli— require iron as cofactor of many metabolic enzymes and regulatory proteins because of its ability to exist in two stable oxidation states. Although iron is one of the most abundant elements in the environment, it is often a limiting factor for bacterial growth. This is so because of the formation of insoluble ferric hydroxide complexes under aerobic conditions at neutral pH, which impose severe restrictions on the availability of the element. Consequently, bacteria have evolved specialized high-affinity transport systems in order to acquire sufficient amounts of this essential element.

Most bacteria have the ability to produce and secrete molecules—called *siderophores*—to fulfill their iron requirements. Siderophores are special iron-chelating agents that facilitate iron solubilization and uptake. They are water-soluble, low-molecular weight molecules that bind ferric ions strongly. The ability of bacteria to utilize siderophores is associated with the presence of transport systems that can recognize and mediate uptake of the ferric–siderophore complexes into the cell. These iron-acquisition systems are regulated in response to iron availability, and their action thus increases under iron limitation conditions.

As discussed in Chapter 2, iron forms a variety of oxidized or reduced compounds in a given environment depending on the pH and redox potential, which leads to a heterogeneous distribution of various iron-containing compounds. Under conditions ranging from alkaline to neutral, ferrous iron is inherently unstable in the presence of O_2 as it is spontaneously oxidized to ferric ion. In such conditions, microorganisms have little chance to extract energy from the oxidation processes. Under acidic conditions in oxygenated environments, however, ferrous iron is relatively stable and acidophiles such as *Thiobacillus ferroxidans, Leptospirillum ferroxidans*, and some strains of *Sulfolobus acidocaldarius* are capable of producing the chemolithotrophic oxidation of ferrous iron:

$$2Fe^{2+} + \frac{1}{2}O_{2(g)} + 2H^+ \rightarrow 2Fe^{3+} + H_2O_{(l)} \tag{7.16}$$

With the exception of *L. ferroxidans*, the same microorganisms can also oxidize sulfur compounds.

There are also non-acidophilic iron bacteria, such as the prosthecates *Hyphomicrobium,*

Example 7.5

Determine the $\Delta G^{0'}$ of reaction 7.16.

Answer

According to Table 7.5:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad E^{0'} = 0.816$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E^{0'} = 0.771$$

and:

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad E^{0'} = -0.771$$

$$E^{0'} = 0.816 - 0.771 = 0.045V$$

$$\begin{aligned}\Delta G^{0'} &= -nF\Delta E^{0'} \\ &= -2(96.496 \text{ kJ V/mol})(0.045V) \\ &= -8.68 \text{ kJ/mol}\end{aligned}$$

Pedomicrobium, and *Planctomyces*, and the filamentous *Sphaerotilus* and *Leptothrix* that derive energy from ferrous iron oxidation. The activity of iron-oxidizing bacteria can lead to substantial iron deposits; most iron in the biosphere exists in the oxidized state. Where anaerobic conditions are created as a result of limited oxygen diffusion and vigorous heterotrophic microbial activity—as in the hypolimnion of stratified lakes, waterlogged soils, and aquatic sediments—ferric ion may act as an electron sink and become Fe^{2+}. A large heterogeneous group of heterotrophic bacteria, comprising *Bacillus*, *Pseudomonas*, *Proteus*, *Alkaligens*, *Clostridia*, and *Enterobacteria*, are thought to be involved in iron reduction. Magnetite (Fe_3O_4) and siderite ($FeCO_3$) are the major end products of Fe(III) reduction.

7.4.9 Interrelations Among Cycles

Biogeochemical cycles interact with each other extensively in space and time. This is true not only for C, H, and O, which are cycled by the same two processes of photosynthesis and respiration, but also for cycles that are driven by different biochemical processes and performed by distinct microorganisms.

The reductive portions of the N, S, and Fe cycles are driven by chemical energy fixed in organic substances during photosynthesis. The chemolithotrophic reoxidation of N, S, and Fe is, in turn, linked to the conversion of CO_2, into cell material, again involving the cycling of C, H, and O. This is shown in Figure 7.10.

Solubilization, uptake, and precipitation of Ca and Si are directly (or at least energetically) linked to the photosynthetic and respiratory cycling of C, H, and O. Acids from nitrification and sulfur oxidation aid phosphorus mobilization; photosynthesis or respiration is required for the uptake and conversion of phosphorous into high-energy phosphate. Sulfur is oxidized (with the concomitant reduction of nitrate) by *Thiobacillus denitrificans*; likewise, some extremely thermophilic methanogens can transfer hydrogen not only to CO_2, but also to S. These are a few examples of interrelations involved in biogeochemical cycles.

Under each given set of circumstances, the process that allows for the maximal energy flow is selected. Many of the biogeochemical cycling reactions of individual elements are actually connected by factors such as redox potentials. Individual minerals are oxidized only at specific redox potentials. This leads to zonations in soil and aquatic environments where minerals accumulate in specific chemical forms and where specific microbial populations proliferate.

From the pool of potential electron acceptors, microorganisms within a given community use the specific electron acceptor that they are genetically capable of using, which yields the maximum energy from the available substrate. Each electron acceptor is utilized at a different redox potential, which is in part due to metabolic regulation within a single population and, to some degree, due to competition between populations with diverse metabolic capabilities. Through various regulatory mechanisms, facultatively anaerobic microorganisms shut

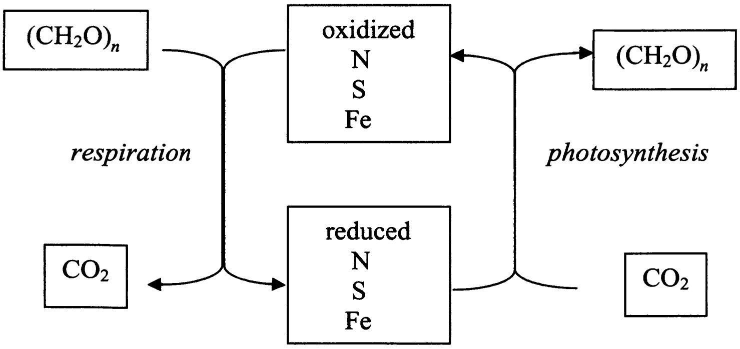


FIGURE 7.10. Interrelations among cycles.

TABLE 7.6. Relative energy yield of electron acceptors (AH_2 is an oxidizable substrate)

Type of metabolism	Schematic reaction (not balanced)	Energy yield
Aerobic	$AH_2 + O_2 \rightarrow CO_2 + H_2O$ + energy	decreasing energy ↓
Anoxic	$AH_2 + NO_3^- \rightarrow N_2 + H_2O$ + energy	
Facultative-anaerobic	$AH_2 + SO_4^{2-} \rightarrow H_2S + H_2O$ + energy	
	$AH_2 + CO_2 \rightarrow CH_4 + H_2O$ + energy	

off their less efficient fermentative or dissimilatory nitrate reduction pathways in the presence of dioxygen. In the absence of oxygen or Fe(III), the most oxidizing electron acceptor is NO_3^-. From a substrate equally utilizable by nitrate and sulfate reducers, the former will obtain a higher energy yield and, therefore, will produce more biomass per unit of substrate utilization. Nitrate reducers also outdo the sulfate reducers because the latter have lower thresholds for carbon substrates.

Nitrate and iron are usually scarce in aquatic sediments and become rapidly depleted, leaving sulfate as the most oxidizing electron acceptor. When competing for a common substrate (i.e., H_2), methanogens have lower utilization efficiency and a higher threshold for hydrogen uptake than sulfate reducers. Consequently, methanogens cannot effectively compete with sulfate reducers until most of the sulfate (or all of it) is depleted. In low-sulfate freshwater sediments this occurs fairly rapidly; in sulfate-rich marine sediments, it occurs much more slowly.

The sequence of electron-acceptor utilization can be spatially observed in horizontal layers of increasing depth in aquatic water columns and sediments. In a typical littoral marine sediment, only the first few millimeters of the sediment are oxygenated and nitrate serves as the electron acceptor. Below this, for several meters, sulfate is the principal electron acceptor. Methanogenesis is usually confined to the sulfate-depleted deeper sediment layers; methane may diffuse upwards into the sulfate-reduction zone.

Hydrogenogens (i.e., hydrogen-producing fermentative microorganisms) are at thermodynamical disadvantage if hydrogen accumulates. They live syntrophically with *hydrogenotrophs* (i.e., hydrogen consumers such as sulfate reducers, methanogens and acetogens) and supply them with the hydrogen necessary for SO_4^{2-} or CO_2 reduction, respectively. Most of the H_2-dependent methanogenesis in these ecosystems occurs via interspecies hydrogen transfer.

Then, electron acceptors are sequentially used in the following general descending order: dissolved dioxygen, nitrate, sulfate, and carbon dioxide. Therefore, hydrogen sulfide formation follows nitrate reduction but precedes methane production as shown in Table 7.6.

Due to the lack of electron acceptors in anaerobic decompositions, the low energy yield per unit of substrate is a limiting factor that results in the incomplete breakdown of the substrate. Metabolism and synthesis cease when the supply of biologically available energy is exhausted. On the other hand, biologically available carbon is the limiting factor in aerobic metabolisms, with no shortage of electron acceptors because of the abundance of dioxygen. However, the supply of carbon-containing substrates is rapidly exhausted because of carbon dioxide metabolism and organic synthesis.

Related Experiment in the Companion Book

22. Microorganisms in soil, water and air

Additional Related Experiments/Activities

Andino, J. M.; Wallington, T. J.; Hurley, M. D.; Wayne, R. P. "A Classroom Demonstration of the Formation of Aerosols from Biogenic Hydrocarbons," *J. Chem. Educ.* **2000**, *77*, 1584–1586.

Norman, J.; Cedergren, H. "Phosphorus Cycling—An Ecology Experiment," *J. Coll. Sci. Teach.* **1987**, *16*, 529–531.

Pepper, I.; Gerba, C. *Environmental Microbiology: A Laboratory Manual*, 2nd ed.; Academic Press: San Diego, 2005.

- Experiment 1: Dilution and Plating of Bacteria and Growth Curves
- Experiment 2: Soil Moisture Content Determination, Examination of Soil Microorganisms via Microscopic and Cultural Assays
- Experiment 3: Contact Slide Assay
- Experiment 4: Filamentous Fungi
- Experiment 5: Bacteria and Actinomycetes
- Experiment 6: Algae: Enumeration by MPN Microbial Transformations and Response to Contaminants
- Experiment 7: Oxidation of Sulfur in Soil
- Experiment 8: Dehydrogenase Activity of Soils
- Experiment 9: Nitrification and Denitrification
- Experiment 10: Enrichment and Isolation of Bacteria that Degrade 2, 4- Dichlorophenoxyacetic acid
- Experiment 11: Adaptation of Soil Bacteria to Metals
- Experiment 12: Biodegradation of Phenol Compounds
- Experiment 13: Assimilable Organic Matter
- Experiment 14: Biochemical Oxygen Demand, Water Microbiology
- Experiment 15: Membrane Filter Technique
- Experiment 16: Bacteriological Examination of Water: the Coliform MPN Test
- Experiment 17: Detection of Bacteriophages
- Experiment 18: Film Medium for the Detection of Coliforms in Water, Food, and on Surfaces
- Experiment 19: Defined Substrate Technology for the Detection of Coliforms and Fecal Coliforms, Advanced Topics
- Experiment 20: Detection of Enteric Viruses in Water
- Experiment 21: Detection of Waterborne Parasites
- Experiment 22: Kinetics of Disinfection
- Experiment 23: Aerobiology: Sampling of Airborne Microorganisms
- Experiment 24: Detection and Identification of Bacteria via PCR and Subsequent BLAST Analysis of Amplified Sequences

Piedrahita, R. H. "Biology in Aquacultural Engineering Instruction," *Proc. Ann. ASEE Conf.* **1995**, *2*, 2529–2533. Anaheim, CA, USA, Jun. 25–28, 1995.

Schmitz, R. A. "The Earth's Carbon Cycle: Chemical Engineering Course Material," *Chem. Eng. Educ.* **2002**, *36*, 296–303.

Shmaefsky, B. R. "Using Elodea as a Live Model of the Eukaryotic Cell," *J. Coll. Sci. Teach.* **2003**, *Dec.*, 52–55.

Watson, J. "How to Collect and see the Microbial Community that Fixes Iron and Maganese in the Natural Environment," U.S. Geological Survery, Department of Interior. http://pubs.usgs.gov/gip/microbes/

References and Further Reading

Alexander, M. *Biodegradation and Bioremediation*; Academic Press: San Diego, CA, 1994.

Atlas, R. M.; Barths, R. *Microbial Ecology. Fundamentals and Applications*; Benjamin Cummings: San Francisco, CA, 1998.

Biology Daily. The Biology Encyclopedia. http://www.biologydaily.com/biology/upload/thumb/3/37/340px-PhylogeneticTree.jpg

Chasteen, T. G.; Bentley, R. "Volatile Organic Sulfur Compounds of Environmental Interest: Dimethyl Sulfide and Methanethiol. An Introductory Overview," *J. Chem. Educ.* **2004**, *81*, 1524–1528.

Doolittle, W. F., Canadian Institute for Advanced Research, Dept. of Biochemistry and Molecular Biology, Dalhousie University, Halifax, Nova Scotia, Canada. "Phylogenetic Classification and the Universal Tree." http://cas.bellarmine. edu/tietjen/Ecology/phylogenetic_classification_and_.htm

Gura, T. "Bones, Molecules... or Both?", *Nature* **2000**, *406*, 230–233.

Khan, H. R.; Adachi, T. "Soil Acidity and its Impact on Acidic-Basic Cations in Recent Sediments as Influenced by Micro-Organisms and Water Contents," *Proc. 1st Int. Conf. Environ. Eng. Educ. Train. (EEET'96)*. Southampton, UK, Apr. 17–19, 1996, pp. 197–206.

Levine, J. S.; Miller, K. R. *Biology: Discovering Life*; D. C. Health: Canada, 1994. p. 711.

Maier, R. M.; Pepper, I. L.; Gerba, C. P. *Environmental Microbiology*; Academic Press: San Diego, CA, 2000.

Margulis, L.; Matthews, C.; Haselton, A. *Environmental Evolution. Effects of the Origin and Evolution of Planet Earth*; The MIT Press: Cambridge. MA, 2000.

Martin, W.; Embley, T. M. "Early Evolution Comes Full Circle," *Nature* **2004**, *431*, 134–135.

Marietta College, Biology. Environmental Biology—Ecosystems. http://www.marietta.edu/~biol/102/ecosystem.html

Nevel, J. B.; Wright, R. T. *Environmental Science. Toward a Sustainable Future*, 8th ed.; Prentice Hall: Upper Saddle River, NJ, 2002.

Nisbet, E. "The Realms of Archaean Life," *Nature* **2000** *405*, 625–626.

Reeburgh, W. S. Department of Earth System Science, University of California, Irvine. "Figures Summarizing the Global Cycles of Biologically Active Elements." http://www.ess.uci.edu/~reeburgh/figures.html

Scheffe, M; Carpenter, S.; Foley, J. A.; Folke, C.; Walker, B. "Catastrophic Shifts in Ecosystems," *Nature* **2001**, *413*, 591–596.

Stern, D. I. "Global Sulfur Emissions from 1850 to 2000," *Chemosph.* **2005**, *58*, 163–175.

Talaro, K. P.; Talaro, A. *Foundations in Microbiology*; McGraw-Hill College: New York, 1999. p. 22.

University of Florida, Dept. of Agricultural and Biological Engineering. http://www.agen.ufl.edu/~chyn/age2062/lect/lect_19/5kingdms.gif

Whitfield, J. "Born in a Watery Commune," *Nature* **2004**, *427*, 674–676.

Wilkinson, D. "At Cross Purposes", *Nature* **2001**, *412*, 485.

Williams, R. J.; Fraústo da Silva, J. J. "The Trinity of Life: Genome, the Proteome, and the Mineral Chemical Elements," *J. Chem. Educ.* **2004**, *81*, 738–749.

Yarnell, A. "Defining Life's Limits," *Chem. Eng. News*, April 4, 2005, pp. 60–63.

Part 3

Effects, Treatment and Prevention of Pollution

8

Effects of Pollutants on the Chemistry of the Atmosphere, Hydrosphere, and Lithosphere

In this chapter we present the main types of useful chemical substances, contaminants, pollutants, and wastes, and give an overview of their key undesirable effects upon the atmosphere, hydrosphere, and lithosphere. In the following chapter, we will deal with their effects on live organisms. The unavoidable overlap with other chapters is addressed in the form of references to the sections where a specific theme is further discussed.

8.1 Importance of the Manufacture and Use of Chemical Substances

Production processes typically depend on materials and substances derived from the chemical industry, which in turn relies on chemical feed stocks. To give an idea of the importance of chemical trade, the United States exports and imports are both on the order of \$$10^{11}$ USD per year. A list of the most important organic and inorganic chemicals is given in Table 8.1.

Key uses for the chemicals described in Table 8.1 include the manufacture of plastics, resins, synthetic rubber and fibers, agricultural chemicals (e.g., fertilizers and pesticides), dyes and pigments, pharmaceuticals and medicines, soap, cleaning compounds and toiletries, and paints and coatings. Table 8.2 gives examples of the production of some of these goods.

8.2 Sources of Chemical Substances as Contaminants and Pollutants

(a) Natural types and sources of pollutants

Nature may be responsible for generating pollutants when natural substances are liberated in amounts that can harm health or cause alterations in ecosystems. This is the case with volcanic eruptions that generate abnormal levels of particles and gases in the atmosphere. Processes such as wind erosion and natural anaerobic processes (involving the production of CO_2, CH_4, and H_2S) may also contribute to abnormal levels of natural substances. Other examples include:

- The contribution of non-methane volatile organic compounds (VOCs) to the atmosphere due to the liberation of volatile phytochemicals.
- The production of NOx and O_3 by lightning.
- The liberation of Rn gas from the lithosphere.
- The action of termites, organic matter decay, geological activity, and biogenic processes.

The majority of natural contributions to pollution (including particles, aerosols, VOCs, and inorganic gases) strongly influence air composition. They make an impact on the hydrosphere generally through the dissolution of substances produced by dry or wet deposition, or by the transport of sediments resulting from runoff or river drainage.

TABLE 8.1. Production of key organic and inorganic chemicals

ORGANICS	Relative production (by weight)*	INORGANICS	Relative production (by weight)*
Ethylene	100	Sulfuric acid	100
Propylene	60.6	Phosphoric acid (as P_2O_5)	29.6
Ethylene dichloride	43.5	Chlorine	28.8
Urea	26.7	Ammonia	28.8
Ethylbenzene	24.3	Sodium hydroxide	23.4
Styrene	22.5	Nitric acid	17.2
Ethylene oxide	15.9	Ammonium nitrate	15.3
Cumene	14.8	Hydrochloric acid	11.0
1,3-Butadiene	8.3	Ammonium sulfate	6.7
Acrylonitrile	6.5	Titanium dioxide	3.8
Vinyl acetate	5.7	Aluminum sulfate	2.5
Aniline	4.2	Sodium chlorate	1.8
Benzene	3.6	Sodium sulfate	1.3

INORGANIC GASES	Relative production (by volume)**
Nitrogen	100
Oxygen	73.3
Hydrogen	53.3

*Data for U.S. production in 2003. The average annual net production of sulfuric acid is approximately 40 × 10^6 tons (metric). The production ratio of sulfuric acid to ethylene (by weight) is typically 1.6 to 1.

**The annual production of each gas is given relative to that of nitrogen (approximately 3 × 10^{10} cubic meters). (Source: *Chem. Eng. News*, July 5, 2004.)

(b) Anthropogenic types and sources of pollutants

As the use of synthetic chemicals increased dramatically after World War II, their possible adverse effects on human health and the environment also increased. As a consequence, the air we breathe, the water we drink and bathe in, the soil in which our crops are grown, and the environments in which populations of animals and plants thrive are often contaminated to different extents with a variety of synthetic chemicals, heavy metals, and/or radionuclides.

TABLE 8.2. Examples of production of goods derived from the chemical industry

Products	Millions of tons (metric)*
PLASTICS AND SYNTHETIC RUBBER	
Thermoplastic resins	35.2
Thermosetting resins	3.7
Rubber	2.2
SYNTHETIC FIBERS	
Non-cellulosic fibers	3.9
Cellulosic fibers	0.1
FERTILIZERS	
Phosphate products	58.3
Nitrogen products	28.4
Potash products	1.4
*PAINTS AND COATINGS***	
Architectural	3.0
Products for manufacturers	1.5
Special purpose	0.7

*U.S. production in 2003.

**In 10^9 liters. (Source: *Chem. Eng. News*, July 5, 2004.)

The main sources of anthropogenic pollutants derive from the following human activities:

- Industrial processes
- Agricultural practices
- Energy-related activities (mainly transportation and combustion)
- Resource exploitation
- Urban refuse

Such pollutants typically involve

- Substances deliberately or inadvertently discharged into waters or soils following their intended use
- Substances generated during water treatment operations

TABLE 8.3. EPA's conventional and non-conventional pollutant categories (code of Federal Regulations, Title 40)

Conventional	Non-conventional
Biochemical oxygen demand	Ammonia
Total suspended solids	Chromium (VI)
Oil and grease	Chemical oxygen demand
pH	COD/BOD_5
	Fluoride
	Manganese
	Nitrate
	Organic nitrogen
	Pesticide active ingredients
	Phenols
	Phosphorus
	Total organic carbon

- Byproducts of manufacturing operations that do not use waste treatment facilities
- Wastes that are inadequately treated
- Derivatives of synthetic substances produced by reactions in the environment
- Consumer products that are discarded as waste after use

Many of these substances are exemplified in Tables 8.3 and 8.4.

The substances in Table 8.4 are not normally found alone in the environment but rather in simple or complex mixtures. These mixtures may be associated with the release, storage, or transport of chemicals in surface or groundwater, waste-treatment systems, soils, or sediments. Although many of these chemicals are either consumed or destroyed, a significant portion find their way into the air, waters and soils far away from their original discharge sites.

The major polluters in industrialized countries are typically the

- Electric utilities
- Metal mining corporations
- Chemical and petroleum industries
- Agro and food industries

The first three together contribute around two-thirds of the total toxic releases. Air emissions alone involve more than 3×10^5 tons per year. In the same vein, approximately 10^6 tons of petroleum are released annually into the oceans due to natural seeps, or extraction–transportation–consumption processes.

(c) Point and non-specific (or multimedia) pollution sources

The environmental effects of pollutants and wastes have traditionally been confronted with actions at the immediate vicinity level. A typical example involves the emissions resulting from fossil fuel burning in industrial and power plants, where taller stacks were built in the past to disperse pollutants in the air (mainly sulfur oxides) in a more efficient way. However, it is now recognized that these oxides can have important effects even in regions far away from the emission source due to environmental transport phenomena. Consequently, increasing the height of the stacks did not solve the problem.

The boundary between the effects of *point sources* (i.e., localized discharges) and *non-point* or *non-specific sources* (*NPS*) to local and global pollution is becoming more and more blurred, and the latter sources have become more relevant due to the difficulty in evaluating and controlling them. Because local regulations are insufficient to tackle such overall problems, national, regional, and international regulations as well as other concerted efforts have become essential strategies.

Non-point specific pollution is caused, for example, by

- Runoff due to rainfall or melting snow that dissolves and transports pollutants as it moves
- Industrial diffuse or fugitive releases and leaks
- Accidental spills
- Atmospheric wet and dry deposition
- Local air contamination sources (e.g., forest fires and highly transited highways or streets)

The pollutants thus transported include fertilizers, pesticides, oil, grease, other organic and inorganic industrial chemicals, sediments, salts, acid mine drainage, nutrients, radionuclides, microorganisms, and noxious gases.

8.3 Transport, Mobility, and Partition of Pollutants

From the previous discussion it is clear that pollutants may be transported away from their sources by physical, chemical, or biological means, or a combination thereof. They may also accumulate in various media. Assessment of their chemical fate requires knowledge of many factors including those

TABLE 8.4. Main types and examples of anthropogenic pollutants

ORGANICS

Pesticides

These include herbicides for weed control, insecticides for insect control, and fungicides for fungi control. Chemically speaking, they typically belong to one of the following three groups: (a) chlorinated hydrocarbons, (b) organic phosphates, or (c) carbamates, as seen in the following list.

Herbicides (e.g., alachlor, atrazine, butachlor, cyanazine, and dioxin)

Insecticides (e.g., chlordane, dieldrin, heptachlor, and DDT)

Fungicides (e.g., quinones, dithiocarbamates, halogenated thiocarbamides, halogenated and nitrated benzenes, oxathines, benzoimidazoles and pyrimidines)

The most common pesticide used for many years was DDT. This was discussed briefly in Chapter 1 and it is discussed in more detail further ahead in Section 9.1.

Organic solvents and hydrocarbons (HC)

Organic solvents are derived mainly from petroleum and are widely used in industry to dissolve non-polar (or slightly polar) organic compounds for further processing or separation. Examples include the members of the BTEX family (benzene, toluene, ethylbenzene, and xylene), acetone, and chlorinated solvents (e.g., chloroform trichloroethylene and methylene chloride). These are all generally considered VOCs. They typically have low boiling points (also high vapor pressures at ambient conditions); therefore, they are partially transferred to the atmosphere. Another source of hydrocarbon pollution involves petroleum exploitation and processing, as well as incomplete combustion or oxidation of fossil fuels.

Polychlorinated organic compounds: polychlorinated biphenyls (PCBs), polychlorodibenzodioxins (PCDD), and polychlorodibenzofurans (PCDF)

Polychlorinated biphenyls (PCBs) are mixtures of biphenyls with 1 to 10 chlorine atoms per molecule. They are oily fluids with high boiling points, great chemical resistance, and low electrical conductivity, and have been used as plasticizers in polyvinyl polymers, insulators and coolants in transformers and heat exchange fluids. Dioxins and furans (see Section 9.1) are not produced intentionally but are derived from combustion processes of chlorinated aromatic hydrocarbons, pesticides and chlorinated solvents.

Trihalomethanes (THMs)

These halogenated organic substances (e.g., chloroform and carbon tetrachloride) are generated as disinfection byproducts from the use of chlorine in water treatment.

Polycyclic aromatic hydrocarbons (PAHs)

They are typically produced in coal furnaces, through petroleum use and exploitation, in tobacco smoke, and other sources. The most important examples are benzo(*a*)pyrene and cyclopenta(*cd*)pyrene.

Dyes, colorants, pigments, and paints

Modern commercialization strategies rely heavily on product appeal. Dyes and paints play a key role in luring consumers toward certain products. Unfortunately, production processes involving, for example, textile dyes, which are complex organic molecules (generally of difficult biodegradation and some even toxic, see Section 9.1.2), are intrinsically wasteful in the sense that a large percentage of the dye load is lost to the environment (typically in the dyeing bath). Paints generally have an organic synthetic resin and one or more solvents that are combined with a series of inorganic pigments. When applied, paints release solvents into the atmosphere and, when dry, they eventually degrade and/or erode, resulting in the release of dust particles.

Surfactants

Chemicals with surface activity are used for a myriad of applications, including detergents for household and industrial cleaning, and personal care products (e.g., soaps and shampoos). Large amounts of surfactants enter ecosystems through wastewaters. Detergents are formed by complex organic molecules with a series of additives. They originally consisted of highly branched organic compounds but, owing to their low biodegradability (see Section 9.1.2), they were replaced by the more linear compounds alkyl benzene sulfonates (LAS), even though some of the substances used in their production are environmentally problematic. Another former difficulty associated with detergents involved the use of polyphosphates as additives which, when discharged, enhanced eutrophication in water. Additives such as citrates may slowly replace phosphates.

Other industrial organics

Chlorofluorocarbons (CFCs) such as freons (e.g., CCl_2F_2 and CCl_3F) were traditionally used as propellants for different liquids and as refrigerants. Fortunately, their use has decreased dramatically owing to increased awareness of their negative effect on our planet's protective ozone layer (see Section 8.4.1.5).

Formaldehyde is used in the conservation of organs and in polymer preparation. It is toxic and its high vapor pressure makes it rather volatile.

Phenols are used, for example, in general disinfection and in the manufacture of resins, medicines, industrial organic compounds, and dyes.

TABLE 8.4. (*Continued*)

Monomers, plastics adhesives and resins are consequences of the production and use of polymers. They have a strong environmental impact in waters and soils due to their low biodegradability. It is very common to find plastic residues in marine sediments, soils, seashores, lakes, and rivers. Furthermore, some of the monomers used in their production are volatile and toxic (e.g., acrylamide, isocyanates, and vinyl chloride).

Paper, glass and other solid wastes (*i.e., trash*) are derived from urban activities. These products can usually be recycled.

Food wastes, human and animal detritus and waste, oxygen-demanding substances

These are simple or complex organic substances (e.g., carbohydrates, proteins and lipids derived from urban wastewater and agroindustrial discharges) which, when dissolved in water or present as highly concentrated colloids, strongly promote the lowering of the dissolved oxygen level, thus affecting the aquatic ecosystem. See Section 8.4.2. They can also be solid or semisolid wastes.

INORGANICS

Gases

They are used for chemical synthesis, water and waste treatment, disinfection, neutralizations, and the like. They can also be produced in atmospheric photochemical reactions and as undesirable products, for example, in the combustion of fuels and industrial processes. The most important inorganic gases are ammonia, carbon oxides, nitrogen oxides, ozone and sulfur oxides.

Metals and metal cations

Pb, Hg, As, Cd, Sn, Zn, and Cu are widely used in industry, particularly in metal-working and metal-plating processes, and in products such as batteries, electronic components, certain pesticides, and medicines. Owing to the brilliant colors of certain heavy metal compounds, they are also used in paint pigments, glazes, inks, and dyes.

Metalloids

Arsenic is an ubiquitous element in many ores and minerals. Toxic As_2O_3 is typically produced upon smelting them. Arsenic is used for example in the hardening of some metals and alloys, and in the production of some types of glass.

Selenium is found in the sulfide ores of many heavy metals. It is used for example in photographic baths, pigments, photocells, electronic devices, arc lights, rubber vulcanizing, and as a catalyst.

Acids and Bases

Acids and bases are among the most abundant industrial discharges. They may alter the pH of aquatic ecosystems and consequently the life of resident organisms.

Anions

Cyanide is produced mainly as a residue in the mining industry because it can selectively form stable complexes with certain metals. It is very toxic.

Perchlorate is produced mainly for military and construction applications owing to its explosive nature.

Chromate is derived from metal working and finishing, and from old tannery processes.

As will be discussed in Section 9.1.1, Cr(VI) is highly mobile and toxic.

Phosphates come from waste nutrients (see below) and cleaning products (see above).

Other important anions include F^-, Br^-, SO_4^{2-}, and Cl^- released from many industrial and agricultural processes. They are part of the salt pollution burden in the environment.

OTHER IMPORTANT POLLUTANTS

Nutrients

Nutrients are sources of N and P such as ammonia, nitrites, nitrates, orthophosphates, metaphosphates, and polyphosphates. They are present in fertilizers and are formed during biodegradation of organic matter in wastewater discharges or dead organic matter.

Particles, fumes, and dusts

These are produced, for example, during incomplete combustion processes, and mineral extraction and processing. They can be organic or inorganic, and can form aerosols in which hydrocarbons may be present (these hydrocarbons may have toxic effects). Examples include coal dust and asbestos.

Radionuclides

There are nearly 100 radioisotopes whose beta and/or gamma radiation is used in diagnosis, therapy, or research in nuclear medicine. As discussed in Chapter 3, radioactive decay kinetics enables dating of materials. Some of the radionuclides in the environment (e.g., ^{3}H, ^{85}Kr, and ^{14}C) are emitted in gaseous or liquid wastes during the processing and use of radioactive materials in nuclear reactors. ^{129}I is emitted during the nuclear fuel reprocessing. Others are emitted during the explosion of nuclear weapons and nuclear accidents (e.g., ^{137}Cs, ^{134}Cs, ^{90}Sr, and ^{99}Tc). Some other low-radiation products are intentionally used in consumer products such as ceramic glazes, or in luminous paints in timepieces and diverse indicator instruments.

Source: Rajeshwar and Ibanez, 1997.

mentioned below. (The corresponding characterization parameters are given in parentheses).

- Organic carbon water-partitioning at equilibrium (K_{oc})
- Chemical partitioning between soil and water (K_d)
- Partitioning between air and water (*Henry's law constant*, $K_{H,i}$)
- Solubility constant (K_{sp})
- Vapor pressures (p_i)
- Partitioning between water and octanol ($K_{o,w}$)
- Bioconcentration factors (see Section 9.5)

To understand the factors involving partitioning between one medium and another, one must understand the concept of *partition coefficient* which is of paramount importance. This is discussed next.

Partition or distribution coefficients

Environmental phenomena frequently involve the transfer of a substance, *i* (or solute) from one medium (*phase 1*) into another (*phase 2*). The amount transferred can be quantified by measuring the equilibrium concentration of *i* in both media (phases). If the overall attraction between *i* and *phase 1* is weaker than that between *i* and *phase 2*, the substance will prefer to be in *phase 2*. The resulting *distribution* or *partitioning* of *i* can be estimated quantitatively by defining a *partition or distribution coefficient* ($K_{i1,2}$) as follows:

$$K_{i1,2} = \frac{\text{equilibrium concentration of } i \text{ in phase 1}}{\text{equilibrium concentration of } i \text{ in phase 2}} \quad (8.1)$$

As with any physicochemical equilibrium, a greater tendency for transfer from one phase into another is the result of a free energy decrease, as given by the generalized equation:

$$-\Delta G_{i1,2} \propto \ln K_{i1,2} \quad (8.2)$$

At constant temperature this becomes

$$-\Delta G_{i1,2} \propto T \ln K_{i1,2} \quad (8.3)$$

which can be rewritten by using A as the proportionality constant:

$$-\Delta G_{i1,2} = AT \ln K_{i1,2} \quad (8.4)$$

or in the form of the familiar ΔG expression:

$$\Delta G_{i1,2} = -AT \ln K_{i1,2} \quad (8.5)$$

The amount transferred depends on the type and strength of the interactions between *i* and the source and receptor phases. The key interaction types are the dipole–dipole and hydrogen bonding. *Surface* or *interface adsorption* may also play a key role in certain partitioning phenomena; however, only *bulk interactions* (i.e., dipole – dipole and hydrogen bonding) are considered in the present discussion.

The strength of the interaction between *i* and its host phase can be understood with a simple cavity model, based on the idea that the molecular transfer from one phase into another involves two steps (see Goss and Schwarzenbach, 2003):

(a) The removal of a molecule of *i* from *phase 1*, and
(b) Its insertion into *phase 2*.

Step *a* requires some *energy expenditure* for the breaking of the cohesive forces between *i* and *phase 1*, whereas step *b* also *requires energy* for the creation of a physical space inside *phase 2* (i.e., a *cavity*) so as to receive the molecule of *i*; however, it *releases energy* due to the formation of new bonds between *i* and the molecules of *phase 2*. Obviously, the bigger the molecule, the more energy is required to form a larger cavity. The final energy balance determines the outcome of the process, and appears reflected in the value of $K_{i1,2}$.

In turn, all of these steps depend on the Van der Waals and hydrogen-bond interaction forces, which become stronger with the number of interactions. For example, a non-polar compound only interacts through Van der Waals forces, whereas a monopolar compound (i.e., an H-donor *or* H-acceptor) interacts through Van der Waals and hydrogen bonding forces. A bipolar compound (i.e., an H-donor *and* H-acceptor) interacts through Van der Waals, hydrogen donor, and hydrogen acceptor forces. Therefore, one can expect that the partition coefficient for a non-polar solute between a non-polar solvent and air will be much smaller than that of a bipolar solute between a bipolar solvent and air. In fact, the (dimensionless) value of $K_{i\,\text{solvent, air}}$ for *n*-octane in *n*-hexane (i.e., non-polar/non-polar) is 9.3×10^3, whereas that for phenol in *n*-octanol (i.e., bipolar/bipolar) is 2.2×10^6. This means that more solute goes into the air in the first case than in the second, because the interaction between the solute and the solvent is weaker in the first case.

Owing to the impossibility of compiling partition coefficients for a substance into every possible set of solvents/phases, a reference that is commonly accepted is the *octanol/water* partition coefficient, $K_{io,w}$. This solvent (i.e., the 1-octanol) is a good reference choice as it mimics (to a reasonable extent) the solvent behavior of lipids in biota as well as that of humic substances in soils. Extensive tables of $K_{io,w}$ values are readily available (see for example, the *CRC Handbookfor Chemistry and Physics*). Such data help predict the environmental fate of many substances (see Casey and Pittman, 2005).

If one has the value of $K_{io,w}$ for a given substance i as well as its partition coefficient between water and a different medium (x), one can calculate the value of the partition coefficient between 1-octanol and x, $K_{io,x}$ by noting that the ΔG values are additive, assuming that the values of A and T are constant:

$$\Delta G_{io,x} = \Delta G_{io,w} + \Delta G_{iw,x}$$
$$-AT \ln K_{io,x} = -AT \ln K_{io,w} + (-AT \ln K_{iw,x}) \tag{8.6}$$

Dividing by $-AT$ one obtains

$$\ln K_{io,x} = \ln K_{io,w} + \ln K_{iw,x} \tag{8.7}$$
$$e^{\ln K_{io,x}} = e^{\ln K_{io,w} + \ln K_{iw,x}} \tag{8.8}$$
$$K_{io,x} = K_{io,w} K_{iw,x} \tag{8.9}$$

See Example 8.1.

8.4 Air, Water, and Soil Pollution and Their Effects

The pollution of air, water, or soil may or may not be intentional. Deliberate contamination may involve a myriad of paths, such as the disposal of pollutants into water, or the control of animals, plants, or microorganisms with biocides, open-air incineration, and distorted industrial disposal practices. Non-intentional routes mainly involve biogenic and accidental pollution. An example of the former is the production of methane by biodecay processes. Accidental contamination may result from short-term or long-term aerial transport, natural disasters (e.g., flooding by rivers or seas, or hurricanes), collision of trains or tankers carrying toxic chemicals, among many others. Regardless of the sources and intentions, a pollutant produced in one or another form has similar effects. A summary of their effects is presented next.

8.4.1 Effects of Pollutants on the Atmosphere

The main sources of air pollution include combustion processes, industrial processes, natural resource exploitation and processing, commercial services (e.g., dry-cleaning or painting), and biogenic or non-anthropogenic processes. The most abundant air pollutants can be grouped and classified into 10 groups (see below). The last six groups include many substances listed on the U.S. EPA official Hazardous Air Pollutants lists (*HAPs*), derived from the Clean Air Act. The majority are *primary* pollutants (i.e., those that are directly emitted to the atmosphere), while others may form as *secondary* pollutants through photochemical or other reactions in the atmosphere.

8.4.1.1 Main Air Pollutants

(a) *CO and CO_2:* These two oxides are directly related to fossil fuel and biomass combustion, biogenic processes, and photochemical transformations in the atmosphere. CO_2 is produced as a consequence of complete combustions and metabolic processes. Its main importance is that of a greenhouse gas, as discussed in Chapter 4. CO is derived from incomplete combustion processes and from

Example 8.1 Calculate the partition coefficient of aniline between 1-octanol and air.

Answer

One looks up the $K_{io,w}$ for aniline and its water/air partition coefficient. Often times such data are found in logarithmic form as log $K_{ia,b}$. (See Goss and Schwarzenbach, 2003 and any *CRC Handbook of Chemistry and Physics*).

$\log K_{aniline\, o,w} = 0.90$, and thus $K_{aniline\, o,w} = 7.94$.

Because $K_{aniline\, w,air} = 7.2 \times 10^3$, then
$K_{aniline\, o,air} = 7.94 \times 7.2 \times 10^3 = 5.7 \times 10^4$

the photochemical transformation of methane and other non-methane VOCs by the hydroxyl radical generated in the atmosphere:

$$CH_4 + {}^{\bullet}OH \rightarrow CH_3^{\bullet} + H_2O \qquad (8.10)$$

$$CH_3^{\bullet} + O_2 + h\nu \rightarrow CO + H_2 + {}^{\bullet}OH \qquad (8.11)$$

In turn, these products may react to form CO_2 in the atmosphere. The main hazard of CO is its toxicity since it can substitute dioxygen uptake in hemoglobin.

(b) *NOx and N_2O:* This nomenclature represents the NO, NO_2, and N_2O gases. The last of these is of biogenic origin (released by soil bacteria) and can be transformed in the atmosphere into NO. The latter is a combustion product through oxidation of air nitrogen at high temperatures, and can also be produced in the atmosphere by lightning. In turn, it oxidizes into NO_2, which is a precursor of acid rain and smog formation (this will be further discussed below).

(c) *SOx:* This nomenclature represents the SO_2 and SO_3 gases as well as the SO_4^{2-} ion, all of which are generally related to the oxidation of sulfur-containing fuels and the oxidation of H_2S. The latter is a toxic gas produced from the biological decay of organic matter (e.g., sulfate reduction), geothermal action, or industrial processes such as wood pulping. The oxidation of H_2S gas can take place in the atmosphere with the presence of oxidants such as ozone (plus water, probably as vapor):

$$H_2S_{(g)} + O_{3(g)} \rightarrow H_2O_{(g)} + SO_{2(g)} \qquad (8.12)$$

In turn, SO_2 can react photochemically with dioxygen to yield SO_3:

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)} \qquad (8.13)$$

(d) *Photochemical oxidants:* These are secondary pollutants because they are formed through photochemical reactions based on other primary pollutants. The main photooxidant is ozone, generated in nature by lightning or through photochemical reactions based on NO_2 as the precursor. Other photochemical oxidants include PBzN (peroxybenzoyl nitrate) and PAN (peroxyacyl nitrates), both produced as a consequence of reactions among HC, ozone, or other ambient oxidants (e.g., the ${}^{\bullet}OH$ radical), and NO derivatives in the atmosphere.

(e) *Particulates and aerosols:* These are generated by wind-blown dust and wildfires, volcanic eruptions, incomplete combustion, industrial and mineral processing, and the formation of aerosols. The particles may be minute ocean salt crystals, soil particles, minerals, and metallic compounds, condensed hydrocarbons or other organic compounds, and sulfuric and nitric acid aerosols. Particulate matter is generally classified as $PM_{2.5}$ (i.e., particulate matter of diameter ≤ 2.5 μm) and PM_{10} (i.e., particulate matter $2.5\ \mu m \leq d \leq 10\ \mu m$). The most dangerous type is the former because the body is unable to release these particles that often consist of aerosols containing carcinogenic substances. Such particles also play a relevant role as reaction nuclei for smog formation or other photochemical reactions. Although they may comprise compounds from other air pollutant groups, it is common to consider them separately. They are part of the criteria pollutants of the U.S. National Ambient Air Quality Standards (*NAAQS*).

(f) *Metal and metalloid compounds and vapors:* These may consist of hazardous particulate matter or vapors of metals such as Pb, Hg, As, Ni, Be, and Cu that are generated by combustion and incineration processes, engine wear, lubricating oil components, lamp wastes, and mineralization of geologic formations.

(g) *PAHs (polycyclic aromatic hydrocarbons and derivatives)*: These are aromatic compounds of at least three fused aromatic rings. Those containing up to 6 rings are called "small PAH", and those containing more are "large PAH". When the molecular weight (MW) is below 230, the PAH is generally a gas, whereas for larger MW values they are particles. All PAHs are hazardous air pollutants (e.g., dibenzo(*a*)anthracene, and pyrene) and are found as products of the incomplete combustion of fossil fuels and vegetable matter, petroleum refineries, and in petroleum products. These compounds may have a half-life in the troposphere of 3.5 to 10 days and they may react with hydroxyl radicals, ozone, and nitro radicals, generating in the last case mutagenic nitro-PAHs.

(h) *VOCs (methane and non-methane volatile organic compounds)*: These are light hydrocarbons (e.g., of the BTEX family) and unsaturated hydrocarbons. Methane—one of the greenhouse gases and a natural contaminant—is also included in this case, as well as partially oxidized compounds such as formaldehyde and other aldehydes, ketones, and alcohols. Sources of VOCs include incomplete combustion processes, fugitive sources, industrial processes, petroleum processing, and painting and other solvent-intensive processes. There is also a non-methane VOC contribution due to biogenic processes (i.e., the phytochemical liberation of light hydrocarbons). The most abundant biogenic VOCs include the highly reactive isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$) (e.g., α-, β-pinene, limonene, and d-3-carene), sesquiterpenes ($C_{15}H_{24}$), methylbutenol, and other reactive oxygenates such as aldehydes, ketones, and esters. These emissions are influenced by five factors: (a) ambient temperature, (b) vegetation type, (c) vegetation density, (d) solar radiation, and (e) cloud coverage. These compounds are precursors of smog formation and organic aerosols, and many are also classified as HAPs.

(i) *Halogenated hydrocarbons and polychlorinated organic compounds:* Volatile chlorinated hydrocarbons used as solvents (e.g., chloroform, carbon tetrachloride, methylene chloride, and perchloroethylene) fall into this category. The polychlorinated dibenzo compounds dioxins and furans also belong to this group (see Section 9.1.4); they are related to the PAHs, mainly produced and emitted through incineration processes and car emissions. The CFCs (chlorofluorocarbons and similar polyhalogenated compounds) are also included here. The first two types are very hazardous compounds and the others are responsible for the destruction of the ozone layer (see Section 8.4.1).

(j) *Radionuclides:* Their presence is due to natural gas or particulate emissions from natural deposits of uranium where radon is liberated, as well as emissions from uranium processing, nuclear reactors, and fuel-reprocessing wastes.

From the analysis of air pollutants and their effects, the *NAAQS* described above were developed by the US EPA based on requirements of the Clean Air Act. This was done by defining the criteria pollutants to measure air quality, and then by determining the acceptable concentrations under health protection criteria (known as *primary standard*); a *secondary standard* was also defined to protect public welfare and prevent environmental and property damage. The criteria pollutants for air quality thus selected were CO, Pb, NO_2, O_3, PM_{10}, $PM_{2.5}$, and SO_2.

8.4.1.2 Combustion Processes as the Main Air Pollution Source

Where do trace gases originate? For the most part, they come from anthropogenic activities related to the combustion of fossil fuels, leading to the production of the main primary pollutants: CO, NO*x*, VOCs, and SO_2.

The (ideal) combustion of gasoline in internal combustion engines is expressed by the following equation:

$$C_nH_{m(g)} + (n + m/4)O_{2(g)} \rightarrow nCO_{2(g)} + (m/2)H_2O_{(g)} \tag{8.14}$$

If the ratio of hydrocarbons to oxygen is not adequate, partially oxidized compounds of carbon will be emitted, together with unreacted hydrocarbons. On the other hand, an excess of oxygen favors the production of NO because of the exothermicity of the reaction and because the oxygen required comes from the air:

$$N_{2(g)} + O_{2(g)} \rightleftarrows 2NO_{(g)} \tag{8.15}$$

$$2NO_{(g)} + O_{2(g)} \rightleftarrows 2NO_{2(g)} \tag{8.16}$$

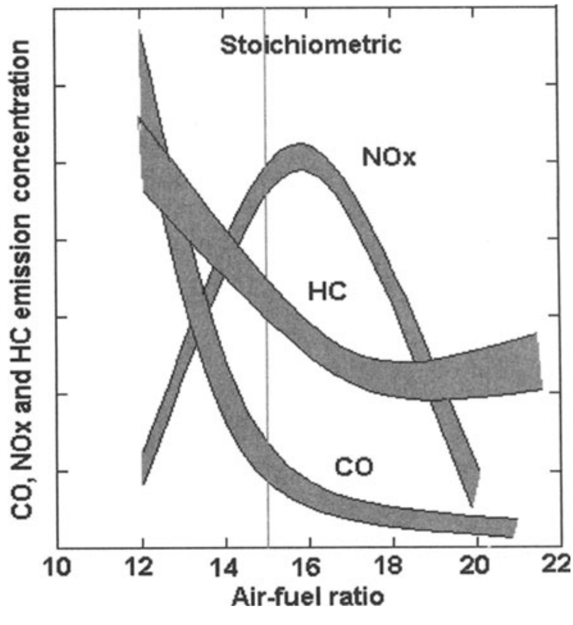


FIGURE 8.1. The effect of air–fuel ratio on exhaust composition (not to scale; only approximate ranges are given). (Adapted from Nishikawa et al. 2000 and Stern, 1976).

Figure 8.1 shows the relative amounts of exhaust gases from a combustion engine at different air-to-fuel ratios.

The sulfur content of the fuels generates sulfur dioxide upon burning:

$$\{S\} + O_{2(g)} \rightarrow SO_{2(g)} \qquad (8.17)$$

Combustion processes also generate many other contaminants. For example, diesel combustion produces more than 40 components including gases, vapors, and fine particles, many of them hazardous.

Furthermore, mercury has been identified as an abundant contaminant from coal-burning processes. Unfortunately, incineration processes and vapor-generating processes also produce toxic dioxins and furans, among other contaminants.

8.4.1.3 The Greenhouse Effect

An additional effect of combustion gases is the strong anthropogenic contribution to the *greenhouse* effect, a global air pollution problem whose principles are discussed in Section 4.5. This is primarily due to the augmented emissions of CO_2 and NOx into the atmosphere, promoted by unregulated increases in population, transport, and industrial activity. The gas of major concern is CO_2 because its concentration has been steadily increasing over the last 100 years as a result of the combustion of fossil fuels.

The great majority of the anthropogenic emissions from CO_2 are related to energy production. The current concentration of this gas is approximately 370 ppm as opposed to approximately 280 ppm at the beginning of the 19th century. Because an increase in CO_2 concentration increases the greenhouse effect, some estimates indicate that by doubling the concentration of this gas, the Earth's surface temperature could increase 3.5°C.

Other potential greenhouse pollutants are the chlorinated alkyl compounds such as tetrachloromethane, chloroform, the *chlorofluorocarbons* (*CFCs* and their substitutes: the *halons* (e.g., $CBrClF_2$), the *hydrochlorofluorocarbons, HCFCs* (e.g., C_2H_4HCl), and the *hydrofluorocarbons, HFCs* (e.g., CF_3CH_3). The CFCs are double trouble because they are the principal agents in *ozone depletion* and are *greenhouse gases* as well. Although they are trace gases, they are very efficient IR absorbers in the atmosphere, as shown in Table 4.3.

Another contribution to the greenhouse effect involves the increase in methane production. This increase is due to two factors: there is an increasing demand on rice production for a growing population, and methane is produced in the rice pads; and there is also intensive livestock breeding, which is a source of concentrated methane production. (On a humorous note, in 2003 New Zealand considered applying a special tax that would be paid by farmers. This tax was to be derived from the high methane content of the flatulence gases of their livestock and its possible contribution to the greenhouse effect. The proposal was known as the "flatulence tax." It was later suggested that most of the methane from livestock probably comes from burping... and so it could have been considered as the "burping tax" instead. The proposal was dropped).

8.4.1.4 Smog Formation

Smog formation—a local air pollution problem—is a consequence of photochemical reactions based on primary pollutants discharged into the atmosphere. For this effect to occur, the following factors must be present: high solar radiation, dioxygen, NOx, SO_2, hydrocarbons, and particles that serve as reaction nuclei. As stated earlier, HC, NOx, and SO_2 can be provided through anthropogenic and biogenic sources. Smog has many deleterious effects on human health as well as on plants and materials.

The most important reaction in the initiation of smog formation is the production of ozone, a strong oxidant generated through the NO_2 photodissociation cycle known as the *null cycle*:

$$NO^{\bullet}_{2(g)} + h\nu\ (\lambda < 430\,\text{nm}) \rightarrow NO^{\bullet}_{(g)} + O^{\bullet}_{(g)} \qquad (8.18)$$

$$O^{\bullet}_{(g)} + O_{2(g)} + M_{(g)} \rightarrow O_{3(g)} + M_{(g)} \qquad (8.19)$$

$$O_{3(g)} + NO^{\bullet}_{(g)} \rightarrow NO^{\bullet}_{2(g)} + O_{2(g)} \qquad (8.20)$$

where M represents any third atom or molecule needed to absorb the excess energy of the intermediate formed. Ozone is a pollutant of the urban troposphere, but because it is not directly released, it is called a *secondary pollutant*. Its formation depends on the photolysis rate and on the ratio of NO_2/NO. The contribution from hydrocarbon emissions consists in the formation of free radicals after their reaction with strong oxidants such as OH radicals, atomic or molecular oxygen, nitric oxide or ozone, or even photo dissociating in the presence of sunlight. (Note: all the species in the remainder of this section are in the gas phase, but their physical state is omitted for the sake of clarity.)

$$O^\bullet + H_2O \rightarrow 2^\bullet OH \qquad \text{(hydroxyl radical)} \tag{8.21}$$

$$RH + {}^\bullet OH \rightarrow R^\bullet + H_2O \qquad \text{(alkyl radical)} \tag{8.22a}$$

$$RH + O^\bullet \rightarrow RO^\bullet + H^\bullet \qquad \text{(alkoxyl radical)} \tag{8.22b}$$

$$R^\bullet + O_2 + M \rightarrow RO_2^\bullet + M \qquad \text{(peroxyl radical)} \tag{8.22c}$$

$$RO_2^\bullet + RH \rightarrow ROOH + R^\bullet \tag{8.22d}$$

$$RO_2^\bullet + NO \rightarrow RO^\bullet + NO_2^\bullet \tag{8.22e}$$

$$RH(\text{alkene}) + O_3 \rightarrow {}^\bullet OH + \text{products} \tag{8.22f}$$

$$ROR + h\nu \rightarrow RO^\bullet + R^\bullet \tag{8.23}$$

In turn, these free radicals may react with atomic or molecular oxygen, nitric oxide, and nitrogen dioxide without necessarily sacrificing the ozone present.

A series of chain reactions then take place, which depend on radical initiation, propagation, and termination. These are aleatory processes where reactions occur among the species as they come upon each other, depending on the individual reactivities. The oxidation of hydrocarbons in the termination reactions leads to aldehydes, which may be further oxidized to form aldehyde peroxides, peroxides, hydroperoxides, and peroxyacids:

$$RO^\bullet + O_2 \rightarrow R'CHO + HO_2^\bullet \qquad \text{(hydroperoxyl radical)} \tag{8.24}$$

$$RCHO + {}^\bullet OH \rightarrow RCO^\bullet + H_2O \tag{8.25}$$

$$RCO^\bullet + O_2 \rightarrow RC(O)O_2^\bullet \qquad \text{(acylperoxyl radical)} \tag{8.26}$$

$$R^\bullet + O_2 + M \rightarrow RO_2^\bullet + M \tag{8.27}$$

$$RO_2^\bullet + NO \rightarrow RO^\bullet + NO_2^\bullet \tag{8.28}$$

$$RO_2^\bullet + O_2 \rightarrow RO^\bullet + O_3 \tag{8.29}$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \tag{8.30}$$

$$2^\bullet OH \rightarrow H_2O_2 \qquad \text{(peroxide)} \tag{8.31}$$

Some termination reactions also include the formation of acids, alcohols, and nitro compounds. They may take place through combination or disproportionation (dismutation) reactions:

$$2RO_2^\bullet \rightarrow ROOR + O_2 \qquad \text{(organic peroxide)} \tag{8.32a}$$

$${}^\bullet OH + NO_2 + M \rightarrow HNO_3 + M \qquad \text{(acid)} \tag{8.32b}$$

$$R{-}O{-}CH_2O_2^\bullet + HO_2^\bullet \rightarrow R{-}O{-}CHO + O_2 + H_2O \qquad \text{(ester)} \tag{8.32c}$$

$$RO_2^\bullet + HO_2^\bullet \rightarrow ROOH + O_2 \qquad \text{(organic hydroperoxide)} \tag{8.32d}$$

$$RO^\bullet + NO/NO_2 \rightarrow RONO/RONO_2 \qquad \text{(nitro compounds)} \tag{8.32e}$$

$$RO_2^\bullet + NO \rightarrow RONO_2 \tag{8.32f}$$

Combination reaction:

$$2RO^\bullet \rightarrow ROOR \qquad \text{(organic peroxide)} \tag{8.33}$$

Dismutation or disproportionation:

$$RO^\bullet + RO^\bullet \rightarrow R'CH{=}O + R{-}OH \qquad \text{(aldehyde + alcohol)} \tag{8.34}$$

Among the very important secondary pollutants related to smog are the peroxy-nitro compounds, PAN (peroxyacetyl nitrate) and PBN (peroxybenzylnitrate), which are responsible for the phenomenon of eye redness in polluted cities. Ozone—as well as these organic peroxides—is part of the end of the chain mechanisms of photochemical smog. Considering acetaldehyde as the initial organic reactant we have:

$$CH_3CHO + {}^\bullet OH \rightarrow CH_3CO^\bullet + H_2O \tag{8.35}$$

$$CH_3CO^\bullet + O_2 + M \rightarrow CH_3COO_2^\bullet + M \tag{8.36}$$

$$CH_3COO_2^\bullet + NO_2^\bullet + M \rightarrow CH_3COOONO_2(\text{PAN}) + M \tag{8.37}$$

In summary, the main products derived from these photochemical reactions are O_3, peroxides (e.g., PAN, PBN, and H_2O_2), hydroperoxides, aldehydes, ketones, alcohols, nitro compounds (alkyl and benzyl nitrates and nitrites), and acids such as sulfuric, nitric, and nitrous acid.

8.4.1.5 Stratospheric Ozone Destruction or the Ozone Hole

In the winter of 1984, massive losses of stratospheric ozone were detected in Antarctica over the South Pole (Halley Bay). This ozone depletion is known as the *ozone hole.* We know now that it also forms over the Arctic, although not as dramatically as in the Antarctic. Stratospheric ozone protects life on the surface of the Earth by screening harmful UV radiation coming from the sun through a photodissociation mechanism (see Chapter 4).

The ozone hole is geographically defined as the area where the total ozone amount is less than 220 Dobson Units (DU) (see definition in Chapter 4). The ozone hole has steadily grown in size (up to 27 Mkm^2) and length of existence (from August through early December) over the past two decades. As a reference to the size of the "hole," the continental United States has an area of 9.4 Mkm^2. Figure 8.2 shows a comparison of the ozone distribution over

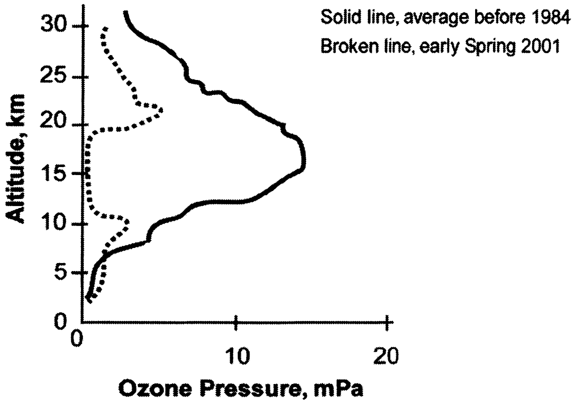


FIGURE 8.2. Ozone distribution over Antarctica in different years.

Antarctica in two different years (before 1984 and in 2001).

During the winter season in the South Pole, a strong circumpolar wind develops in the middle to lower stratosphere. Such strong winds, known as the *polar vortex*, isolate the air over the polar region. In the winter there is no sunlight and the air contained in the vortex becomes very cold (i.e., temperatures below −80°C) leading to the formation of the *polar stratospheric clouds (PSC)*. These *PSC* are composed not only of water but also of nitric acid trihydrate.

It is now an established fact that anthropogenically generated chlorine and bromine compounds in the atmosphere are responsible for the decrease in ozone concentration observed over Antarctica and over the North Pole. Such compounds form HCl and $ClONO_2$ (and the corresponding bromine compounds), which act as chlorine (or bromine) reservoirs. They are then converted into more active forms of chlorine on the surface of the *PSC*, according to the following scheme:

$$HCl + ClONO_2 \rightarrow HNO_3 + Cl_2 \quad (8.38)$$

$$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl \quad (8.39)$$

$$HCl + HOCl \rightarrow H_2O + Cl_2 \quad (8.40)$$

$$N_2O_5 + HCl \rightarrow HNO_3 + ClONO \quad (8.41)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (8.42)$$

The destruction of ozone requires atomic chlorine produced by sunlight:

$$Cl_2 + h\nu \rightarrow 2Cl^\bullet \quad (8.43)$$

Sunlight also drives the following reactions:

Mechanism 1:

$$ClO^\bullet + ClO^\bullet + M \rightarrow Cl_2O_2 + M \quad (8.44)$$

$$Cl_2O_2 + h\nu \rightarrow Cl^\bullet + ClO_2 \quad (8.45)$$

$$ClO_2 + M \rightarrow Cl^\bullet + O_2 + M \quad (8.46)$$

$$(Cl^\bullet + O_3 \rightarrow ClO^\bullet + O_2) \times 2 \quad (8.47)$$

The net reaction is

$$2O_3 \rightarrow 3O_2 \quad (8.48)$$

Mechanism 2:

$$ClO^\bullet + BrO^\bullet \rightarrow Br^\bullet + Cl^\bullet + O_2 \quad (8.49)$$

$$Cl^\bullet + O_3 \rightarrow ClO^\bullet + O_2 \quad (8.50)$$

$$Br^\bullet + O_3 \rightarrow BrO^\bullet + O_2 \quad (8.51)$$

The net reaction is the same as above:

$$2O_3 \rightarrow 3O_2 \quad (8.52)$$

These catalytic cycles are largely responsible for the depletion of ozone. One chlorine atom may destroy more than 100,000 ozone molecules before it is transformed into a non-reactive species. Despite the substantial reduction of chlorine and bromine compounds released into the atmosphere as a result of the Montreal Protocol, this has not shown any significant impact on the reduction of the size of the ozone hole. If such a trend continues, it may still take some half a century for the recovery of ozone to the levels it had prior to 1984.

8.4.1.6 Acid Rain

We may think of rain as a way that nature has to clean the atmosphere by washing-off substances from it. The cleaning process is carried out in two forms: one, by dissolution of the soluble compounds, and the other by sweeping away suspended particles.

Under "normal" conditions the pH of rain is acidic (approximately 5.7) due to the dissociation of dissolved carbon dioxide in water, as discussed in Chapter 6:

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+ \quad (8.53)$$

However, in polluted environments there are also oxides of sulfur and nitrogen present, which are stronger acids than carbon dioxide. When these oxides dissolve in rain droplets, the pH reaches values lower than 5.7, thus forming what is known as *acid rain* or — in a broader sense — *acid deposition.*

Sulfur dioxide from the combustion of sulfur-containing fossil fuels (e.g., diesel oil and coal) is oxidized in the atmosphere to form sulfur trioxide that reacts with water to form sulfuric acid.

$$SO_2 + O^\bullet \rightarrow SO_3 \tag{8.54}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{8.55}$$

$$H_2SO_4 \rightarrow HSO_4^- + H^+ \tag{8.56}$$

Although the oxidant in combustion reactions is dioxygen, nitrogen oxides form because dioxygen comes from air which contains approximately 78% nitrogen. The following reaction scheme explains the formation of nitric acid, another component of acid rain:

$$N_2 + O_2 \rightarrow 2NO^\bullet \tag{8.57}$$

$$2NO^\bullet + O_2 \rightarrow 2NO_2^\bullet \tag{8.58}$$

$$3NO_2^\bullet + H_2O \rightarrow 2HNO_3 + NO^\bullet \tag{8.59}$$

$$HNO_3 \longrightarrow NO_3^- + H^+ \tag{8.60}$$

In addition to low pH values, acid rain containing nitrates can oxidize materials such as copper or iron. Other consequences of acid rain include the deterioration of marble or any carbonated exterior material due to the decomposition reaction:

$$CaCO_{3(s)} + 2H^+ \rightarrow CO_{2(g)} + H_2O_{(l)} + Ca^{2+} \tag{8.61}$$

Volcanic eruptions are natural sources of sulfur oxides, and lightings are natural sources of nitrogen oxides and ozone, while combustion processes are the main anthropogenic sources of these two pollutants.

8.4.1.7 Indoor Pollution

Air quality in homes and workplaces is affected by human activities, construction material, underground minerals, and outside pollution. The most common indoor pollutants are radon, carbon oxides, nitrogen oxides, tobacco smoke, formaldehyde, and a large variety of organic compounds. Indoor atmospheres can also be contaminated with fine particles such as dust, aerosols (from spray cans), fungal spores, and other microorganisms.

Water vapor itself is not usually considered a pollutant, but the amounts generated in closed spaces such as in kitchens (that use gas for cooking) can favor the growth of house dust mites, moulds, and fungi, which in many cases lead to allergic reactions.

(a) Radon

Why is radon, a noble gas, a pollutant? Although Rn is a member of the noble gas family, ^{222}Rn is a radioactive gas (half-life = 3.8 days) that decays first into ^{218}Po (half-life = 3 min), ending in ^{210}Pb (half-life = 22.3 years). Radon enters a building from the subjacent ground, either carried by a convective flow of soil gas or dissolved in the groundwater.

Indoor moderate airborne concentrations of radon daughters can increase considerably in the presence of particles such as those found in cigarette smoke. The size of these particles (now radioactive) allows them to reach the lungs and remain there, increasing the probability of consequences in health.

The amount of radon that enters a building depends on the geology of the zone, the concentration of the gas, the pathways into the building and its ventilation rate. The US EPA recommended limit indoor radon concentration is 4 pico Curies/L.

(b) Carbon oxides

Carbon dioxide is not a toxic gas. However, when individuals are exposed for prolonged periods to 1.5% CO_2 (vol/vol in air), this apparently causes metabolic stress. Exposure to 7–10% will produce unconsciousness within minutes.

Carbon monoxide is a toxic gas that binds hemoglobin more efficiently than dioxygen, and therefore its presence decreases the oxygen uptake by cells, ultimately leading to asphyxia.

These two pollutants can be found concentrated inside buildings due to unvented heaters, leaking chimneys, furnaces, and stoves, in addition to automobile exhaust from garages, and tobacco smoke. These are among the most common pollutants that cause deaths in underdeveloped countries during winter, when people warm themselves using wood stoves.

(c) Nitrogen oxides

Most health effects associated with nitrogen oxides (NOx) are attributed to nitrogen dioxide. The main source of NOx in homes can be traced to gas stoves and heaters, where combustion takes place to produce heat. The combustion first produces NO, which then oxidizes rapidly to NO_2. High levels of NO_2 (approximately 150 ppm) can be lethal, while concentrations in the range of 50–150 ppm can produce lung disease. Lower concentrations may lead to eye, nose, and throat irritation.

(d) Tobacco smoke

Tobacco smoke contains both particulate matter (see Chapter 4) and a large number of gaseous and vapor components. These components include CO, CO_2, NO, NO_2, acrolein, pyridine, methyl chloride, acetaldehyde, formaldehyde, and dimethylnitrosamine. Particulate matter comprises, for example, nicotine, pyrene, benzo(*a*)pyrene, naphthalene, methyl naphthalene, aniline, and nitrosonornicotine.

The health effects associated with direct or indirect (i.e., passive smoking) exposure are multiple, but their discussion is beyond the scope of this chapter. This is even more worrisome because it is not only the smoker but the non-smoker as well who is exposed to all these toxic substances; in fact, the side stream smoke (which also reaches all the non-smokers in the room) may contain higher concentrations of the toxicants than the mainstream smoke. Strict prohibitions, therefore, have been established for smoking in public spaces.

(e) Formaldehyde

Formaldehyde is an important industrial chemical for the production of synthetic resins. These resins are applied primarily as adhesives in the production of a large number of consumer products and construction materials that end up in homes. Other sources of indoor formaldehyde include urea-formaldehyde foam insulation, textile additives, as well as combustion and tobacco smoke. Formaldehyde is one of the many VOCs present indoors and it is considered the most abundant among them. It has important toxic effects in the 0.1–5 ppm concentration range.

(f) Other volatile organic compounds

Most of the 300+ organic vapors that may be found in indoor pollution are derived from paints, paint strippers and other solvents, wood preservatives, aerosol sprays, cleansers and disinfectants, moth repellents, air fresheners, in addition to fuels and automotive products, and dry-cleaners. Many of these compounds are halogenated hydrocarbons, PAH, ketones and aldehydes, which exhibit different degrees of toxicity.

(g) Particulates

As stated above, indoor pollution has a high content of particulate matter (solids and aerosols), including that in tobacco smoke. Particulates may originate inside a closed area or drift inwards into a building from the outside. Other important sources include combustion processes inside the homes, where carbon and soot particles are generated from sources such as fireplaces, woodstoves, and heaters. Particulate matter also arises from contaminated soil and dust, deteriorating paint, and damaged insulation and floor tiles. These last two are key sources of Pb and asbestos, two of the main toxic pollutants. Additional sources of particles and aerosols include the pesticides used inside or outside residences.

8.4.2 Effects of Pollutants on the Hydrosphere

The effects of pollutants on the hydrosphere are quite notorious. For example, an estimated 40% of the U.S. waterways are too polluted for swimming or fishing. Thus, it is important to understand the sources of these pollutants, their interactions and effects.

The main sources of water pollutants are point and non-point sources: for example, domestic sewage, industrial discharges, agricultural and livestock breeding runoff, accidental spills, storage tank leaks, urban runoff, and contaminated rain. The main industrial discharges come from the following industries: chemical, petroleum and petrochemical, beverages and food, paper, textile, sugar, mining and metallurgy, tannery, fishing and fish processing, and fertilizer production.

Many thousands of chemicals enter water bodies from anthropogenic sources. These chemicals have significantly different properties, which makes it impossible to monitor or measure such a variety. Consequently, when these water pollutants are considered, they are generally grouped into substance types, and a *priority* or *indicator substance* is used to estimate their presence.

The main types of water pollutants and their sources are listed in Table 8.5.

8.4.2.1 Oxygen-Demanding Materials

Anything that can be oxidized in the receiving water with the consumption of dissolved molecular oxygen is termed *oxygen-demanding material.* This usually consists of biodegradable organic matter (see Chapter 9), but it may also include certain inorganic compounds. The consumption of *dissolved oxygen (DO)* poses a threat to fish and other higher forms of aquatic life that require it for respiration. The critical level of DO varies greatly

TABLE 8.5. Principal water pollutants

	Point sources		Non-point sources	
Water pollutant type	Urban	Industrial	Field, agricultural, other runoff	Urban runoff
Oxygen-demanding substances (*BOD*)	★	★	★	★
Nutrients	★	★	★	★
Suspended particles/sediments	★	★	★	★
Salts		★	★	★
Toxic metallic and metalloid compounds		★		★
Surfactants	★	★		★
Acids and bases		★		
Toxic organic substances		★	★	★
Toxic inorganic salts		★		★
Oil and grease			★	★
Plastic, polymers, etc. (trash)				★
Pathogens	★	★	★	★
Heat		★		

among species. For example, brook trout require about 7.5 mg/L of DO, while carp may survive at 3 mg/L. Oxygen-demanding materials in domestic sewage come primarily from human waste and food residues. Particularly noteworthy among the many industries that produce oxygen-demanding wastes are the food processing and paper industries. Almost any naturally-occurring organic matter such as animal droppings, crop residues, or leaves that reach the water from non-point sources, contribute to DO depletion.

The amount of oxygen required for oxidizing a substance to carbon dioxide and water may be stoichiometrically calculated if the chemical composition of the substance is known. In contrast, the *chemical oxygen demand* (*COD*) does not rely on knowledge of the chemical composition of the substances in the water. The COD test measures the amount of dioxygen required to achieve a complete chemical oxidation of 1 L of sewage sample using a strong chemical oxidizing agent (i.e., Cr^{6+}, typically as dichromate in 50% sulfuric acid) mixed with a water sample and then heated to 150°C for 2 h. The difference between the amount of oxidizing agent at the beginning and at the end of the test is assumed to have been used for the complete oxidation of the oxidizable contaminants present in the aqueous sample, and is used to compute the COD, reported in mg/L of dioxygen (see Examples 8.2 and 8.3). Since this analysis produces toxic chromium

Example 8.2 A general reaction that occurs in the COD test is represented as follows:

$$C_nH_aO_bN_c + dCr_2O_7^{2-} + (8d + c)H^+ \rightarrow nCO_2 + \frac{a + 8d - 3c}{2}H_2O + cNH_4^+ + 2dCr^{3+}$$

where organic nitrogen is assumed to be in its most reduced oxidation state (i.e., −3). With this information, show that the number of moles of dichromate, *d* required for the oxidation of one mole of the organic substance, is given by:

$$d = 2n/3 + a/6 - b/3 - c/2$$

Answer

From the oxygen balance,

$$b + 7d = 2n + \frac{a + 8d - 3c}{2}$$

Solving for *d* one obtains

$$3d = 2n - b + a/2 - (3/2)c$$

and

$$d = 2n/3 + a/6 - b/3 - c/2$$

Example 8.3 Assuming acidic media,

(a) Write the half-reaction for the reduction of one mole of dichromate ions into Cr (III).

(b) Write the half-reaction for the reduction of one mole of dioxygen in water.

(c) If in a real COD test one required 1 mole of dichromate for the oxidation of a given amount of organic matter, how many moles of dioxygen would this be equivalent to?

Answer

(a) $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

(b) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

(c) Then 6/4 (or 1.5) times that required for the dichromate is the number of moles of O_2 needed for oxidation of the organic matter (i.e., for removal of the same number of electrons as dichromate).

residues, alternative oxidants are actively sought, for example Mn(III).

If oxidation of the compounds in wastewater is carried out by microorganisms, the dioxygen consumed is known as the *biochemical oxygen demand* (*BOD*). Dioxygen is consumed by heterotrophs that use organic matter as food and energy source (*carbonaceous BOD*, or *CBOD*) and by autotrophs, such as nitrifying bacteria, for the oxidation of NH_4^+ to nitrite and nitrate (i.e., *nitrogenous oxygen demand* or *NOD*). During the BOD test, a mixed population of microorganisms oxidizes organic and inorganic compounds in the dark at 20°C over a period of 5 days (and therefore it is often called the BOD_5 test). The corresponding reaction is written as follows:

$$C_nH_aO_bN_c + (n + a/4 - b/2 - 3c/4)O_2 \rightarrow nCO_2 + (a/2 - 3c/2)H_2O + cNH_3 \quad (8.62a)$$

NOD is significant in nitrified wastewater effluents. The reaction is:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad (8.62b)$$

One must inhibit nitrification in order to distinguish between carbonaceous and nitrogenous BOD.

Sewage discharged into surface waters should have values for COD and BOD that fall below the established limits. Values which are above these limits indicate that the organic content of the sewage is too high for its discharge into receiving waters. Such a discharge could cause a substantial reduction in the oxygen level of the water with serious consequences for aquatic organisms. In practice, the quality of sewage effluents varies enormously from country to country and from place to place. Because of the high cost of sewage treatment, nothing more is done other than what the regulation-requires. This even occurs in developed countries.

There are thousands of naturally-occurring organic compounds, not all of which can be degraded with equal ease. Simple sugars and starches are rapidly degraded; cellulose (a polysaccharide) degrades much more slowly, and hair and fingernails (fibrous proteins) are almost non-degradable in the BOD test or in normal wastewater treatment. Other compounds lie between these extremes.

Microorganisms are limited in their ability to utilize organic compounds as carbon and energy sources. Consequently, many organic compounds can only be degraded by a small group of microorganisms.

8.4.2.2 Nutrients

Nitrogen and phosphorus—two nutrients of primary concern—are considered pollutants because they are essential nutrients for living organisms to grow. Thus, they must be present in rivers and lakes to support the natural food chain. Problems arise when these nutrient levels become excessive and the food web is grossly disturbed, causing some organisms to proliferate at the expense of others. As discussed in Section 6.1.3.2, excessive nutrient concentrations often lead to *eutrophication*—a process in which lakes gradually become shallower and more productive through the introduction and cycling of nutrients.

Oligotrophic lakes have a limited supply of nutrients and a low capacity to support a food web. These lakes gradually pass through the *mesotrophic* and *eutrophic* stages, as nutrient availability increases and algal growth supplies food for higher organisms. A more productive lake will usually have a higher fish population, but water quality is reduced as algal death and its decomposition is sufficient to deplete dioxygen. *Senescent* lakes have thick organic sediments and rooted plants in abundance until they fill up completely. The time for this process to occur depends on the original size of the lake and on the rate at which sediments and nutrients are introduced. In some lakes the natural eutrophication process is so slow that thousands of years may pass with little change in water quality. *Cultural eutrophication* is caused when human activity speeds natural processes by increasing the rate at which sediments and nutrients are added to the lake. Some major sources of nutrients include phosphorus-based detergents, fertilizers, and food-processing wastes. Thus, lake pollution can be seen as the intensification of a natural process.

8.4.2.3 Pathogenic Organisms

Untreated sewage is a major public health hazard because it is a major pathway in the spread of many infectious diseases. The excrement from humans and other animals infected with certain pathogens (e.g., disease-causing bacteria, viruses, and other parasitic organisms) contains large numbers of these organisms or their eggs. Even after the symptoms of disease disappear, an infected person or animal may still harbor low populations of the pathogen, thus continuing to act as a disease carrier. If wastes from carriers contaminate drinking, swimming, or bathing water or food, the pathogens can gain access to and infect other individuals (Table 8.6).

Before the connection between disease and sewage-carried pathogens was recognized in the mid-18th century, disastrous epidemics were common. For example, typhoid fever and cholera killed thousands of persons in different cities. Today, public-health measures have prevented this disease cycle; examples include purification and disinfection of public water supplies with chlorine or other agents, sanitary collection and treatment of sewage wastes, and maintenance of sanitary standards in all facilities where food is processed or prepared for public consumption.

TABLE 8.6. Infectious agents present in polluted wastewater

Infectious agent	Disease
Salmonella typhi (bacteria)	typhoid fever
Vibrio cholerae (bacteria)	cholera
Salmonella SP (bacteria)	salmonellosis
Escherichia coli (bacteria)	diarrhea
Hepatitis A virus	infectious hepatitis
Shigella sp. (bacteria)	dysentery
Entamoeba histolytica (protozoan)	dysentery
Giardia intestinales (protozoan)	giardiasis
Roundworms, flatworms	several parasitic diseases

Nevertheless, in many parts of the world—and largely because of poor sanitation regarding water and sewage—a significant portion of the world's population is chronically infected. More than 250 million new cases of water-borne disease are reported each year, about 10 million of which result in death (about 50% of these are children under five).

The routine examination of environmental samples for the presence of intestinal pathogens is often a tedious, difficult, and time-consuming task. Thus, it has been customary to tackle such examinations by looking for certain microorganisms whose presence indicates that pathogenic microorganisms may also be present. For example, coliform bacteria, which normally occur in the intestines of all warm-blooded animals, are excreted in great numbers in feces. In polluted water, coliform bacteria are found in densities roughly proportional to the degree of fecal pollution. Many countries have adopted coliforms as official standards for drinking water, recreational bathing waters, wastewater discharges, and various foods.

For example, the average density of fecal coliforms in human excreta is 1.3×10^7/g. The US EPA has set a standard of no detectable coliforms per 100 mL in drinking water. In contrast, the Clean Water Act indicates 200 fecal coliforms/100 mL for wastewater discharges.

8.4.2.4 Suspended Solids

Wastewater contains a wide variety of suspended solid materials. The classification of the various solids is shown in Figure 8.3. *Total solids* are obtained by evaporating a sample of wastewater to dryness at 103–105°C. A filtration step separates the *total suspended solids* (*TSS*), which remain on the filter, from the *total dissolved solids* (*TDS*), which pass in the filtrate. The residue that remains after the *TS* are ignited at 500°C is called the *total fixed solids* (*TFS*), and they represent the inorganic salts in the sample. The solids that are volatilized

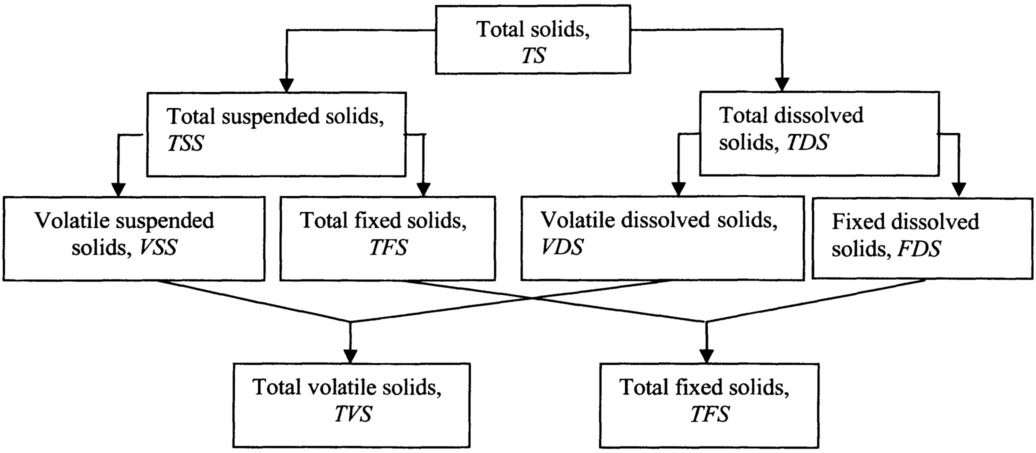


FIGURE 8.3. Types of solids in water and wastewater.

and burned off are the *total volatile solids (TVS)* and they represent the organic matter, including microorganisms. As can be seen in Figure 8.3, both *TSS* and *TDS* include volatile and fixed solids. They are all reported as mg/L.

The term *settleable solids* applies to suspended solids that settle under quiescent conditions because of the influence of gravity. Their measurement is important in engineering practice to determine the need for sedimentation units and the physical behavior of waste streams entering natural water bodies. Colloidal particles do not settle readily and cause the turbidity found in many surface waters.

In turbid waters, most of the harmful organisms are exposed to the action of a disinfectant. However, in cases in which turbidity is caused by municipal wastewater solids, many of the pathogenic organisms may be encased in the particles and protected from the disinfectant. For this and for aesthetic reasons, the U.S. Environmental Protection Agency has placed a maximum contaminant level of 0.5 to 1.0 units of turbidity in public water supplies, depending on the treatment process.

Turbidity is a measure of the light-transmitting properties of water. The measurement of turbidity is based on comparison of the intensity of light scattered by a sample to the light scattered by a reference suspension under the same conditions. The most widely used standards are prepared with hydrazine sulfate and hexamethylenetetramine in water, and give rise to the Formazin Turbidity Units (FTU).

The amount of suspended matter in wastewater increases with the degree of pollution. Sludges represent an extreme case in which most of the solid matter is suspended. The determination of suspended solids is therefore valuable in the analysis of polluted waters. It is one of the major parameters for evaluating the "strength" of domestic wastewaters and for determining the efficiency of treatment units.

8.4.2.5 Oil and Grease Spills

Oil spills represent an important hydrocarbon input into oceans, surface water, and groundwater. They are produced by accidents (e.g., ship, train, or truck wreckages), lack of maintenance (e.g., corroded pipelines), neglectfulness (e.g., car oil changes that end up in the sewage), and the like. Oil spills imply the discharge of mineral oils and petroleum products. They are composed of low- and high-molecular weight aliphatic, aromatic, and naphtenic (mono and polycyclic) hydrocarbons, as well as high-molecular weight unsaturated heterocyclic compounds (e.g., resins and asphaltenes). Generally, the oil will spread in the bodies of water in dissolved, film, emulsion, or sorbed fractions, and there will be a transformation of some of these compounds through microbiological, chemical, and photochemical processes. The lighter fractions (VOCs) will tend to volatilize, whereas the most persistent will be the heavy high-molecular weight PAHs.

The effects of oil in aquatic media are multiple. Besides physically affecting aquatic organisms, many of these substances are toxic and carcinogenic. Oil-transporting ship wreckages represent a serious danger to the physical environment and living species surrounding the accident area. As an example, it is estimated that the tragic accident involving a major oil-spill on the coast of Spain, back in 2001, will still take many years to clean-up.

Another effect of oil spills consists in the formation of oil emulsions that block the entrance of light into bodies of water, with the concomitant decrease in biological activity and cleansing action. Lastly, oil-polluted water is very negative to the public eye.

One effect of immediate concern is the fact that the large majority of water treatment plants throughout the world use chlorine as a disinfecting agent. Unfortunately, chlorine is capable of halogenating many organic materials (including oil components) which produce harmful organochlorinated compounds.

8.4.2.6 *Metallic and Metalloid Compounds*

As discussed earlier, many metals and their ions have become widespread in the environment through many human activities, the main ones being industrial processes (e.g., mining and smelting). The mining of metals may bring about considerable amounts of mine drainage, deleterious to the surroundings. This point is discussed below (Section 8.4.3).

As discussed in Chapters 3 and 6, the availability and chemical form of aqueous metal species depend on several factors, the most important of which are, as a rule, the pH of the solution and the nature and concentration of complexing agents present. As mentioned in those chapters, the ensuing distribution of species (*speciation*) plays a key role in their effects (e.g., toxicity, as discussed in Chapter 9). Prediction of such effects with laboratory tests becomes increasingly difficult when the metal-containing stream undergoes drastic changes during its normal course (e.g., mixing with acid rain) or when it is discharged into receiving waters with very different pH values.

Metals may become "locked up" in the bottom sediments of aquatic systems by chemical reactions, where they may remain for many years. However, metal solubility increases if the pH falls and they become more mobile. In fact, one of the knock-on effects of acid rain is the transport of metals to lower levels in the soil profile, where they may damage deep-rooted plants and contaminate groundwater. A further example of the effect of pH is the metal ion uptake by crops which can multiply several times by a one unit pH decrease.

In addition to health concerns, the presence of metal ions in water can bring about side effects such as bad taste, increase in turbidity and coloration, staining of fixtures in contact with water, and the like. Iron and manganese ions may also promote bacterial growth with its concomitant drawbacks (e.g., foul smell). Fortunately many methods of treatment are available, as discussed in Chapter 10.

8.4.2.7 *Radionuclides*

Aside from accidents in nuclear facilities (e.g., Chernobyl), the main source of anthropogenic radioactive pollution is probably derived from medical applications. Documented reports of radioactive residue mismanagement indicate that sometimes these substances end up in garbage dumps, with the consequent danger of public exposure. The main radioactive isotopes in medical applications are listed in Table 8.7.

The main natural source of dangerous radioactivity is probably Rn. (See Section 8.4.1).

8.4.2.8 *Detergents (Surfactants) and Nutrient Enrichment*

The most common synthetic type of detergent used up to the late 1960s was an alkyl aryl sulfonate that turned out to be very slowly biodegradable due to its branched structure (see Section 9.1.3). This problem is now avoided by replacing the branched alkyl part with less branched (or more linear) structures such as in the anionic detergent, dodecyl benzenesulfonate, ABS. In the formulation of a commercial product, the detergent molecule itself constitutes only between 1/3 and 1/10 of the total preparation. Polyphosphate anions (e.g., $P_3O_{10}{}^{5-}$) are still widely used in some parts of the world as detergent builders, because they can complex the Ca and Mg ions that are responsible for the hardness of water and for the inability of detergents and soaps to exert their surfactant effects. The complexing ability of polyphosphate can be readily understood in Figure 8.4.

As discussed above, excessive algae growth (*eutrophication*) results when phosphates from detergents and nutrients enter surface waters. Upon

TABLE 8.7. Radioactive isotopes used in medicine*

Isotope name	Symbol	Half-life	Use
Cobalt-60	^{60}Co	5 years	Radiation therapy for cancer
Radium-226	^{226}Ra	1590 years	Radiation therapy for cancer
Iodine-131	^{131}I	8 days	Thyroid function, cancer therapy, liver function
Cobalt-57	^{57}Co	270 days	Vitamin B-12 uptake
Phosphorus-32	^{32}Po	14 days	Skin cancer detection
Sodium-24	^{24}Na	15 hours	Detection of blocked arteries
Chromium-51	^{51}Cr	28 days	Red blood cell volume
Technetium-99	^{99}Tc	6 hours	Images of brain, lung, heart, liver, kidney
Americum-241	^{241}Am	432 years	Osteoporosis detection, heart imaging
Cerium-141	^{141}Ce	32.5 days	Gastrointestinal tract diagnosis, measuring regional myocardial blood flow
Europium-155	^{155}Eu	4.73 years	Osteoporosis detection
Gallium-68	^{68}Ga	68.1 min	Study of thrombosis and atherosclerosis, PET imaging, detection of pancreatic cancer, attenuation correction
Thallium-201	^{201}Tl	3.04 days	Radionuclide injected into patients to allow analysis of heart conditions
Ytterbium-169	^{169}Yb	32 days	Gastrointestinal tract diagnosis

*Note: The principles of radioactivity and associated definitions are discussed in Section 3.4.

death of the algae, their microbial degradation can dramatically increase the water's oxygen demand and thus lower its quality by reducing its life-sustaining ability. Furthermore, algae impede the access of incoming light into lower regions of the water reservoirs and thus affect their natural photochemical processes. Polyphosphates can act as ligands and as such they show additional environmental effects, including alteration of metal ion solubility and the dissolution of solid natural oxides (see Section 8.4.3).

8.4.2.9 Salts

A high concentration of salts is discharged by many industries. Furthermore, the use of salt on roads during winter causes high salt levels in urban runoff, especially during the spring snowmelt. Of particular concern in arid regions, where water is extensively used for irrigation, is the fact that water picks up salts every time it passes through the soil on its way back to the river. In addition, evaporation causes the salts to become further concentrated. Thus, salt concentration continuously increases as the water moves downstream. If this parameter becomes too high, crop damage or soil poisoning may ensue. A different problem occurs in normally fresh water, because as salt concentration increases the water may reach the point where either the natural population of plants and animals is threatened or the water is no longer useful for public water supply or irrigation.

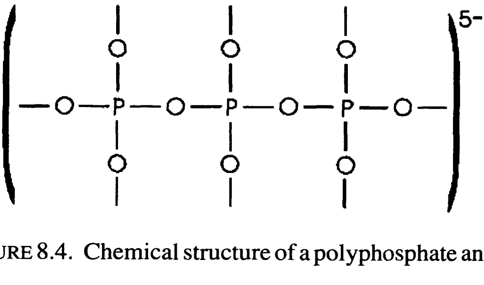


FIGURE 8.4. Chemical structure of a polyphosphate anion.

Salts can be determined as TDS or by measuring the conductivity of the solution (i.e., the ability of a solution to conduct an electric current). The electrical conductivity in SI units can be expressed as milliSiemens/m (mS/m) or in micromhos per centimeter (μmho/cm); 1mS/m is equivalent to 10 μmho/cm, and 1S = 1mho.

8.4.2.10 Heat

Although heat is not often recognized as a pollutant, individuals in the electric power industry are well aware of the problems involved in the disposal of waste heat. Furthermore, waters released by many industrial processes are much hotter than the receiving waters. While in some cases an increase in water temperature can be beneficial (e.g., the production of clams and oysters can increase), in other cases it can have negative impacts. For example, many important commercial and game fish (e.g., salmon and trout) live only in cool waters. Higher water temperatures also increase the rate of dioxygen depletion in areas where oxygen-demanding wastes are present.

The quality of sewage discharged into surface waters depends on the quality of the raw sewage received by the sewage works and its treatment.

8.4.2.11 Other Contributions

Many other pollutants enter water reservoirs daily and to present them in this limited space would be virtually impossible. One example involves plastic debris, which can erode and become microscopic fragments in the form of granules or fibers small enough so as to be ingested by small organisms, posing a substantial threat to their lives. Larger pieces of plastic (e.g., bags) can be dangerous to animals such as turtles that may ingest them or be strangled by them; to make matters worse, in the ocean such materials resemble food (e.g., jelly fish).

8.4.2.12 Groundwater Pollution

Groundwater (see definition in Chapter 6) may be contaminated by several anthropogenic sources, the main ones being septic systems and cesspool effluents, animal wastes, agricultural runoff, re-use of irrigation water, industrial wastewater impoundments, acid mine drainage, underground wells for waste injection, underground storage tanks, highway de-icing salts, leaking pipelines, accidental spills, and landfill leachates. Leachates are liquid effluents generated at landfill sites—they contain soluble and/or suspended pollutants resulting from the percolation of water through the waste.

Natural pollution of groundwater can also occur, albeit to a lesser extent; examples include the mineralization of soluble aquifers and arsenic dissolution. Groundwater pollution is much less reversible than that of surface waters and also considerably more difficult to tackle, because most cleansing microorganisms work aerobically (see Chapters 7, 9, and 11), and groundwater is normally not in contact with a fresh dioxygen supply. Furthermore, light-promoted cleansing processes obviously cannot occur here.

8.4.2.13 Surface Waters

The discharge of sewage into surface waters is a major global source of pollutants. Domestic and industrial wastes are mainly discharged into sewage systems (industrial wastes are sometimes directly discharged into surface waters). The sewage quality depends on the quality of the raw sewage received by the sewage works and on its treatment. Urine, feces, paper, soap, and synthetic detergents are important constituents of domestic waste. Industrial wastes are many and quite varied; their quality depends on the nature of the individual source operations. A diversity of treatments may be carried out at sewage works to improve the quality of sewage before it is discharged into surface waters (see Chapters 10 and 11).

Pollutants in surface waters are transported by rivers either in the dissolved or in the particulate states, and they may later accumulate in lakes or in the estuaries into which they flow. Ocean currents can transport pollutants over long distances.

8.4.3 Effects of Pollutants on the Lithosphere

Of particular importance is the contamination of soil, because it receives pollutants from the atmosphere (e.g., sulfates and nitrates resulting from oxidation of nitrogen and sulfur oxides, and metals from smelters) and from the hydrosphere (e.g., sediments that concentrate heavy metals from aqueous bodies and mining operations). In multimedia mass-balance models, soil is an important sink as well as a conduit for mass transfer to vegetation and shallow groundwater.

Soils are the main and ultimate culprit of many different human exposure pathways to pollutants through the food chain, partly because lipophilic compounds that reside mainly in soils dissolve pesticides, herbicides, and the like.

8.4.3.1 Transformation of Pollutants in Soils

Soil pollutants may percolate and end up in groundwater, or be retained by a soil matrix due to their affinity for specific soil components (e.g., insoluble organic compounds in humic substances). There, they may stay inactive, decompose, or react with soil components or with other pollutants. Reactions from these types of pollutants with soil include oxidation, reduction, combination, precipitation, dissolution, and metathesis. The main decomposition pathways include biodegradation (see Section 9.1.2), chemical degradation, and photolysis (only for surface species); the final product(s) may or may not be more environmentally friendly than the starting material. For instance, trichloroethylene photodecomposes on clays (e.g., on Ca-montmorillonite), and primarily yields the carcinogenic dichloroacetic acid, whose potency is greater than that of trichloroethylene.

8.4.3.2 Transport, Mobility, and Partitioning of Pollutants in Soils

A given pollutant may penetrate in soil down to a specific depth, and therefore transport calculations need individual depth data. Owing to mass transport restrictions, residence times of many pollutants in soils are (unfortunately) much longer than those in the gas or liquid phases. In addition, partitioning effects in soils can be dramatic; a case in point is the concentration effect that occurs with uranium, which sometimes reaches levels up to 10^4 times higher than its concentration in water with which the soil is in equilibrium. Biota plays a key role in the transport and mobilization of pollutants from soil, because for example, many of them bioaccumulate in vegetation and cattle (see Section 9.2).

Land is also contaminated by aerially-transported materials. Smoke and dust from chimneys can fall on neighboring land, carrying along a variety of organic and inorganic pollutants. Gases such as sulfur dioxide and nitrogen oxides, released from chimneys, may cause damage to vegetation in the neighborhood of industrial premises. Additionally, as with surface waters, atmospheric pollutants reach land after traveling considerable distances. They are carried down by rain or snow, in solution or suspension, or by dust particles.

Partitioning and mobility of metal ions, metal complexes, and ligands in soils or sediments are affected by their adsorption onto a variety of substrates. As mentioned earlier (see Section 6.3.1), natural oxides offer suitable adsorption sites for some of these species and may even undergo dissolution as a result. Here, an understanding of the bonding phenomena is crucial. For example, the adsorption of [Co(III)EDTA] (here written as $[ML]^-$) on hydrated aluminum oxide surfaces (written as $\equiv AlOH$) can be represented as:

$$\equiv AlOH + [ML]^- + H^+ \rightarrow \equiv AlOH_2^+ \text{—} ^-[LM] \qquad (8.63)$$

It involves an outer-sphere mechanism (see Section 3.1.4) because the four carboxylate groups in the monovalent $[Co(III)EDTA]^-$ complex are coordinated to the metal center, whereas in the divalent $[Co(II)EDTA]^{2-}$ complex, one carboxylate group is free to coordinate with the surface and thus it adsorbs through an entirely different path.

Polyphosphates also play a role in the chemistry of natural metal oxides. For example, if the concentration of polyphosphates is smaller than that needed to saturate the available sites of a solid oxide surface, their presence *enhances* the sorption of surrounding metal ions; by contrast, if their concentration exceeds that needed to saturate the surface, their presence *decreases* metal ion sorption due to two effects:

(a) Competition between dissolved and surface polyphosphates for the target metal ions.
(b) Dissolution of the oxide itself by the action of the polyphosphates. For example, phosphates compete so successfully with metal–EDTA species for adsorption sites onto natural iron oxides (e.g., goethite), that the metal complex can be desorbed completely under appropriate conditions of pH and concentration.

As discussed above, soil pH may play a major role in its interactions with pollutants. Species distribution diagrams (see Chapter 2) set the framework to know which species are predominant at a given pH. For example, phosphates have the predominance-zone diagram shown in Figure 8.5.

Because soils typically have surface hydroxyl groups, low pH values allow their protonation and render the surface positive or neutral. The OH_2 groups thus formed are easier to displace from the surface-bonding sites than the OH groups, and therefore ligand exchange reactions with the negatively-charged phosphate groups occur more easily at low pH. On the other hand, at high pH the excess of OH^- in solution removes protons from the surface, making it negative; as a result, the negatively-charged phosphate groups become electrostatically repelled and adsorption does not occur.

8.4.3.3 Agriculture and the Chemistry of Soils

Soils receive vast amounts of fertilizers, soil additives (e.g., gypsum and sulfur), pesticides, and

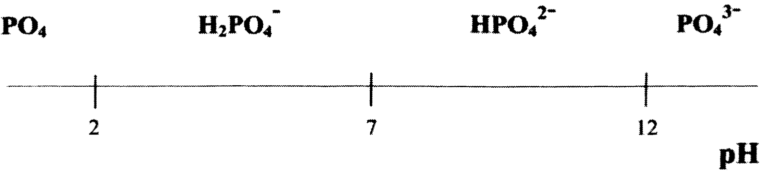


FIGURE 8.5. Predominance-zone diagram for phosphates.

herbicides as a result of their application to crops. Biocides are used for the control of vertebrate and invertebrate pests, weeds, and other vectors of disease. This is important in areas of intensive agriculture, where a variety of different pesticides are used during the course of a farming year; they are applied in different forms, as sprays, granules, dusts, and seed dressings. The method of application and the nature of the formulation influence the ways in which pesticides are distributed in the crops and soils. They sometimes move through the soil to contaminate groundwater, especially where there are cracks in the soil profile that allow rapid percolation of water.

Apart from agricultural applications, pesticides are applied over large areas for other purposes such as the control of the tsetse fly and locust swarms in Africa.

The use of sewage sludge as fertilizer on agricultural land is another source of pollution. Heavy metals, nitrates, phosphates, and detergents are all added to soil in this way.

As mentioned earlier, high salt contents in water (e.g., Na, Ca, and Mg sulfates) in contact with soils produce *salinization* (i.e., excess salinity). Other causes of salinization include high water tables, high evaporation rates, and low annual rainfall. Excessive salinity makes it more difficult for plant roots to take in water, which considerably reduces crop yields and also degrades the quality of shallow groundwater and of surface water.

8.4.3.4 Metals and Mining Processes

Metals constitute an important source of pollution in soils. As discussed in Chapters 5 and 6, they can bind to soils through humic substances, surface complexation, or ion exchange. In some cases more than one type of interaction can occur, as in clay minerals (e.g., montmorillonite and vermiculite) that bind metals through ion exchange as well as surface complexation. The extent of such interactions obviously affects metal ion leaching, plant uptake, and related phenomena. It is then clear that an inevitable overlap exists between the discussion of this subject here and that in the sections dealing with the effects of metallic pollutants in the hydrosphere.

Metal contamination of soils is primarily due to the application of sewage sludge, manure, phosphate fertilizers, atmospheric deposition, and traffic emissions. The most common heavy metal ions found in soils are Zn, Cu, Ni, Pb, Cr, and Cd. As mentioned earlier (see Section 6.3.1.4), sequential extraction techniques can differentiate among the metal forms in a soil, typically the *acid soluble* fraction (e.g., carbonates), the *reducible* fraction (e.g., iron/manganese oxides), and the *oxidizable* fraction (i.e., metals in low oxidation states).

Among other minerals, metal sulfides are nearly ubiquitous in the environment. When they become exposed to air as a result of mining processes, they become oxidized. Microorganisms typically mediate this process, although pure chemical oxidation is also possible. After coming into contact with water (mainly rainwater), these minerals form aqueous solutions that are notably acidic and are generically called *acid mine drainage* (*AMD*). Because Fe is often the main metal present, AMD can be represented by the equation

$$FeS_{2(S)} + H_2O_{(l)} + 7/2O_{2(g)} \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{8.64}$$

The Fe^{2+} thus produced oxidizes to Fe^{3+} in air at low pH, albeit very slowly. Then, Fe^{3+} can either hydrolyze and form insoluble Fe(III) hydroxide, or act as a secondary oxidant to FeS_2:

$$\begin{aligned} &FeS_{2(s)} + 14Fe^{3+} + 8H_2O_{(l)} \\ &\quad \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \end{aligned} \tag{8.65}$$

TABLE 8.8. Extremely acidic solutions in the environment

Site	Location	pH	Comments
Kawah Ijen	Java Island	0 to 0.2	Lake waters
Kilauea Iki	Hawaii	−0.3	HCl – HF fumarolic condensates
Poas crater	Costa Rica	−0.9	Lake waters
Ebeko volcano	Kurile Islands, Russia	−1.7	HCl – H_2SO_4 hot springs
Iron Mountain	California	1.5 to −3.6	AMD

Source: Nordstrom, 2000.

The residues obtained after the main mineral or metal has been extracted are called *mine tailings*. They normally appear in a substantially divided form (as a result of crushing and grinding) and therefore have high surface areas that favor the previous reactions. The ensuing production of protons and sulfate ions yields H_2SO_4, which can dissolve minerals and therefore increase the metal and non-metal ion content and acidity in nearby surface waters, in groundwaters, and in the corresponding receiving bodies of water. For example, arsenic builds up in particular areas when the sulfide minerals contain this element. In addition, the AMD process promotes downstream deposition of insoluble Fe(III) species. When the water table is near the surface, capillary rise and evaporation may also contaminate the upper soil layers. Amazingly, tailing dumps can be oxidized at depths of even 5 m.

As shown in Table 8.8, quite acidic solutions exist in the environment as a result of AMD and other natural environmental phenomena (mainly produced by magmatic gases: HCl, HF, H_2SO_4).

8.4.3.5 *Other Wastes and Pollutants in Soil*

The dumping of wastes at landfill sites is a widespread practice. Indeed, many old sites can be regarded as ecological "time bombs." Hazardous substances in landfills are typically mixed with other wastes and with soil itself, which unfortunately makes their treatment rather complicated. The wastes at landfills commonly involve:

- Solid wastes. These mainly include waste paper, food, yard, and street wastes, plastic trash, metal objects, and septic tank residues.
- Industrial wastes. They vary widely, including items such as thick organic waste (e.g., tars), residual construction materials, pollution-treatment wastes, scrap, personal waste and safety items, and other various types of solid trash.
- Sewage sludge. This is the solid material produced in wastewater treatment plants. It contains residues from residential and commercial settings, storm-water runoff, and others.

On the other hand, there is the question of disposal of domestic and general industrial wastes. There are toxic wastes which require more careful handling. Of particular concern are radioactive wastes from nuclear power stations. With the latter, there are stringent regulations for safe disposal to minimize contamination of the land surface and neighboring surface waters.

Lastly, non-ionic organic pollutants can also adsorb onto soil from water. This constitutes a major process in pollutant transport/mobility in subsurface environments. Both the organic fraction of soils and the clay minerals can play key roles as adsorption sites.

Related Experiments in the Companion Book

2. Dissolved oxygen in water
3. Alkalinity and buffering capacity of water
7. Air oxidation of metal ions
8. Photoassisted reduction of metal complexes
9. Anionic detergents and *o*-phosphates in water
11. Acid mine (or acid rock) drainage
15. Removal of nitric oxide by complex formation

Additional Related Experiments/Activities

Adelheim, M.; Höhn, E.-G. "A Simple Demonstration of the Greenhouse Effect," *J. Chem. Educ.* **1993**, *70*, 73–74.

Abney, J. R.; Scalettar, B. A. "Saving your Students' Skin. Undergraduate Experiments that Probe UV Protection by Sunscreens and Sunglasses," *J. Chem. Educ.* **1998**, *75*, 757–760.

Andino, J. M.; Wallington, T. J.; Hurley, M. D.; Wayne, R. P. "A Classroom Demonstration of the Formation of Aerosols from Biogenic Hydrocarbons," *J. Chem. Educ.* **2000**, *77*, 1584–1586.

Baedecker, P. A.; Reddy, M. M. "The Erosion of Carbonate Stone by Acid Rain—Laboratory and Field Investigation," *J. Chem. Educ.* **1993**, *70*, 104–108.

Baker, R. C., Jr. "Checking Trace Nitrate in Water and Soil Using an Amateur Scientist's Measurement Guide," *J. Chem. Educ.* **1995**, *72*, 57–59.

Bauer, R.; Birk, J.; Sawyer, D. *Laboratory Inquiry in Chemistry*, 2nd ed.; Brooks-Cole: Stamford, CT, 2005.

- How much cobalt is in the soil? (Experiment 17)

Betterton, E. A. "Acid Rain Experiment and Construction of a Simple Turbidity Meter," *J. Chem. Educ.* **1991**, *68*, 254–256.

Bilanovic, D.; Loewenthal, R. E.; Avnimelech, Y.; Green, M. "Potentiometric Measurement of Chemical Oxygen Demand," *Water SA* **1997**, *23(4)* 301–309.

Blume, R.; Bader, H. J. *Environmental Chemistry in Classroom Experiments*; IUPAC Publication, S. M. V. Traders and Printers: Delhi, 1990.

- Preparation of NO and NO_2 (Experiment 2)
- Preparation of nitrogen dioxide (Experiment 3)
- The test of NO*x* and nitrite ions: Lunge's reagent (Experiment 5)
- The test of NO*x* in exhaust gases and cigarette smoke (Experiment 6)
- The oxidizing effect of nitrogen oxides (Experiment 7)
- Preparation and detection of hydrogen sulfide (Experiment 11)
- Model experiment on the effect of H_2S as a respiratory poison (Experiment 13)
- Reducing properties of hydrogen sulfide (Experiment 14)
- Roasting of pyrites (Experiment 21)
- Model experiment on the limestone process (Experiment 25)
- Preparation of carbon monoxide (Experiment 28)
- Test for carbon monoxide (Experiment 29)
- Test for carbon monoxide in tobacco (Experiment 30)
- Test for carbon monoxide in exhaust gases (Experiment 31)
- Test for freons (CFC's) in the propellant gas of sprays (Experiment 45)
- Model experiment on the reactive nature of chlorine atoms (Experiment 46)
- Combustion products of PVC (Experiment 49)
- Analysis of rain water (Experiment 50)
- Effect of heavy metal salts on the activity of enzymes (Experiment 56)
- Model experiment on ground water pollution (Experiment 57)
- Model experiment on the processes in a refuse incineration plant (Experiment 61)
- Determination of degree of pollution of water (Experiment 109)
- Test for nitrate and nitrite in drinking water reduction; reduction of nitrate to nitrite (Experiment 119)
- Phosphate determination in surface water (Experiment 122)
- Adsorption of phosphate ions by aluminum oxide (Experiment 124)
- Emulsifying action of detergents (Experiment 125)
- Water softeners in action (Experiment 126)
- Sequestering a detergent by adsorbing resins (Experiment 128)

Boehnke, D. N.; Delumyea, R. D. *Laboratory Experiments in Environmental Chemistry*; Prentice-Hall: New York, 1999.

- Determination of oils and greases by Soxhlet extraction (Experiment 14)
- Determination of oil-spill sources using pattern recognition of known petroleum product gas chromatograms (Experiment 17)
- Properties of detergents: surface tension measurement of critical micelle concentration (Experiment 20)
- Introduction to air sampling: particulates in urban air (Experiment 21)
- Collection and chemistry of acid rain (Experiment 23)

Brouwer, H. "Demonstration Properties of Sulfur Dioxide," *J. Chem. Educ.* **1991**, *68*, 417.

Brouwer, H. "Acid Volatile Sulfides (AVS) in Sediment. An Environmental Chemistry Experiment," *J. Chem. Educ.* **1995**, *72*, 182–183.

Buell, P.; Girard, J. *Laboratory Manual for Chemistry Fundamentals*, 2nd, ed.; Jones and Bartlett: Boston, MA, 2002.

- Nuclear radiation (Experiment 8)
- Acid rain (Experiment 11)
- Environmental sampling (Experiment 22)

Butala, S. J.; Zarrabi, K.; Emerson, D. W. "Sampling and Analysis of Lead in Water and Soil Samples on a University Campus- A Student Research Project," *J. Chem. Educ.* **1995**, *72*, 441–444.

Caldararu, F.; Patrascu, S.; Caldararu, M.; Paraschiv, A. "Higher Education Level Laboratory for Real Time Pollution Monitoring," *Int. Geosci. Remote Sens. Symp. (IGARSS)* **2003**, *7*, 4587–4589. IEEE. Toulouse, France, Jul 21–25 2003.

Casey, R. E.; Pittman, F. A. "Intermolecular Forces as a Key to Understanding the Environmental Fate of Organic Xenobiotics," *J. Chem. Educ.* **2005**, *82*, 260–264.

Christensen, J. K.; Hoyer, B. L.; Kryger, L.; Pind, N.; Kong, L. S. "Sulfides in the Anaerobic Environment: The Determination of Hydrogen Sulfide and Acid-Soluble Metallic Sulfides in Sea-Floor Sediment," *J. Chem. Educ.* **1998**, *75*, 1605–1608.

Cirsp, P. T.; Eckert, J. M.; Gibson, N. A. "The Determination of Anionic Surfactants in Natural and Waste Waters", *J. Chem. Educ.* **1983**, *60*, 236–238.

Clemson University. *Introductory Chemistry Lab Experiments in Environmental Chemistry*; Environmental Chemistry Library. National Science Foundation, 2002. http://www.ces.clemson.edu/ecl/labs/general/index.html

- Phosphate determination
- Sulfate determination
- Chloride determination
- Total suspended solids
- Total dissolved solids
- Soap and detergents
- Fertilizer and water quality

Dacko, B. M.; Giulano, L. "Why do Some Turds Float? Wastewater Chemistry in the Classroom," *214th Am. Chem. Soc. Nat. Meet.*, Chem. Ed. Division Paper # 068. Las Vegas, NV, Sept. 7–11, 1997.

Daniel, D. W.; Allen, Alisha G.; Brown, Gregory R.; Chandrupatla, Hareesh; Fowler, Steve A.; Richmond, Deondre J.; Skipper, Shaun W.; Taylor, Jason A.; Waslak, Amy E. "A Simple UV Experiment of Environmental Significance," *J. Chem. Educ.* **1994**, *71*, 83.

Dingrando, L.; Tallman, K.; Hainen, N; Wistrom, C. *Chemistry: Matter and Change (Lab Manual)*; Glencoe Science/McGraw-Hill Ryerson: New York, 2005.

- Growth of algae as a function of nitrogen concentration (Experiment 26.2)

Dolan, E.; Zhang, Y.; Klarup, D. "The Distribution Coefficient of Atrazine with Illinois Soils: A Laboratory Exercise in Environmental Chemistry," *J. Chem. Educ.* **1998**, *75*, 1609–1610.

Driscoll, J. A. "Acid Rain Demonstration: The Formation of Nitrogen Oxides as By-Products of High Temperature Flame in Connection with Internal Combustion Engines," *J. Chem. Educ.* **1997**, *74*, 1424–1425.

Dunnivant, F. M.; Moore, A.; Alfano, M. J.; Brzenk, R.; Buckley, P. T.; Newman, M. E "Understanding the Greenhouse Effect: Is Global Warming Real? An Integrated Lab-Lecture Case Study for Non-science Majors," *J. Chem. Educ.* **2000**, *77*, 1602–1603.

Epp, D. N.; Curtright, R. "Acid Rain Investigations", *J. Chem. Educ.* **1991**, *68*, 1034–1035.

Gleason, G. I. "Nitric Acid in Rain Water," *J. Chem. Educ.* **1973**, *50*, 718–719.

Godfrey, P. J. "Acid Rain: The Scientific Challenge," *Sci. Prob.* **1991**, *1 (3)* 71–80.

Goss, K. U.; Schwarzenbach, R. P. "Rules of Thumb for Assessing Equilibrium Partitioning of Organic Compounds: Successes and Pitfalls," *J. Chem. Educ.* **2003**, *80*, 450–455.

Goss, L. M.; Eddleton, J. E. "A Demonstration of Acid Rain and Lake Acidification: Wet Deposition of Sulfur Dioxide," *J. Chem. Educ.* **2003**, *80*, 39–40.

Greco, T. G.; Rickard, L. H.; Weiss, G. S. *Experiments in General Chemistry: Principles and Modern Applications*, 8th, ed.; Prentice Hall: Upper Saddle River, NJ, 2002.

- Investigation of buffer systems (Experiment 20)
- Determination of water hardness (Experiment 26)
- Analysis of common anions and their salts (Experiment 38)

Hollenberg, J. L.; Stephens, E. R.; Pitts, J. N., Jr. "Demonstrating the Chemistry of Air Pollution," *J. Chem. Educ.* **1987**, *64*, 893–894.

Horan, J. H.; Wildeman, T. R.; Ernst, R. "Acid Mine Drainage Laboratory Experiments," *214^{th} Am. Chem. Soc. Nat. Meet.*, Chem. Ed. Division Paper # 005. Las Vegas, NV, Sept. 7–11, 1997.

Howe, A. C.; Cizmas, L.; Bereman, R. "Eutrophication of Lake Wingra: A Chemistry-Based Environmental Science Module," *J. Chem. Educ.* **1999**, *76*, 924–926.

Ibanez, J. G. "Redox Chemistry and the Aquatic Environment: Examples and Microscale Experiments," *Chem. Educ. Int. (IUPAC)* **2005**, *6*, 1–7.

Jackson, G. B. *Applied Water and Spentwater Chemistry. A Laboratory Manual*; Van Nostrand-Reinhold: New York, 1993.

- Color measurement (Experiment 9)
- Turbidity measurement (Experiment 10)
- Specific conductivity measurement (Experiment 12)
- Total suspended solids measurement (Experiment 16)
- Calcium carbonate stability measurement (Experiment 17)
- Total residual chlorine measurement (Experiment 21)
- Chlorine demand measurement (Experiment 22)
- Chloride measurement (Experiment 23)
- Sulfate measurement (Experiment 24)
- Nitrate-nitrogen measurement (Experiment 25)
- Fluoride measurement (Experiment 26)
- Biochemical oxygen demand measurement (Experiment 28)
- BOD_5 toxicity measurement (Experiment 29)
- Glucose-glutamic acid measurement (Experiment 30)
- Chemical oxygen demand measurement (Experiment 32)
- Oil and grease measurement (Experiment 33)
- Volatile acid to alkalinity ratio measurement (Experiment 34)
- Phosphate measurement (Experiment 35)
- Ammonia and organic nitrogen measurement (Experiment 36)
- Methylene blue surface active agents measurement (Experiment 37)
- Iron measurement (Experiment 38)
- Manganese measurement (Experiment 39)
- "Jackson's" modified sulfur dioxide measurement (Experiment 40)
- Residual sulfur dioxide measurement (Experiment 41)

JCE Editorial Staff. "Acid Raindrops Keep Fallin' in my Lake," *J. Chem. Educ.* **2003**, *80*, 40A.

Klausen, J.; Meier, M. A.; Schwarzenbach, R. P. "Assessing the Fate of Organic Contaminants in Aquatic Environments: Mechanism and Kinetics of Hydrolysis of a Carboxylic Ester," *J. Chem. Educ.*, **1997**, *74*, 1440–1444.

Kelter, P. B.; Grundman, J.; Hage, D. S.; Carr, J. D.; Castro-Acuna, C. M. "A Discussion of Water Pollution in the U.S. and Mexico, with High School Laboratory Activities for Analysis of Lead, Atrazine, and Nitrate," *J. Chem. Educ.* **1997**, *74*, 1413–1421.

King, D. M.; Lampman, G. M.; Smith III, J. H. "Nitrate Analysis—A Laboratory Experiment for the Non Science Major Course," *J. Chem. Educ.* **1971**, *48*, 647.

Kohn, H. W. "Student Flowmeter and an Air Pollution Experiment," *J. Chem. Educ.* **1972**, *49*, 643.

Koubek, E. "The Absorption of UV Light by Ozone," *J. Chem. Educ.* **1989**, *66*, 338.

Kriz, Jr., G. S.; Kriz, K. D. "Analysis of Phosphates in Detergents," *J. Chem. Educ.* **1971**, *48*, 551–552.

Lauren, Paul M. "Oxidizing Action of Sulfur Dioxide", *J. Chem. Educ.* **1969**, *46*, A55.

Lee, C. M. "Speciation of Aluminum in Acidified Waters," Environmental Chemistry Library. NSF-Clemson University. Environmental Engineering and Science, Clemson University, 2002. http://www.ces.clemson.edu/ecl/modeling/visual_M/fish/index.html

Lisensky, G.; Reynolds, K. "Chloride in Natural Waters—An Environmental Application of a Potentiometric Titration," *J. Chem. Educ.* **1991**, *68*, 334–335.

Lynam, M. M.; Kilduff, J. E.; Weber, W. J. "Adsorption of *p*-Nitrophenol from Dilute Aqueous Solution: An Experiment in Physical Chemistry with an Environmental Approach," *J. Chem. Educ.* **1995**, *72*, 80–84.

MacLeod, M.; Mackay, D.; Webster, E. "Contaminant Fate Models for Undergraduate and Graduate Education in Environmental Chemistry," *Prepr. Ext. Abstr., Am. Chem. Soc. Nat. Meet., Div. Environ. Chem.* **1999**, *39(2)*, 232–234.

Marsella, A. M.; Huang, J.; Ellis, D. A.; Mabury, S. A. "An Undergraduate Field Experiment for Measuring Exposure to Environmental Tobacco Smoke in Indoor Environments," *J. Chem. Educ.* **1999**, *76*, 1700–1701.

Martin, David P. "Demonstrating the 'Greenhouse' Effect," *J. Coll. Sci. Teach.* **1996**, *25*, 225–228.

Meserole, C. E.; Mulcahy, F. M.; Lutz, J.; Yousif, H. A. "CO_2 Absorption of IR Radiated by the Earth," *J. Chem. Educ.* **1997**, *74*, 316–317.

Mihok, M.; Keiser, J. T.; Bortiatynski, J. M.; Mallouk, T. E. "An Environmentally-focused General Chemistry Laboratory," *J. Chem. Educ.* **2006**, *83*, 250.

http://jchemed.chem.wisc.edu/Journal/Issues/2006/FebACS/ACSSub/ACSSupp/JCE2006p0250W.pdf

- Acid rain deposition (Experiment 7)

Molirig, J. R. "An Introductory Experiment on Phosphates in Detergents," *J. Chem. Educ.* **1972**, *49*, 15–18.

Moore, B. III. "Environment, Education, and Health: The Environment," *Proc. 31st Goddard Mem. Symp., Am. Astronaut. Soc. Sci. Technol. Ser.* **1994**, *83*, 51–56. Arlington, VA, USA, Mar. 9–10, 1993.

Morrison, R. J.; Dandy, A. J. "Phosphate Fertiliser in Soils," *Educ. Chem.* **1979**, *16 (6)* 176–177.

Newton, T. A. "Partition Coefficients—A Lecture Demonstration," *J. Chem. Educ.* **1982**, *59*, 973.

Ophardt, C. E. "Acid Rain Analysis by Standard Addition Titration," *J. Chem. Educ.* **1985**, *62*, 257–258.

Osorio, V. K. L.; de Oliveira, W.; El Seoud, O. A. "Hard Water and Soft Soap: Dependence of Soap Performance on Water Hardness. A Classroom Demonstration," *J. Chem. Educ.* **2005**, *82*, 257–259.

Peterson, J. B.; May, A. "Characterization of Mining/Mineral Processing Waste Using Oxidation/Reduction Potential and pH Measurements," *Proc. Western Reg. Symp. Mining & Min. Process. Wast.* (Soc. for Mining, Metallurgy & Exploration) **1990**, 53–59. Berkeley, CA, USA, May 30–Jun 1 1990.

Powers, D. C.; Higgs, A. T.; Obley, M. L.; Leber, P. A.; Hess, K. R.; Yoder, C. H. "Analysis of Natural Buffer Systems and the Impact of Acid Rain. An Environmental Project for First-Year Chemistry Students," *J. Chem. Educ.* **2005**, *82*, 274–277.

Ramachandran, B. R.; Allen, J. M.; Halpern, A. M. "Air-Water Partitioning of Environmentally Important Organic Compounds: An Environmental Chemistry or Integrated Laboratory Experiment," *J. Chem. Educ.* **1996**, *73*, 1058–1061.

Roesky, H. W.; Mockel, K. *Chemical Curiosities*; VCH: Weinheim, 1996.

- A simple experiment to demonstrate the greenhouse effect (Experiment 94)

Romero, A.; Hernandez, G.; Suarez, M. F. "Photocatalytic Oxidation of Sulfurous Acid," *J. Chem. Educ.* **2005**, *82*, 1234–1236.

Sawyer, C. N.; McCarty, P. L.; Parkin, G. F. *Chemistry for Environmental Engineering*; McGraw-Hill International Editions, Civil Engineering Series: New York, 1994.

- Biochemical oxygen demand (Chapter 22)
- Chemical oxygen demand (Chapter 23)
- Phosphorous and phosphate (Chapter 29)

Schilling, A. L.; Hess, K. R.; Leber, P. A.; Yoder, C. H. "A Simulation of the Interaction of Acid Rain with Soil Minerals," *J. Chem. Educ.* **2004**, *81*, 246–247.

Schonbeck, N. D. "Visualization of Buffer Action and the Acidifying Effect of CO_2," *J. Chem. Educ.* **1985**, *62*, 436–437.

Seeley, J. V.; Bull, A. W.; Fehir, R. J. Jr.; Cornwall, S.; Knudsen, G. A.; Seeley, S. K. "A Simple Method for Measuring Ground-Level Ozone in the Atmosphere," *J. Chem. Educ.* **2005**, *82*. 282–285.

Seymour, P. "Chromium Pollution: An Experiment Adapted for Freshman Engineering Students," *J. Chem. Educ.* **1999**, *76*, 927–928.

Shooter, D. "Nitrogen Dioxide and its Determination in the Atmosphere— A Simple Method for Surveying Ambient Pollution Concentrations," *J. Chem. Educ.* **1993**, *70*, A133–A140.

Solomon, S. Oliver-Hoyo, M.; Hur, C. "Generating Water-Soluble Noxious Gases: An Overhead Projector Demonstration," *J. Chem. Educ.* **1998**, *75*, 1581–1582.

Sipos, L. "Inhibition of Sulfite Oxidation by Phenols: Screening Antioxidant Behavior with a Clark Oxygen Sensor," *J. Chem. Educ.* **1998**, *75*, 1603–1605.

Stephens, E. R. "Gasoline Vapor: An Invisible Pollutant," *J. Chem. Educ.* **1997**, *54*, 682–684.

Suplinkas, R. J. "Air Pollution Measurements in the Freshman Laboratory," *J. Chem. Educ.* **1972**, *49*, 24–25.

Szafran, Z.; Pike, R. M.; Foster, J. C. *Microscale General Chemistry Laboratory with Selected Macroscale Experiments*, 2nd ed.; Wiley: New York, 2003.

- Determination of the source of iron pollution (Experiment 15)

Tandon, R. K.; Finlayson, P.; Adeloju, S. B; "Testing the Waters," *Educ. Chem.* **1994**, *31(6)* 159–161.

Tratnyek, P. G.; Reilkoff, T. E.; Lemon, A. W.; Scherer, M. M.; Balko, B. A.; Feik, L. M.; Henegar, B. D. "Visualizing Redox Chemistry: Probing Environmental Oxidation–Reduction Reactions with Indicator Dyes," *Chem. Educ.* **2001**, *6(3)* 172–179.

Tripp, T. B.; Nadenu, J. L. "Roadside Salt Pollution and the Absorption-Emission Spectra of Sodium—A General Chemistry Experiment," *J. Chem. Educ.* **1974**, *51*, 130.

Urbansky, E. T. "Carbinolamines and Geminal Diols in Aqueous Environmental Organic Chemistry," *J. Chem. Educ.* **2000**, *77*, 1644–1647.

Walczac, M. M. "Should We Build a Copper Mine?", 214th Am. Chem. Soc. National Meeting, Las Vegas, NV, Sept. 7–11, 1997. Chem. Ed. Division Paper #003.

Walczak, M. M.; Lantz, J. M. "A Case on Septic Systems and Well Water Requiring In-Depth Analysis and Including Optional Laboratory Experiments," *J. Chem. Educ.* **2004**, *81*, 218–220.

West, P. W.; Sachdev, S. L. "Air Pollution Studies—The Ring Oven Techniques," *J. Chem. Educ.* **1969**, *46*, 96–98.

Whisnant, D. M.; McCormick, J. A. "BCTC for Windows: Abstract Issue 9903W," *J. Chem. Educ.* **1999**, *76*, 719.

Wildeman, T. R. "Mineral Acidity, APP, ANP, NNP: The Stoichiometry and Quantitative Chemistry of Acid Rock Drainage Explained," *214th Am. Chem. Soc. Nat. Meet.*, Chem. Ed. Division Paper# 006. Las Vegas, NV, Sept. 7–11, 1997.

Wu, R. S. S. "Change of Forms of Cadmium in the Aquatic Environments," *J. Chem. Educ.* **1995**, *72*, 264–265.

Xia, K.; Pierzynski, G. "Competitive Sorption between Oxalate and Phosphate in Soil: An Environmental Chemistry Laboratory Using Ion Chromatography," *J. Chem. Educ.* **2003**, *80*, 71–75.

Xiao, D.; Lin, L., Yuan, H.; Choi, M. M. F.; Chan, W. "A Passive Sampler for Determination of Nitrogen Dioxide in Ambient Air," *J. Chem. Educ.* **2005**, *82*, 1231–1233.

Yappert, M. C.; DuPre, D. B. "Complexometric Titrations: Competition of Complexing Agents in the Determination of Water Hardness with EDTA," *J. Chem. Educ.* **1997**, *74*, 1422–1423.

References and Further Reading

Batty, L. C.; Younger, P. L. "Critical Role of Macrophytes in Achieving Low Iron Concentrations in Mine Water Treatment Wetlands," *Environ. Sci. Technol.* **2002**, *36*, 3997–4002.

Casey, R. E.; Pittman, F. A. "Intermolecular Forces as a Key to Understanding the Environmental Fate of Organic Xenobiotics," *J. Chem. Educ.* **2005**, *82*, 260–264.

Climate Monitoring and Diagnostic Laboratory. http://www.cmdl.noaa.gov/ozone.html

Domènech, X.; Ayllón, J. A.; Peral, J. "Use of Physicochemical Parameters to Assess the Environmental Fate of Organic Pollutants: The Fugacity Model," *J. Chem. Educ.* **2006**, *83*, 237–240.

Fukushi, K.; Sato, T.; Yanase, N. "Solid-Solution Reactions in As(V) Sorption by Schwertmannite," *Environ. Sci. Technol.* **2003**, *37*, 3581–3586.

Grisham, J. "EPA Proposes Plan to Clean up Waterways," *Chem. Eng. News*, Aug. 23, 1999. pp. 10–11.

Goss, K.-U.; Schwarzenbach, R. P. "Rules of Thumb for Assessing Equilibrium Partitioning of Organic Compounds: Successes and Pitfalls," *J. Chem. Educ.* **2003**, *80*, 450–455.

Gustafsson, J. P.; Pechova, P.; Berggren, D. "Modeling Metal Binding to Soils: The Role of Natural Organic Matter," *Environ. Sci. Technol.* **2003**, *37*, 2767–2774.

Halstead, J. A. "Spring Shock! Impact of Spring Snowmelt on Lakes and Streams," *J. Chem. Educ.* **1998**, *75*, 400A.

Hogue, C. "Scuffle over Perchlorate," *Chem. Eng. News*, Nov. 3, 2003. p. 14.

Hogue, C. "North American Pollution," *Chem. Eng. News*, Jun. 7, 2001. p. 8.

Howard, A. G. *Aquatic Environmental Chemistry*; Oxford Chemistry Primers. Oxford Science Publications: Oxford, 1998. Chapter 5.

Howe, A. C.; Cizmas, L.; Bereman, R. "Eutrophication of Lake Wingra: A Chemistry-Based Environmental Science Module," *J. Chem. Educ.* **1999**, *76*, 924–926.

IUPAC (International Union of Pure and Applied Chemistry). Commission on Atmospheric Chemistry, "Glossary of Atmospheric Chemistry Terms", *Pure Appl. Chem.* **1990**, *62*, 2167–2219.

IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F. Jr.; Hynes, R. G.; Jenkin, M. E.; Kerr, J. A.; Rossi, M. J.; Troe, J. "Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry," http:// www.iupac-kinetic.ch.cam.ac.uk/summary/IUPACsumm_web_March2005.pdf

Jones, J.C. "Greenhouse Gases and Non-gray Behavior," *J. Chem. Educ.* **2005**, *82*, 837.

Kaasaainen, M.; Yli-Halla, M. "Use of Sequential Extraction to Assess Metal Partitioning in Soils," *Environ. Poll.* **2003**, *126*, 225–233.

Klausen, J.; Meier, M. A.; Schwarzenbach, R. P. "Assessing the Fate of Organic Contaminants in Aquatic Environments: Mechanism and Kinetics of Hydrolysis of a Carboxylic Ester," *J. Chem. Educ.* **1997**, *74* 1440–1444.

Langmuir, D.; Chrostowski, P.; Chaney, R. Vigneault, B. "Issue Paper on the Environmental Chemistry of Metals," *U.S. Environmental Protection Agency, Risk Assessment Forum*; Draft, Contract # 68-C-98-148: Washington, August 2003.

Lajeunesse, S. "Plastic Bags," *Chem. Eng. News* Sept. 20, 2004. p. 51.

Lewis, A.; Bumpus, J. A.; Truhlar, D. G.; Cramer, C. J. "Molecular Modeling of Environmentally Important Processes: Reduction Potentials," *J. Chem. Educ.* **2004**, *81*, 596–604.

Lide, D. R. *Handbook of Chemistry and Physics.* Chemical Rubber Company (CRC): Boca Raton, FL (USA) (any modern edition).

McKone, T. E.; Bennett, D. H. "Chemical Specific Representation of Air-Soil Exchange and Soil Penetration in

Regional Multimedia Models," *Environ. Sci. Technol.* **2003**, *37*, 3123–3132.

Naicker, K.; Cukrowska, E.; McCarthy, T. S. "Acid Mine Drainage Arising from Gold Mining Activity in Johannesburg, South Africa and Environs," *Environ. Poll.* **2003**, *122*, 29–40.

NASA website. http://www.nas.nasa.gov/Services/Education/Resources/TeacherWork/Ozone/Ozonehomepage.html

Nishikawa, S.; Hill, L.; Kihara, N. "Clean up in Engine R & D: Your Guide to Lowering Exhaust Emissions," *Engine Technol. Intern.* **2000**, *4*, 112–114. http://www.emd.horiba.com/engmeas/techpdf/cleanup_engine_corr.pdf

Nordstrom, D. K.; Alpers, C. N.; Ptacek, C. J.; Blowers, D. W. "Negative pH and Extremely Acidic Mine Waters from Iron Mountain, California," *Environ. Sci. Technol.* **2000**, *34*, 254–258.

Northern Arizona University. Department of Chemistry. Flagstaff, AZ. Use of the Internet to Support on- and off-Campus Environmental Chemistry Courses. http://jan.ucc.nau.edu.doetqp/

Rajeshwar, K.; Ibanez, J. G. *Environmental Electrochemistry: Fundamentals and Applications in Pollution Abatement*; Academic Press: San Diego, 1997. Chapter 1.

Rebhun, M.; Kalabo, R.; Grossman, L.; Manka, J.; Rav-Acha, Ch. "Sorption of Organics on Clay and Synthetic Humic-Clay Complexes Simulating Aquifer Processes," *Wat. Res.* **1992**, *26*, 7–84.

Reese, K. M. "Flatulence Tax Goes Away," *Chem. Eng. News* Dec. 1, 2003. p. 56.

Ritter, S. "Plastic Fallout in the Oceans," *Chem. Eng. News* May 10, 2004. p. 10.

Roundhill, D. M. "Novel Strategies for the Removal of Toxic Metals from Soils and Waters," *J. Chem. Educ.* **2004**, *81*, 275–282.

Sawyer, C. N.; McCarthy, P. L.; Parkin, G. F. *Chemistry for Environmental Engineering.* McGraw-Hill International Edition, Civil Engineering Series: New York, 1994. Chapter 33.

Schilling, A. L.; Hess, K. R.; Leber, P. A.; Yoder, C. H. "A Simulation of the Interaction of Acid Rain with Soil Minerals," *J. Chem. Educ.* **2004**, *81*, 246–247.

Stern, A. C. (Ed.), *Air Pollution* 3rd ed.; Vol. I. Academic Press: New York, 1976. p. 56.

Storck, W. J.; McCoy, M.; Reisch, M. S.; Tullo, A. H.; Short, P. L.; Tremblay, J.-F. "Facts & Figures for the Chemical Industry," *Chem. Eng. News*, July 5, 2004, pp. 23–63.

Tao, T.; Yang, J. J.; Maciel, G. E. "Photoinduced Decomposition of Trichloroethylene on Soil Components," *Environ. Sci. Technol.* **1999**, *33*, 74–80.

Turner, S. M. "Ground Water," Information pamphlet, American Chemical Society: Washington, 1989.

University of Adelaide, Australia. "Data on the Environmental and Toxicological Effects of Chemical Substances," http:/www.adelaide.edu.au/library/guide/sci/Chemistry/env.html

U.S. Environmental Protection Agency. http://www.epa.gov/owow/tmdl

U.S. Environmental Protection Agency. Proposed Guidelines for Carcinogen Risk Assessment, *Fed. Registry* **1996**, *61* (79), 17959–18001.

U.S. Environmental Protection Agency. U.S. Department of Agriculture. Natural Resources Conservation Service. Proposal to Clean up the U.S. Waterways. www.nssc.nrcs.usda.gov

U.S. Environmental Protection Agency. Ozone depletion. http://www.epa.gov/ozone/

Wang, J. W.; Bejan, D.; Bunce, N. J. "Removal of Arsenic form Synthetic Acid Mine Drainage by Electrochemical pH Adjustment and Coprecipitation with Iron Hydroxide," *Environ. Sci. Technol.* **2003**, *37*, 4500–4506.

Wang, J. S.; Wai, C. M. "Arsenic in Drinking Water—A Global Environmental Problem," *J. Chem. Educ.* **2004**, *81*, 207–213.

Wentz, C. A. *Hazardous Waste Management*; McGraw Hill: New York, 1989.

Weston, R. E., Jr. "Climate Change and its Effect on Coral Reefs," *J. Chem. Educ.* **2000**, *77*, 1574–1577.

Williams, K. R. "Refrigeration—From Ice Man to Ozone Hole," *J. Chem. Educ.* **2000**, *77*, 1540–1541.

Yonkos, L. T.; Fisher, D. J.; Burton, D. T.; Whitekettle, W. K.; Petrille, J. C. "Effectiveness of the Sulfur(IV) Compound, Sodium Bisulfite, in Reducing Chlorine, Chlorine Dioxide, and Chlorite Toxicity to Daphnia Magna in Well Water and Pond Water," *Environ. Toxicol. Chem.* **2001**, *20*, 530–536.

9

Effects of Pollutants on the Biosphere: Biodegradability, Toxicity, and Risks

As shown in the previous chapter, numerous pollutants may be classified in terms of the environmental sector on which they make an impact (e.g., air pollutants). They can also be classified according to the transformations that they undergo in the environment (e.g., chemical substances may be biodegradable or recalcitrant, as discussed below). More importantly, they can be classified by the hazards they pose to human health and the ecosystems. The latter aspects are closely related to the chemical structure and characteristics of the discharged substances and their interactions with the environment and its organisms.

9.1 Types of Pollutants According to Their Capacity to Undergo Biotransformation

Many pollutants can be degraded by certain microorganisms (i.e., they are *biodegradable*), while others lack the mechanisms necessary to break them apart or assimilate them through metabolism. Alternatively, the degradation of a substance may occur very slowly, in such a way that the incorporation of its atoms into biogeochemical cycles will require a long time. These last types of substances are called *non-biodegradable* or *recalcitrant*. In the following sections the two concepts are discussed in more detail.

9.1.1 Biodegradable Substances and Biodegradation Processes

Although abiotic transformations of organic compounds may occur in the environment, such processes seldom, if ever, totally convert organic compounds into inorganic substances. These processes are generally linked to oxidation, hydrolysis, or photolysis reactions. On the other hand, biological processes may modify organic molecules at their discharge sites or during transport. Such processes are largely a result of microbiological activity, and they frequently bring about extensive modification in the structure and toxicological properties of pollutants or potential pollutants (see below).

As discussed in Chapter 7, microorganisms require organic or inorganic carbon sources, nitrogen, phosphorus, sulfur, certain trace minerals, water, and an energy source for their maintenance and activity. That is, the biochemical liberation of energy in the absence of light requires electron donors (e.g., oxidizable organic or inorganic substances) and electron acceptors (e.g., molecular oxygen, sulfate ions, nitrate ions, ferric compounds, carbon dioxide, or simple organic compounds).

Biodegradation can be defined as the biologically-catalyzed reduction of the complexity of a substance. Several conditions must be satisfied for biodegradation to occur:

- An organism must exist at the site and possess the necessary enzymes.

- The target substance must be physically accessible to the degrading organism. (Inaccessibility may result if the substance is present in a different microenvironment, dissolved in a solvent that is not miscible with water, or sorbed onto a solid surface).
- If the degrading enzyme is extracellular, the target bonds in the molecule must be exposed to this enzyme.
- If the degrading enzyme is intracellular, the target molecule must penetrate the surface of the cell into the internal enzyme-acting sites.

The population (or biomass) of bacteria or fungi acting on many synthetic compounds is typically small, and therefore the surrounding conditions must allow their proliferation for biodegradation to take place. The occurrence and abundance of microorganisms in an environment are determined not only by the available carbon, but also by physical and chemical factors such as dioxygen and nutrient availability, temperature, pH, salinity, and water activity.

Biodegradation frequently leads to the conversion of organic compounds into inorganic substances. Such a conversion is called *mineralization*, which refers to the capacity of chemoheterotrophic microorganisms to transform organic compounds into inorganic products with the recovery of carbon and energy for the purpose of cell growth. Thus, the organism mineralizes organic carbon, nitrogen (e.g., as proteins), phosphorous (e.g., as phospholipids or nucleic acids), and sulfur (e.g., as organic sulfates or cysteine) to produce CO_2 as well as inorganic forms of N, P, and S (e.g., NH_3, PO_4^{3-}, SO_4^{2-} and S^{2-}) all of which are released and enter the surrounding environment. Plant and animal respiration are mineralization processes that degrade numerous organic molecules of living organisms; on the other hand, the mineralization of *xenobiotics* (see definition below) is almost always observed in microorganisms. Because of their ability to mineralize anthropogenic compounds, microorganisms play key roles in the biodegradation processes in polluted soils, waters, and sediments.

A *xenobiotic* is a compound "foreign" to a particular organism (i.e., it does not participate in its normal biochemistry). A chemical that is "normal" to one organism may be foreign to another, and so xenobiotics may be natural or synthetic. They may produce beneficial effects (e.g., pharmaceuticals) or toxic effects (e.g., Pb).

Microorganisms bring about biodegradation in many different types of environments. Of particular relevance are sewage treatment systems, soils, underground sites for the disposal of chemical wastes, groundwater, surface waters, oceans, sediments, and estuaries. Natural microorganism communities in these various habitats possess an amazing physiological versatility. They are able to metabolize, and often mineralize, an enormous number of natural and xenobiotic organic molecules.

There are cases when a substrate is not used for growth, but is metabolized in the presence of a second substrate that is used to support microorganism reproduction. This type of transformation is called *cometabolism*. Cometabolic conversions that apparently involve a single enzyme include hydroxylations, oxidations, denitrations, deaminations, hydrolyses, acylations, and cleavages of ether bonds. Many of these conversions are complex and involve several enzymes. This may be explained by the existence of enzymes that perform a single type of reaction, but which act on a series of closely related molecules.

9.1.2 Biotic Transformation Reactions

A. Aerobic conditions

Aerobic microorganisms can completely oxidize organic carbon to carbon dioxide, using dioxygen as the terminal electron acceptor.

A.1 Aliphatic compounds

Aliphatic hydrocarbons include straight chain and branched structures. Industrial solvents, petroleum hydrocarbons, and the linear alkyl benzene sulfonates (LAS) are the primary sources of aliphatic hydrocarbon pollutants. Many microorganisms utilize aliphatic hydrocarbons as carbon sources. Long-chain *n*-alkanes are utilized more slowly due to the low bioavailability that results from their extremely low solubility in water. In contrast, short-chain *n*-alkanes show a higher aqueous solubility.

Saturated and unsaturated aliphatics are readily biodegraded. Saturated molecules are oxidized with the aid of enzymes that use molecular oxygen (monooxygenases, see Figure 9.1), while the unsaturated ones become hydrated to form linear fatty acids, which are natural substrates for the

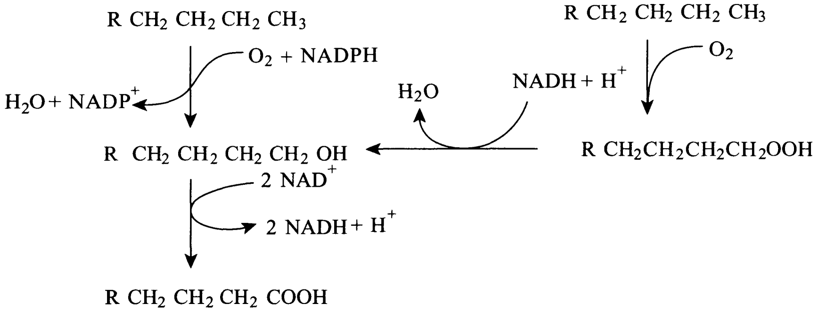


FIGURE 9.1. Oxidation of linear aliphatic hydrocarbons.

β-oxidation pathway (see Figure 9.2). They are degraded to acetylCoA and then mineralized by respiration.

The biodegradability of aliphatics is negatively influenced by branches in the hydrocarbon chain. The degree of resistance to biodegradation depends on both the number of branches and their position in the molecule, because the β-oxidation pathway may be blocked. Therefore, compounds with a quaternary carbon atom are extremely stable due to steric effects.

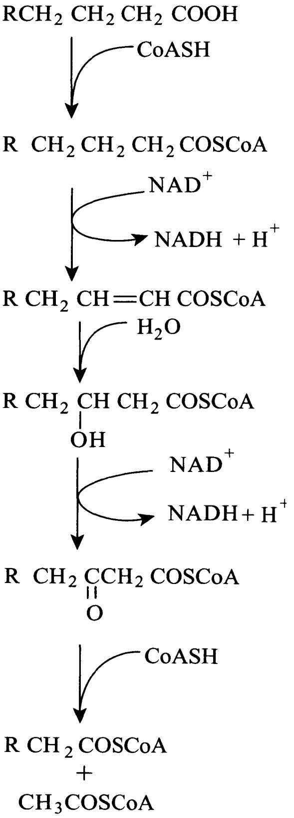


FIGURE 9.2. β-Oxidation pathway of fatty acids.

A.2 Halogenated Aliphatics

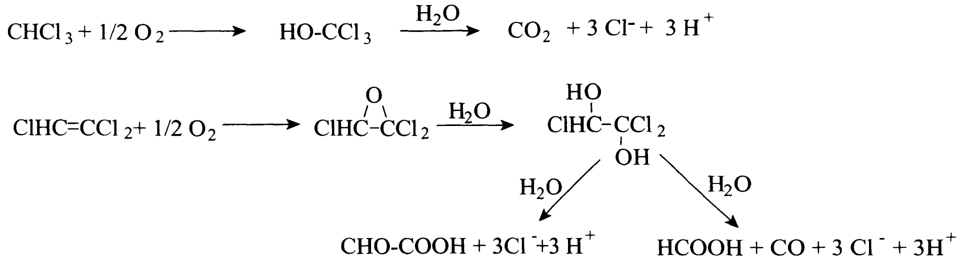
The biodegradability of aliphatics is also negatively influenced by halogen substitution. While monochloro-*n*-alkanes can be biodegraded, the presence of two or three chlorines on the same carbon significantly slows down this process. Chlorinated solvents are used extensively as industrial solvents. As a result of improper use and disposal, they are among the types of organic pollutants most frequently detected in groundwater. Biodegradation of halogenated aliphatics occurs by:

(a) *Substitution.* The halogens of a mono- or dihalogenated compound are substituted by a hydroxyl group as follows:

$$CH_3CH_2Cl + H_2O_{(l)} \rightarrow CH_3CH_2OH + H^+ + Cl^- \tag{9.1}$$

(b) *Oxidation.* This is catalyzed by mono and dioxygenase enzymes that act on highly chlorinated C_1 and C_2 compounds. These enzymes are produced by bacteria to oxidize methane, ammonia, toluene, and other non-halogenated compounds. They do not show high substrate specificity and can participate in the cometabolic degradation of chlorinated aliphatics. As an example, the chemoautotroph *Nitrosomonas europaea* has NH_3 as its natural energy source and CO_2 as its carbon source. It cometabolizes trichloroethylene, 1,1-dichloroethylene, di- and tetrachloroethanes, chloroform, and other monochloroethanes (even fluoro-, bromo-, and iodomethane). See Figure 9.3.

Aerobic conditions generally favor the biodegradation of compounds with a small number of halogens, while anaerobic conditions favor the



$$CHCl_3 + 1/2\,O_2 \longrightarrow HO\text{-}CCl_3 \xrightarrow{H_2O} CO_2 + 3\,Cl^- + 3\,H^+$$

FIGURE 9.3. Biodegradation of chloroform and trichloroethylene.

biodegradation of compounds with a greater number of substituents. Complete biodegradation of highly halogenated aliphatics is difficult under anaerobic conditions.

A.3 Alicyclic hydrocarbons

Alicyclic hydrocarbons are major components of petroleum (comprising from 20% to 67% of its volume) as well as components of plant oils and paraffins, microbial lipids, and pesticides. They range from simple molecules (e.g., cyclopentane and cyclohexane) to complex molecules (e.g., the pesticides aldrin and kepone shown in Figure 9.4).

Alicyclic hydrocarbon degradation is thought to occur primarily by comensalistic and cometabolic reactions as shown in Figure 9.5, where one organism converts cyclohexane into cyclohexanone (steps 1 and 2), but it is unable to lactonize and open the ring. A second organism, which is unable to oxidize cyclohexane to cyclohexanone, can perform reactions 3, 4 and the mineralization of the remaining aliphatic compounds. The rate of degradation of alkyl derivatives of this type of hydrocarbons decreases with the number of substituents.

A.4 Aromatic hydrocarbons

Most aromatic hydrocarbons are natural products, but their addition to the environment has increased dramatically through activities such as fossil fuel processing and utilization. Biodegradation of aromatic compounds is accomplished by a wide variety of bacteria and fungi under a variety of environmental conditions. The most common initial transformation under aerobic conditions is hydroxylation, which involves the incorporation of molecular oxygen. See Figure 9.6. In general, bacteria transform aromatics by an initial dioxygenase attack to form *cis*-dihydrodiols. The molecule is then aromatized to form catechol.

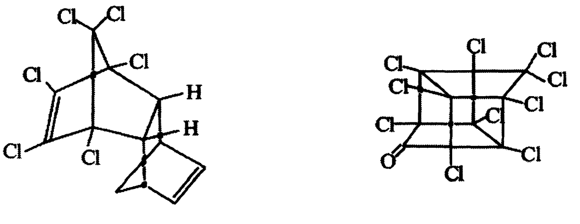


FIGURE 9.4. Alicyclic pesticides (aldrin and kepone, respectively).

Other non-halogenated aromatic compounds are transformed into either catechol or protocatechuate. Then, through a series of oxidative cleavage reactions, catechol and protocatechuate are processed to yield either acetylCoA and succinate, or pyruvate and acetaldehyde. In general, aromatics composed of one, two, or three condensed rings with several types of substitutions are also transformed into catechol. See Figures 9.7a and 9.7b.

The catechol ring is cleaved by a second dioxygenase, either between the two hydroxyl groups (*ortho* pathway, Figure 9.8) or next to one of the hydroxyl groups (*meta* pathway), as shown in Figure 9.9.

Eukaryotic microorganisms initially attack aromatics with a cytochrome P-450 monooxygenase, incorporating one atom of molecular oxygen into the aromatic species and reducing the second one to water, which results in their conversion into an arene oxide. This is followed by the enzymatic addition of water to yield a *trans*-dihydrodiol. See Figure 9.10. Alternatively, the arene oxide can be isomerized to form phenols, which can be conjugated with sulfate, glucuronic acid, or glutathione, compounds that aid in the elimination of aromatics from the organism.

In general, aromatics composed of one to three condensed rings can be transformed and mineralized, whereas aromatics containing four or more condensed rings are transformed very slowly due to their increased hydrophobicity and toxicity.

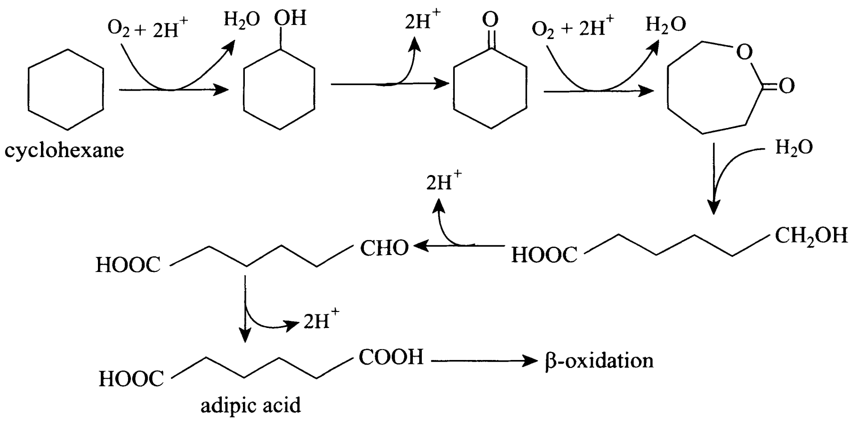


FIGURE 9.5. Biodegradation of cyclohexane.

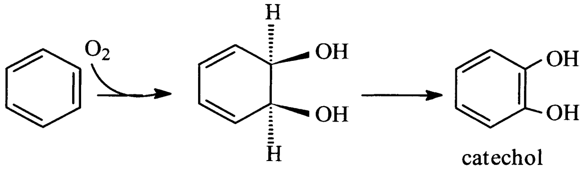


FIGURE 9.6. Bacterial oxidation of benzene.

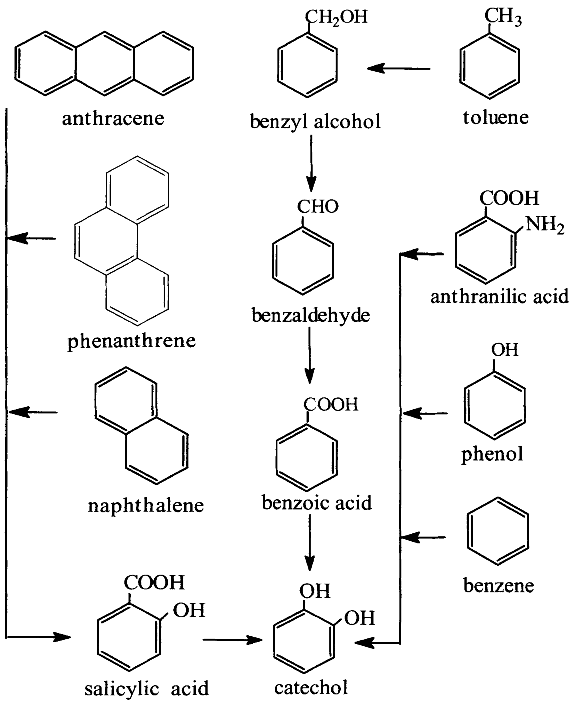


FIGURE 9.7a. Pathways for the enzymatic conversion of aromatic compounds to catechol.

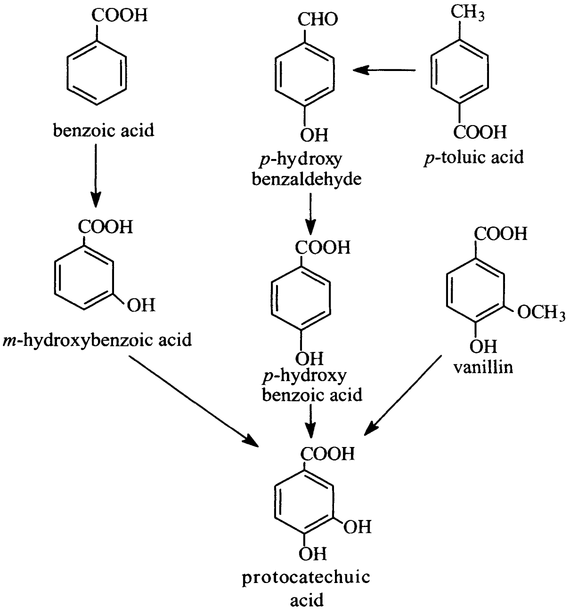


FIGURE 9.7b. Pathways for the enzymatic conversion of aromatic compounds into protocatechuic acid.

Chlorinated aromatics are of special interest due to their extensive use as solvents and fumigants (e.g., dichlorobenzene), wood preservatives (e.g., pentachlorophenol), and as parent compounds for pesticides (e.g., 2,4-dichlorophenoxiacetic acid, also known as 2,4-D). An example of their biodegradation is that of 2,4-D, which takes place through a modified *ortho*-cleavage pathway by enzymes that are not specific for their substrates. See Figure 9.11. The products, acetylSCoA and succinate, are part of

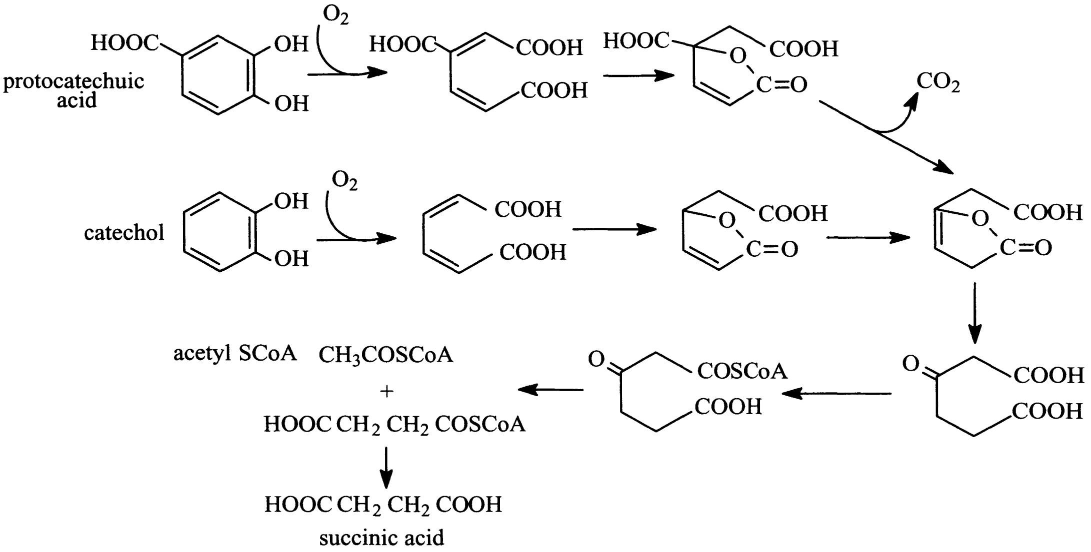


FIGURE 9.8. The *ortho*-cleavage pathway for the enzymatic conversion of catechol and protocatechuic acid.

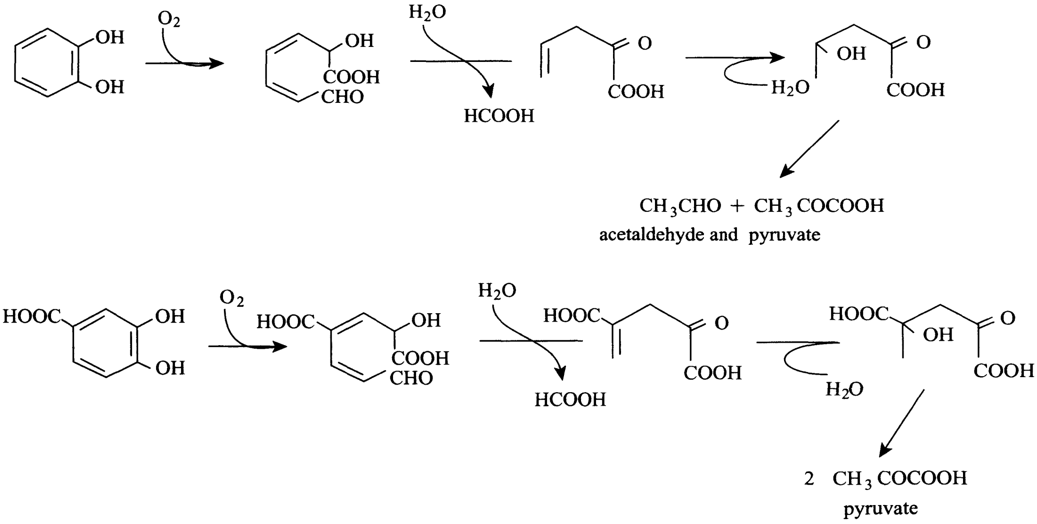


FIGURE 9.9. The *meta*-cleavage pathway for the enzymatic conversion of catechol and protocatechuic acid.

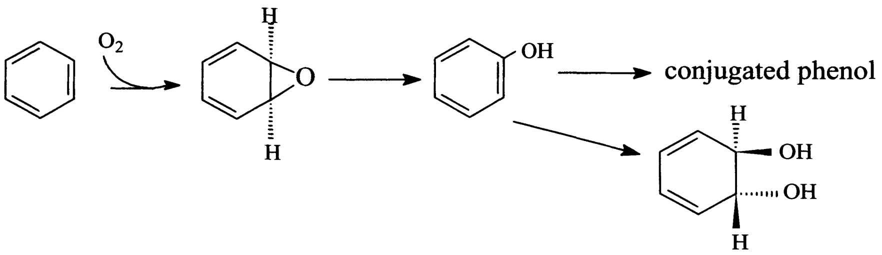


FIGURE 9.10. Fungal oxidation of benzene.

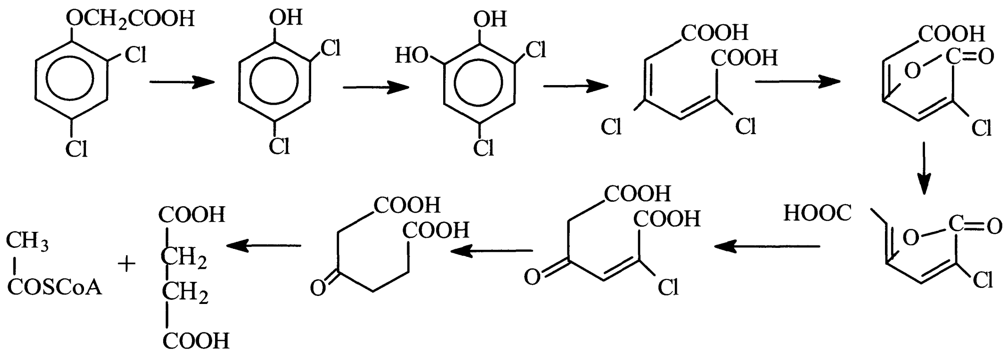


FIGURE 9.11. Biodegradation of 2,4-D.

the tricarboxylic acid pathway and they are mineralized.

B. Anaerobic conditions

In the absence of dioxygen, organic materials can be mineralized to carbon dioxide, although this is a less efficient process than that of aerobic respiration. Anaerobic biodegradation requires alternative electron acceptors, the use of which depends on their availability. The degree of easiness for biodegradation follows a sequence in order of decreasing affinity for electrons (i.e., nitrate > iron > sulfate > carbonate).

Some compounds that are easily degraded aerobically are difficult to degrade anaerobically (e.g., saturated aliphatics). On the other hand, highly halogenated compounds that are not degraded aerobically can be partially or completely degraded anaerobically. Under anaerobic conditions, organic compounds are often degraded by an interactive group or consortium of microorganisms. Individuals within the consortium perform different specialized reactions that together lead to the complete mineralization of the target substance.

C. Biotic transformation of heavy metals and radionuclides

Because of their large surface-to-volume ratio and high metabolic activity, microorganisms are important vectors in the introduction of heavy metal and radionuclide pollutants into food webs. As discussed in Chapter 5, heavy metals in soils and sediments tend to be immobilized by precipitation at neutral to alkaline pH and/or adsorption to cation exchange sites of clay minerals. Microbial production of acid and chelating agents can reverse this adsorption and mobilize toxic metals. Microbial metabolism products that can chelate metals include dicarboxylic and tricarboxylic acids, pyrocatechol, aromatic hydroxy acids, polyols, and some specific chelators such as ferrioxamines.

Heavy metal mobilization is often followed by microorganism and plant uptake, and intracellular accumulation. Filamentous fungi transport heavy metals and radionuclides along their hyphae. This may be a mechanism of mobilization from mycorrhizal fungi to higher plants. An alternative pathway involves direct root uptake of heavy metals mobilized by microbial acid production or chelation.

Microorganisms can transfer methyl groups to various heavy metals and metalloids (e.g., Se, As), which results in mobilizing these heavy metals and promoting their potentiation as environmental toxicants. Such methylation is attributed to the enzymatic system involved in the anaerobic generation of methane, where the methyl donor is methylcobalamin (methyl vitamin B12). This is exemplified by the case of mercury (see Figure 9.12).

9.1.3 Recalcitrance and Recalcitrant Compounds

Xenobiotics that have molecular structures and chemical bond sequences not recognized by existing degradative enzymes, resist biodegradation or are incompletely metabolized, and therefore they may accumulate in the environment. The substances that resist biodegradation are known as *recalcitrant*.

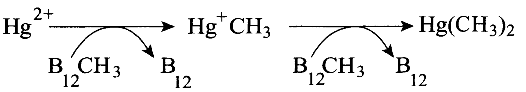


FIGURE 9.12. Mercury biotic methylation.

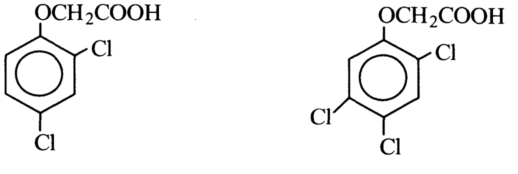


FIGURE 9.13. Structures of 2,4-D and 2,4,5-T, respectively.

There are many reasons for a xenobiotic organic compound to be recalcitrant:

a. Unusual substitutions

Organic compounds may be rendered partially or totally resistant to mineralization by adding a substituent. These substituents may be termed *xenophores*, as they are physiologically uncommon. Thus, addition of a single Cl, NO_2, SO_3H, Br, CN, or CF_3 to simple aromatic compounds, fatty acids, or other readily biodegradable substrates greatly increases their recalcitrance. The groups CH_3, NH_2, OH, and OCH_3 sometimes act as xenophores. The degradation of organic compounds is often stimulated by the presence of OH, COOH, amide, ester, or anhydride groups.

For example, as opposed to the 2,4-D case discussed above, its derivative 2,4,5-trichlorophenoxyacetic acid (known as 2,4,5-T) is recalcitrant due to the chlorine in position 5, which blocks the degradative pathway. See Figure 9.13.

Polychlorinated biphenyls (PCBs) and dioxins are also of special interest. The biphenyl group is able to serve some microorganisms as their carbon and energy source, and thus the mono-, di-, tri-, and tetrachloro biphenyls are, to some degree, subject to biodegradation. However, in more extensively chlorinated biphenyls, the substituents prevent ring hydroxylation. See Figure 9.14.

The PCBs are often contaminated with 2,3,7,8-tetrachlorodibenzodioxin (TCCD), related chlorodibenzodioxins, and chlorodibenzofurans, which are highly recalcitrant and constitute part of the pollutants known as POPs (i.e., *persistent organic pollutants*). See Figure 9.15.

b. Highly condensed aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) with two or three rings may be biodegraded, although this characteristic is lost as the number of rings increases. See Figure 9.16.

c. Unusual bonds or bond sequences (e.g., tertiary and quaternary carbons in surfactants)

As discussed earlier, branching makes biodegradation more difficult. See Figure 9.17.

d. Excessive molecular size

Synthetic polymers represent the most commonly used plastics and fibers, and they are totally resistant to biodegradation as seen in Table 9.1.

However, there are a few synthetic polymers of commercial importance that are biodegradable (see Table 9.2).

e. Partial biotransformations

There are cases in which the original substrate is quickly biodegraded and yields a metabolite that is not. Examples include the following:

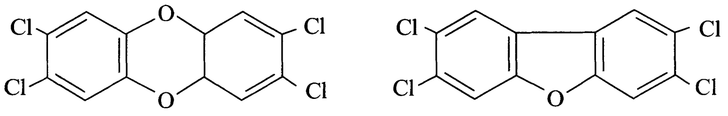
- DDT is slowly converted into a number of products (including DDE) that remain in soils for years. See Figure 9.18.
- The chlorinated insecticides aldrin and heptachlor are microbiologically converted in soils into the corresponding epoxides. The products remain in the treated fields while the parent compounds are essentially absent.
- The surfactant nonylphenol polyethoxylate is readily biodegradable, whereas its biodegradation products are persistent. See Figure 9.19.

In some cases, one portion of the pesticide molecule is susceptible to biodegradation whereas the other portion is recalcitrant. For example,

2, 2′, 5, 5′-tetrachlorobiphenyl

2, 2′, 3′,4, 4′, 5′, 6 -heptachloro biphenyl

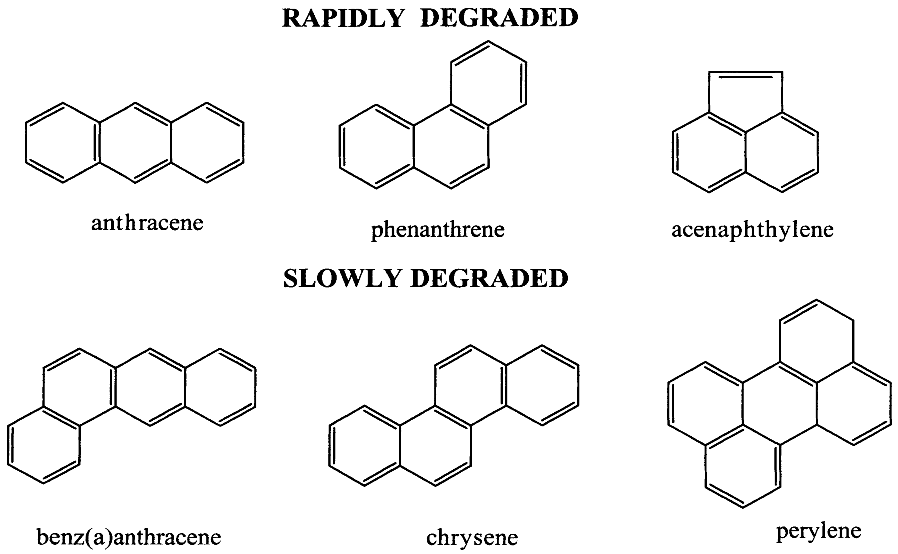
FIGURE 9.14. Examples of two different chloro-substitutions for biphenyls.



2,3,7,8-tetrachlorodibenzo-dioxin

2,3,7,8-tetrachlorodibenzo-furan

FIGURE 9.15. Examples of TCCD and TCBF.



RAPIDLY DEGRADED

anthracene

phenanthrene

acenaphthylene

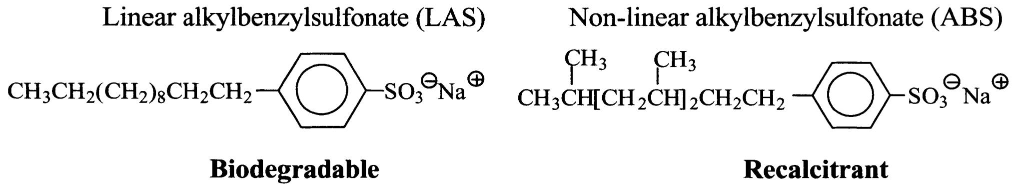
SLOWLY DEGRADED

benz(a)anthracene

chrysene

perylene

FIGURE 9.16. Relative rates of biodegradation of PAHs.



Linear alkylbenzylsulfonate (LAS)

Non-linear alkylbenzylsulfonate (ABS)

Biodegradable

Recalcitrant

FIGURE 9.17. Relative biodegradability of surfactants.

TABLE 9.1. Synthetic polymers resistant to microbial degradation

Nylon	Silicon resins
Phenol formaldehyde	Resorcinol formaldehyde
Poly(tetrafluoroethylene) (Teflon)	Poly(ethylene glycol)terephtalate (Dacron)
Polyacrylonitrile (Orlon)	Polyisobutilene
Cellulose acetate	Polyurethane
Polystyrene	Poly(vinyl chloride)
	Polyethylene (HDPE, high molecular weight)

TABLE 9.2. Biodegradable polymers

Polyethylene glycols	Polyester
Poly (vinyl acetate)	Polyester polycaprolactone
Poly (vinyl alcohol)	

microbial amidases cleave and mineralize the aliphatic portion of some acylamide herbicides, whereas the aromatic portion is stabilized by chlorine substituents and resists mineralization; in fact, it is polymerized to residues that are extremely complex and persistent, as shown in Figure 9.20.

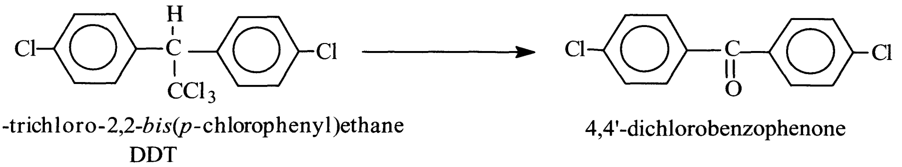


FIGURE 9.18. A DDT degradation product.

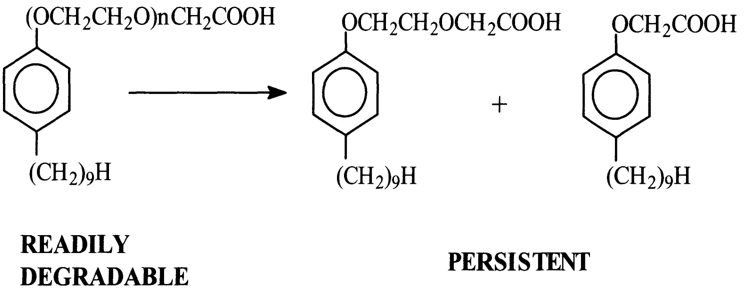


FIGURE 9.19. Degradation products of the surfactant nonylphenol polyethoxylate.

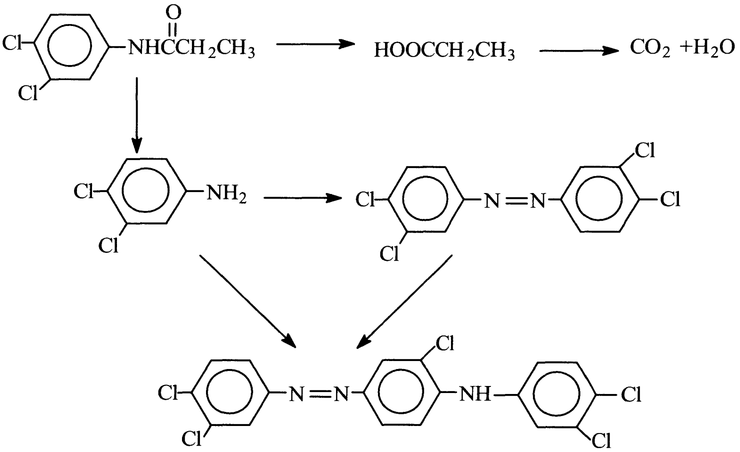


FIGURE 9.20. Partial degradation and polymerization of acylamide herbicides.

9.2 Hazardous and Non-hazardous Substances or Pollutants

Early scientific knowledge recognized two basic types of substances according to their effect on living organisms: beneficial (e.g., foods and medicines) and harmful (those that cause sickness or death). Modern science acknowledges that such a sharp division is not justified. Many chemical substances or mixtures exert a whole spectrum of activities, ranging from beneficial to neutral or lethal. Their effect depends not only on the amount of substance to which an organism is exposed but also on the nature and size of the organism, its nutritional status, the exposure pathway, and several other related factors. Adverse effects may occur in many forms, ranging from immediate death to subtle changes not realized until months or years later. They may occur at various levels within the body (i.e., an organ, a type of cell, or a specific biochemical substance).

9.2.1 Classification of Hazardous Substances

A substance is considered *hazardous* if it exhibits any of the following four characteristics:

- *Flammable:* substances that readily catch fire (e.g., gasoline and alcohol).
- *Corrosive:* substances that corrode storage tanks and equipment (e.g., acids).
- *Explosive:* substances that may cause an explosion (e.g., trinitrotoluene or TNT).
- *Reactive:* substances that are chemically unstable and may explode or create toxic fumes when mixed with water (e.g., explosives, elemental phosphorus, and concentrated sulfuric acid).
- *Toxic:* substances injurious to health when ingested or inhaled (e.g., chlorine, ammonia, pesticides, and formaldehyde).

9.2.2 Toxicity and Related Definitions

The branch of science that studies the adverse effects of chemicals or physical agents on living organisms is known as *toxicology*. This is closely related to what defines a hazardous substance or contaminant.

- A *toxicant* is a substance that has a deleterious effect on living organisms. It may be a discrete toxic chemical (e.g., lead chromate) or a mixture of toxic chemicals (e.g., gasoline).
- A *toxin* is a specific protein produced by living organisms (e.g., mushroom toxin or tetanus toxin).
- A *poison* is a toxicant that causes immediate death or illness when experienced in very small amounts.

A hazardous pollutant is thus defined by its toxicity and impact on human health or its negative effects on organisms in ecosystems.

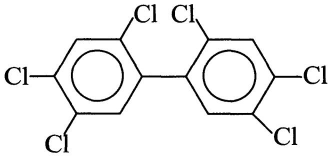
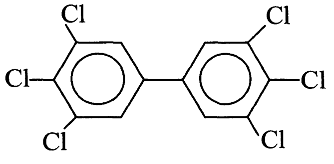
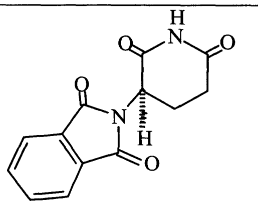
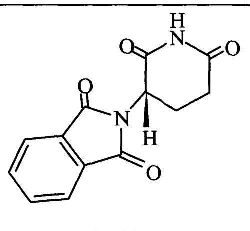
9.2.3 Factors That Affect the Toxicity of Chemical Substances

Several factors influence the toxicity of substances: their structure and innate chemical activity, the dosage, the susceptibility, age and sex of specific organisms, the route of exposure, susceptibility of the substances to being absorbed, the way in which they spread within the receiving organism, their metabolism and excretion, and the presence of other chemicals or conditions.

(a) Structure and activity

The *structure* of a substance may have a profound impact on its toxicity, because receptors and enzymes respond to subtle changes in the three-dimensional molecular structures. See Table 9.3.

TABLE 9.3. Structural differences that affect toxicity

	Low toxicity	**High toxicity**
Structural isomers	 2,2',4,4',5,5'-hexachlorobiphenyl	 3,3',4,4',5,5'-hexachlorobiphenyl
Stereoisomers	 (R)-thalidomide	 (S) thalidomide
Oxidation state	Cr^{3+}	Cr^{6+}

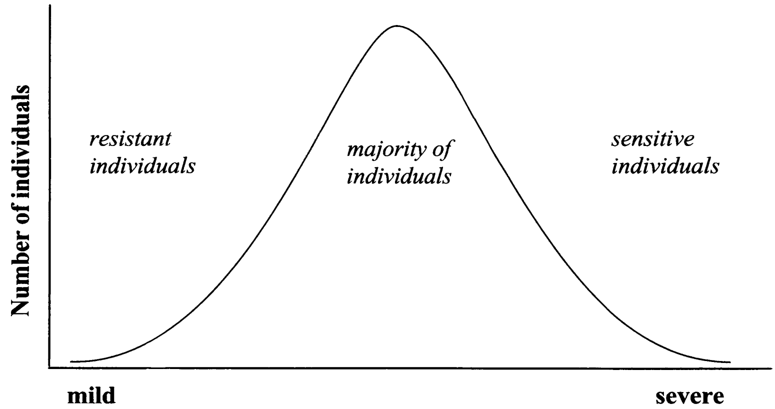


FIGURE 9.21. Response of a population to the same dose of a toxicant. (Adapted from Kamrin, 1988).

The *chemical activity* of substances also varies greatly. Some can quickly damage cells causing their immediate death. Others slowly interfere with a specific cell function. For example:

- Hydrogen cyanide binds cytochrome oxidase, resulting in cellular hypoxia and rapid death.
- Nicotine binds to cholinergic receptors in the central nervous system, altering nerve conduction and inducing gradual onset of paralysis.

The polarity of a substance determines how easily a chemical can enter a body, how easily it is distributed inside the body, and how easily it can be excreted. Because the human body is most efficient at excreting polar compounds, there are enzymes designed to convert foreign non-polar compounds into polar variants so they can be removed from the body; however, some are difficult to excrete and they are stored in the body for long periods of time.

(b) Dosage

The amount of a particular toxic agent to which a body is exposed is termed the *administered dose*. The amount of a chemical that an organism is exposed to is crucial in determining the extent of toxicity that will occur, although the size of the organism is a key factor as well. Thus, instead of using the amount that is administered, one uses the amount per weight of organism (i.e., the *dose*). Metric units are generally used, and toxicity is expressed in milligrams per kilogram of body weight (mg/kg).

(c) Susceptibility of organisms

Another important factor is the susceptibility of the exposed individual as a function of age, sex, diet, health status, genetics, prior exposures to the agent, and exposures to other agents. Within a population, the majority of responses to a toxicant are similar; however, a wide variance in responses may be encountered (some individuals are susceptible while others are resistant). A plot of the individual responses results in a bell-shaped standard distribution curve. See Figure 9.21.

(d) Dose–response relationship

Dose is the major determinant of the extent of toxic action. Scientists often administer a wide variety of toxicant doses to experimental animals so as to determine what dose of a particular chemical causes which kind of toxic effect. What they usually find is that a very small dose causes no observable effect, higher doses cause some toxicity, and a large enough dose causes the organism to die. This gradual increase in toxic effects is known as the *dose–response curve*. Most plots of dose vs. cumulative mortality show a non-linear, S-shaped curve. See Figure 9.22.

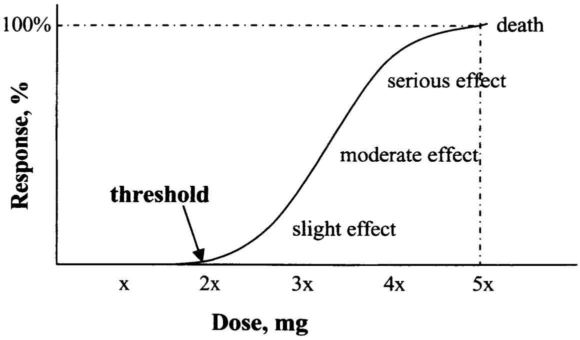


FIGURE 9.22. Dose–response curve. (Adapted from Kamrin, 1988).

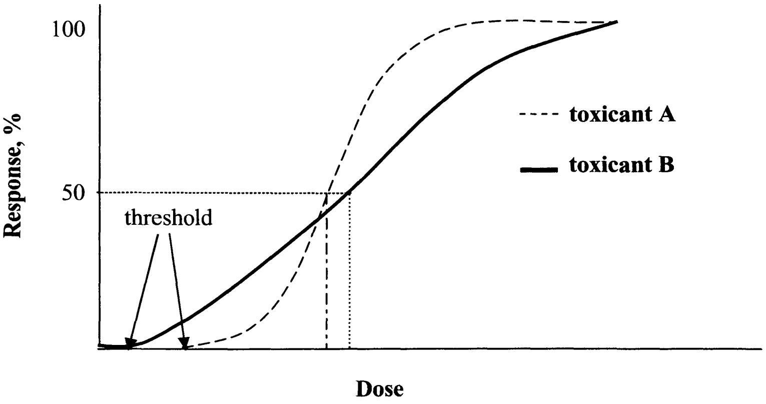


FIGURE 9.23. Dose–response curves for two toxicants (A and B). (Adapted from Kamrin, 1988).

The point at which toxicity first appears is known as the *threshold* dose level. From that point on, the curve rises with higher dose levels. In the hypothetical curve above, no toxicity occurs at x mg, whereas at $5x$ mg, 100% of the individuals experience toxic effects and even death.

The threshold for toxic effects occurs at the point where the body's ability to detoxify a substance or repair toxic injury has been exceeded. For most organs there is a reserve capacity in such a way that the loss of some organ function does not decrease performance. For example, the development of cirrhosis in the liver may not result in a clinical effect until over 50% of the liver has been replaced by fibrous tissue.

Knowing the *shape* and *slope* of the dose–response curve of a substance is extremely important in predicting its toxicity at specific dose levels. Major differences among toxicants may exist not only at the point where the threshold is reached, but also at where it shows the percentage of population responding per unit change in dose (i.e., the *slope*). As illustrated in Figure 9.23, toxicant A has a higher threshold but a steeper slope than toxicant B.

The dose at which only 50% of the organisms remain alive is the median *lethal dose* (LD_{50}). The equivalent for inhaled toxicants is the *median lethal concentration* (LC_{50}), where the dose is expressed as the concentration of the substance present in the inhaled air.

When an acute toxic dose is fractionated into smaller portions and administered over a longer period of time, the toxic effect usually decreases. This will be true if there is an appreciable metabolic deactivation/elimination of the toxicant between exposures. If this process acts fast enough as compared with the interval between doses, no toxic effects will be noted. See Figure 9.24.

Multiple exposures to the same chemical may have an effect similar to a single exposure. This is the case when each dose is too low to cause any adverse effects, and it is excreted by the body before the next dose is administered (see the *short* arrows and the dotted curve in Figure 9.25). But if the exposure period is shortened and the excretion is not complete, the chemical concentration in blood increases from day to day, and finally reaches that of a toxic dose (see the *long* arrows and the solid curve in Figure 9.25). Therefore it is not only the *total* exposure that is critical, but also the exposure *frequency*.

The *rates* at which toxicants are absorbed, metabolized and eliminated are also critical. If the body

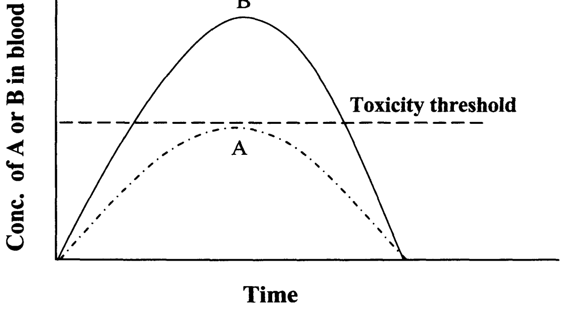


FIGURE 9.24. Effect of different doses over time for toxicants A and B. (Adapted from Kamrin, 1988).

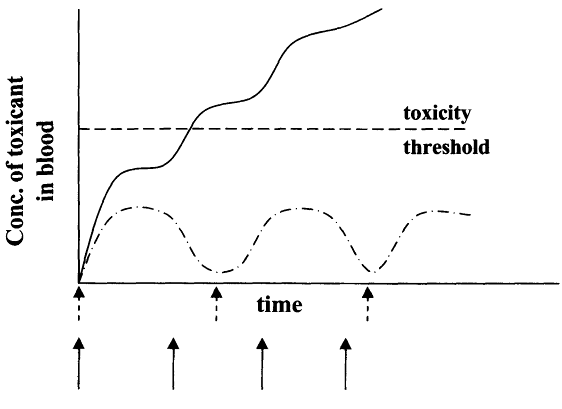


FIGURE 9.25. Relationship between the time course of exposure and the response. (Adapted from Kamrin, 1988).

rapidly eliminates a particular toxicant, then it may tolerate an otherwise toxic dose when the substance is received in controlled portions. If the body eliminates a toxicant fairly slowly, then a low dose over a long period of time could result in its accumulation up to a critical concentration. This is why the duration, concentration, and frequency of exposure are important.

(e) Dose-time relationship or exposure

The period over which a dose is administered is of paramount importance. The following approximate criteria characterize the exposure in humans:

• Acute	1 day
• Subacute	10 days
• Subchronic	2 weeks to 7 years
• Chronic	7 years to lifetime

More specific details about the corresponding responses will now be discussed.

e.1 *Acute toxicity.* Its effects occur almost immediately after an exposure (i.e., within hours/days). An acute exposure is usually a single dose or a series of doses received within a 24-hour period. Death is a major concern in cases of acute exposures. Nonlethal acute effects can also occur.

To compare the acute toxicity of different chemicals on a relative scale, the contact toxic dose LD_{50} is defined as the lethal dose at which 50% of the test population will die when given that dose. The smaller the LD_{50}, the more toxic the substance is. The contact dose may be given by ingestion, inhalation, or absorption through the skin.

For example, chloroform ($CHCl_3$) was used as an anesthetic agent in surgery and as a solvent in industry. It has an LD_{50} of 80 mg/kg. Here, the lethal dose is expressed as the milligrams of chloroform (80 mg) per kilogram of body weight of the test animal (typically rats). This dose tells us that 50% of the rats will die if they are given 80 mg of chloroform per kg body weight of the subject animal. Thus, for a person who weighs 100 kg there is a 50% chance that a dose of (80 mg) × (70 kg) = 5600 mg or 5.6 g may be fatal.

The LD_{50} values of several substances for ingestion in rats are shown in Table 9.4.

e.2 *Subchronic toxicity.* This results from repeated exposures for several weeks or months. It is a common human exposure pattern for some pharmaceuticals and environmental agents. For example, the workplace exposure to Pb over a period of several weeks can result in anemia.

e.3 *Chronic toxicity.* This has to do with cumulative damage to specific organ systems and it may take many months or years to become a recognizable clinical disease. Damage due to subclinical individual exposures may go unnoticed. After repeated exposures or a long-term continued exposure, damage from these subclinical exposures slowly builds-up (i.e., *cumulative damage*) until it exceeds the threshold for chronic toxicity. Ultimately, the damage becomes so severe that the organ can no longer function normally and a variety of chronic toxic effects may result.

TABLE 9.4. Approximate values of LD_{50} for several chemical agents

Substances	LD_{50} (mg/kg)
Sugar (sucrose)	29,700
Polybrominated biphenyls	21,700
Ethanol	14,000
Vinegar	3,310
Malathion	1,200
Aspirin	1,000
Lindane	1,000
2,4-D	375
Ammonia	350
DDT	100
Heptachlor	90
Chloroform	80
Arsenic	48
Dieldrin	40
Strychnine	2
Nicotine	1
Sodium cyanide	0.1
Dioxin	0.001
Botulinus toxin	0.00001

Example 9.1 What is the volume of the fatal dose (LD_{50}) of chloroform that will kill a person who weighs 70 kg? (Density of chloroform = 1.446 g/mL).

Answer

The volume of chloroform for the fatal dose LD_{50} is found from:

$$V = \frac{\text{mass}}{\text{density}} = \frac{5.6\text{ g}}{1.443\frac{\text{g}}{\text{mL}}} = 3.88\text{ mL}$$

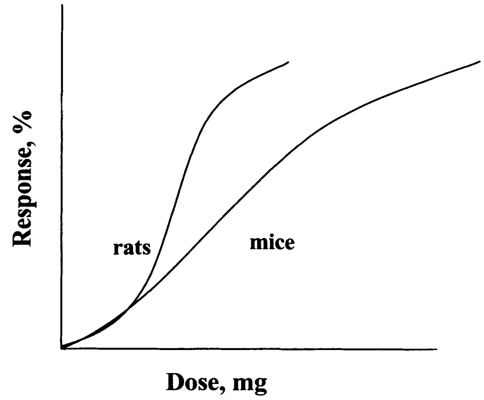


FIGURE 9.26. Effect of dose on different organisms. (Adapted from Kamrin, 1988).

Examples of chronic toxic effects include:

- Cirrhosis in alcoholics who have ingested ethanol for several years.
- Chronic kidney disease in workmen with several years of exposure to lead.
- Chronic bronchitis in long-term cigarette smokers.
- Pulmonary fibrosis in coal miners (called *black lung disease*).

Dosage is the most important and critical factor in determining whether a substance will be an acute or a chronic toxicant. Virtually all chemicals can be acute toxicants if sufficiently large doses are administered. The toxicity mechanisms and target organs are different in acute and chronic toxicities. For example, the acute toxicity of ethanol consists in central nervous system depression, but its chronic toxicity is liver cirrhosis. Cadmium causes hypertension and kidney damage in humans at low chronic exposure; high exposure, however, causes the crippling bone and joint disease.

(f) Species differentiation

Toxic responses vary substantially depending on the *species*. Such variations are attributable to differences in metabolism, which must be considered when toxicity data from animal experiments are applied to human beings. However, this does provide a rough guide to the relative toxicity of various chemicals.

Selective toxicity refers to differences in toxicity between two species simultaneously exposed. See Figure 9.26, where rats show a higher response than mice to a certain dose. This is the basis for the effectiveness of pesticides and drugs. For example, an insecticide is lethal to insects but relatively nontoxic to animals; in the same vein, antibiotics are selectively toxic to microorganisms while virtually non-toxic to humans.

(g) Age

Age may be important in determining the response to toxicants. Some chemicals are more toxic to infants or the elderly than to young adults. For example, the pesticide parathion is more toxic to young animals.

(h) Sex

Although uncommon, toxic responses can vary depending on *sex*. For example, male rats are 10 times more sensitive than females to liver damage from DDT.

(i) Route of exposure

The series of steps starting with a release of toxicants and concluding in their contact with and/or entrance into a human body is referred to as the *exposure pathway*. Gaining entry into the body is the *exposure route*. There are three exposure routes through which environmental pollutants may enter the body:

- Inhalation (respiratory tract)
- Ingestion (gastrointestinal tract)
- Dermal contact (skin)

Some chemicals may be highly toxic by one route but not by others. Two major reasons are the differences in absorption and distribution within the body. Ingested chemicals, when absorbed from the intestine, are firstly distributed to the liver where they may be immediately detoxified, while inhaled toxicants immediately enter the general blood circulation and can be distributed throughout the body prior to being detoxified by the liver.

(j) Toxicokinetics

Exposure marks the beginning of the four basic phases of the passage of a toxic substance through an organism. *Toxicokinetics* is the study of how a substance gets into the body and what happens to it inside the body. Four processes are involved in this activity:

- Absorption
  The substance enters the body.
- Distribution
  The substance moves from the site of entry to other areas of the body.
- Biotransformation
  The body transforms the substance into new chemicals.
- Excretion
  The substance or its metabolites leave the body.

Absorption, distribution, biotransformation, and elimination are interrelated processes as illustrated in Figure 9.27.

j.1 *Absorption*

Reactive chemicals such as acid anhydrides, epoxides, strong acids and bases, acyl chlorides, and corrosive agents cause toxic effects as cell necrosis immediately after coming into contact with animal or human tissue (e.g., skin, eyes, and mucous membranes of the respiratory tract). Such lesions are referred to as *chemical burns*. However, these agents are usually not appreciably taken up into the organism. In contrast, *systemic toxicants* may exert their action at a distant point from the site of absorption. These substances are absorbed, and thereafter they reach the bloodstream and/or lymph. Although the administered dose is important, the amount of toxic chemical that becomes available to the body (absorbed) is the *intake* or *uptake dose*.

The rates and extent of absorption may vary greatly depending on the structure of the chemical, the route of exposure and the susceptibility (or physiological state) of the individual. For example, nearly all alcohols are readily absorbed from the gastrointestinal tract but poorly absorbed through the skin, whereas there is virtually no absorption for most polymers. In the same manner, organic mercury is readily absorbed from the gastrointestinal tract, but inorganic lead sulfate is not. The same processes that govern the absorption of nutrients, dioxygen, and other vital elements and chemicals also govern the absorption of toxic agents.

j.2 *Distribution*

Once the chemical arrives into the bloodstream (or the lymph), it is transported throughout the body to all the organs and tissues. Toxic compounds

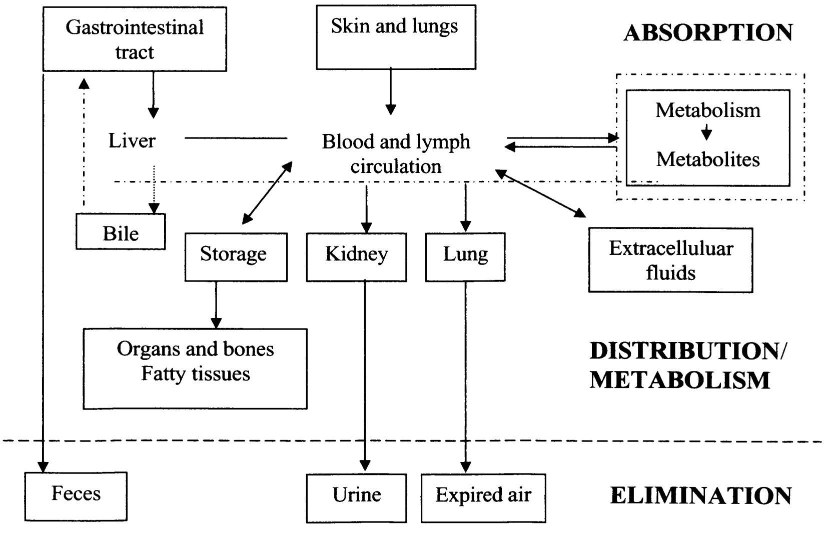


FIGURE 9.27. Toxicokinetics. (Adapted from the United States National Library of Medicine).

are distributed partially and unequally into multiple "compartments" of the body rather than totally to one or equally to all. Absorption is again important because the same processes that govern the passage of the toxic agent into the blood now govern its ability to move from the blood into the tissue of the organs and into the cells. Toxic agents typically attack only one or perhaps a few organs, referred to as *target organs*. A target organ is the *preferential anatomic site* for the expression of toxic effects caused by a substance. The amount reaching the target organ is the *target* or *effective dose*, which depends on how the body's systems interact with the compound.

Other factors influencing distribution are *perfusion* (i.e., the movement of blood through organ tissue), the *route of exposure* and the *tissue affinity*. For example, toxicants absorbed through the lungs, skin, mouth, and esophagus may temporarily bypass the liver, while those absorbed through the stomach and intestines will follow the blood's direct path to the liver, which is the body's primary detoxicant site. Furthermore, the liver is well perfused and its total potential uptake is high. Although the brain is well perfused as well, it is, to a large extent, protected by the blood/brain barrier.

It is generally believed that upon reaching an organ, the toxic chemical must recognize a specific molecule or group of molecules known as *receptors*. The receptor must have a shape complementary to that of the toxicant so that a close fit occurs, and a chemical-receptor complex forms; the exactness of fit is related to the toxic potency. The binding of the toxicant to the receptor initiates a chain of events that leads to the ultimate adverse effect. Some of the most important effects involve the alteration of the structural components of the cell membrane, inhibition of certain enzymes, interference in the biosynthesis or metabolism of proteins, lipids or carbohydrates, and alterations in DNA fidelity that result in mutations and interference with the regulation of cell growth. The location of the receptors has a strong influence on the *site* of toxic effects, and the *number* of receptors influences the *degree* of toxicity. Thus, the toxicant usually interferes with the function of these molecules, perturbing a specific biochemical reaction or its control.

Toxicodynamics is the study of the biochemical and physiological mechanisms of action of toxicants on affected target molecules and tissues. A major portion of toxicodynamic concepts and research involves the study and understanding of receptors.

j.3 *Storage*

Because of their affinity for various tissues, many toxicants accumulate at sites other than the target organ and are released over an extended period of time. This is termed *storage* or *deposition* and typically occurs without any adverse effect on the storage organ. The toxicant concentration in the storage site can be high, sometimes even higher than that in the target organ. The stored fraction and the particular storage site mainly depend on the polarity and affinity of the chemical structure for the storage tissue. Examples of important storage sites include:

- Fat, for non-polar compounds (e.g., organochloride pesticides as DDT and polychlorinated biphenyls)
- Blood plasma, for compounds bound by plasma proteins (e.g., Hg^{2+})
- Kidneys (e.g., Cd)
- Liver (e.g., aflatoxins)
- Bone (e.g., Pb, F and radionuclides such as ^{90}Sr and ^{137}Cs)

j.4 *Biotransformation and elimination*

The body has a remarkable capacity for eliminating a vast range of chemical agents absorbed trough dietary and environmental exposures. The kidney is the main excretory organ of the body for foreign chemicals and is most efficient at eliminating polar molecules. It does not function well with non-polar compounds; consequently, these compounds tend to remain in the body for long periods until they are metabolically transformed by the organism into more polar—and thus more water soluble—metabolites that can be excreted in urine.

The process by which substances circulating in the bloodstream may interact with enzymes and change is called *metabolism* or *biotransformation*; the resulting altered products are called *metabolites*.

Biotransformation of non-polar, non-volatile toxicants is a two-phase biochemical reaction. In the first phase (Phase I), the body's enzyme system introduces a polar group into the toxicant (e.g., by oxidation, reduction, or hydrolysis). See Figure 9.28. The enzymes responsible for these transformations are part of a *mixed function oxidase* system (MFO) of smooth endoplasmatic reticulum present in liver parenchyma cells and in other tissues (e.g., intestine and gill).

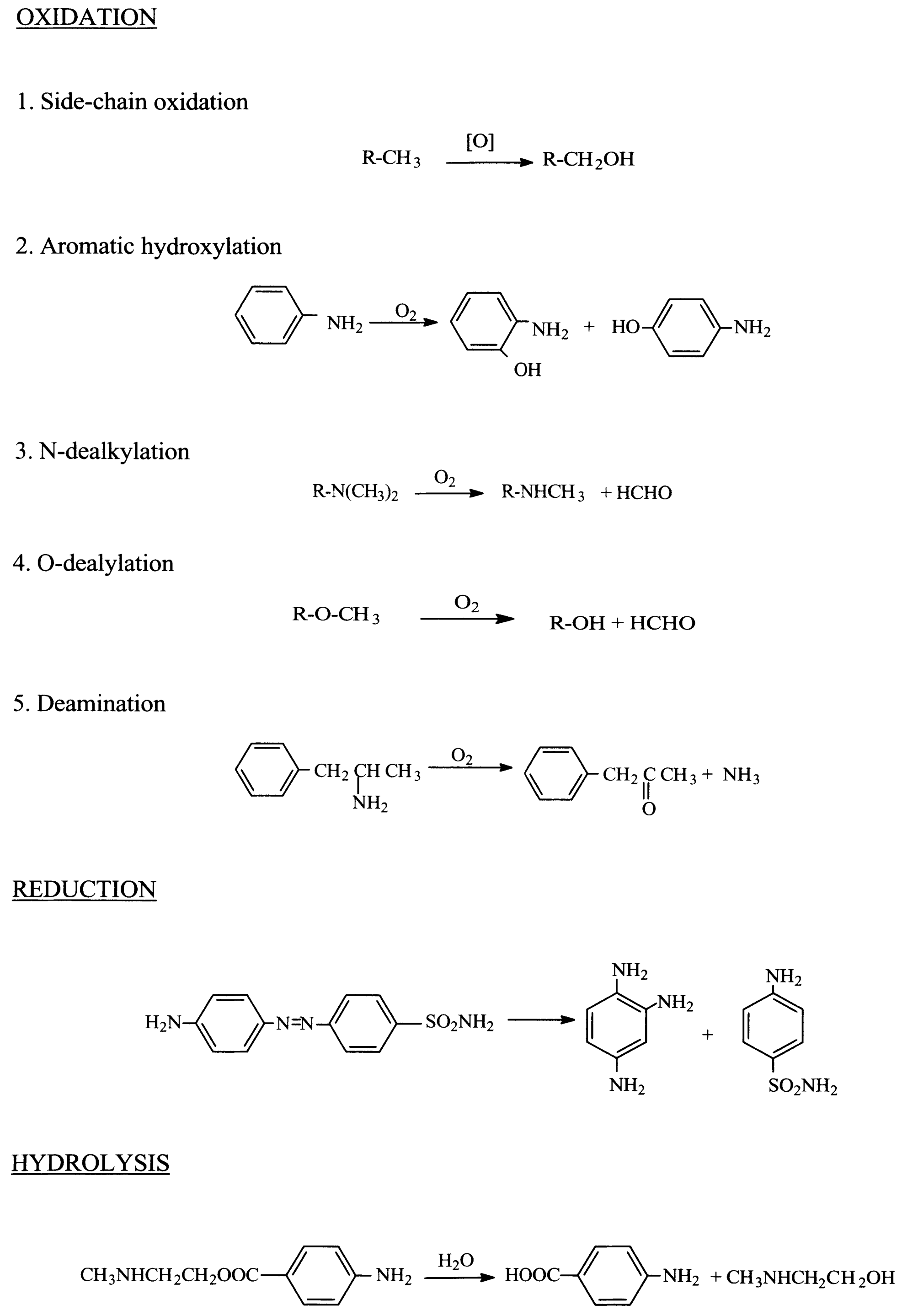


FIGURE 9.28. Examples of Phase I biotransformation reactions.

The second phase in this biotransformation process (Phase II) typically involves linking highly water-soluble moieties to yield products which are more water-soluble (i.e., conjugation), thus facilitating their elimination. Conjugating agents are endogenous to the body. Typical examples include sugars, peptides, glucuronic acid, glutathione, phosphates, and sulfate ions. The enzyme system responsible for this is the cytochrome P450 II present in cytosol. The reactions involved are deamination, acyclic hydroxylation, aromatic hydroxylation, and dealkylation, which further increase hydrophilicity for excretion in bile, urine, and sweat. See Figure 9.29.

There are two types of metabolism of toxicants:

1. *Detoxification*: Conversion of undesirable chemicals into less toxic ones that can be readily excreted by the body.
2. *Bioactivation*: Conversion of a xenobiotic into more reactive or toxic forms.

In this way, two substances with equal toxicity and absorption may be hazardous in different ways depending on the nature of their biotransformation. A substance biotransformed into a more toxic metabolite (i.e., *bioactivated*) represents a greater hazard than a substance biotransformed into a less toxic metabolite (i.e., *detoxified*).

For example, heptachlor and aflatoxin B1 (AFB1) metabolize in the liver to form the corresponding epoxides, which are more toxic than the parent substances because the epoxide form of AFB1 produces DNA adducts by binding to guanine. See Figure 9.30. The aflatoxins are synthesized by the filamentous fungus *Aspergillus flavus* and related aspergilli that affect many seeds and grains including peanuts, corn, cottonseed, and certain tree nuts. Aflatoxins are therefore relatively easy to manufacture by simply practicing poor grain husbandry.

The two most important organs for biotransformation and elimination are the liver and the kidneys.

- The liver is rich in biotransformation enzymes, and quickly transforms substances that it absorbs. Both the original compound to which the body was exposed and one or more metabolites circulate through the bloodstream. They may be stored or excreted, or they may reach the critical site of action in a target organ, at a sufficiently high concentration and for a sufficient length of time to produce toxicity.
- The kidneys filter or otherwise remove water soluble toxicants (of molecular weight < 70,000) and metabolites, and excrete them as concentrated solutes into urine for elimination.

Some toxic agents such as Pb, Hg, other heavy metals, and many organic substances are excreted in the bile as conjugates to the intestinal tract for elimination in the feces. Other common routes of elimination include the lungs for gaseous (e.g., NH_3) and volatile toxicants (e.g., alcohol, sweat, tears, and saliva), as well as breast milk and eggs in females.

Substances with a low or null elimination rate accumulate in the organism (i.e., *bioaccumulation* or *bioconcentration*). If this occurs in small organisms at the base of the food chain and the substance *i* tends to accumulate in all the organisms along the chain, then—because of the energy pyramid—the higher organisms will concentrate this substance within them, where it may reach important levels of toxicity. The process is called *biomagnification* of the substance *i* along the food chain, and it is related to a characteristic environmental parameter known as the *bioconcentration potential factor, BCF* defined in eq. 9.2. The higher the BCF, the higher the potential for bioconcentration and biomagnification.

$$\mathrm{BCF}_i = \frac{\text{Concentration of } i \text{ in an indicator organism (ind) (e.g., fish)}}{\text{Concentration of } i \text{ in water}} = \frac{\mathrm{mg}_i\text{, ind/kg}}{\mathrm{mg}_i\text{, water/L}} \tag{9.2}$$

One of the first substances to set off the alarm for this phenomenon was the pesticide DDT in 1962, when Rachel Carson exposed its long range hazards in her book, *Silent Spring*. DDT has a fish BCF of 54,000 L/kg.

(k) Interactions due to the presence of other chemicals

There are four basic types of interactions, as shown in Table 9.5.

(1) Outcome or endpoint of the toxic effect

Toxic effects are categorized according to the site of the toxic effect. In many cases, the effect occurs at only one site (i.e., the *specific target organ*). See

CONJUGATION

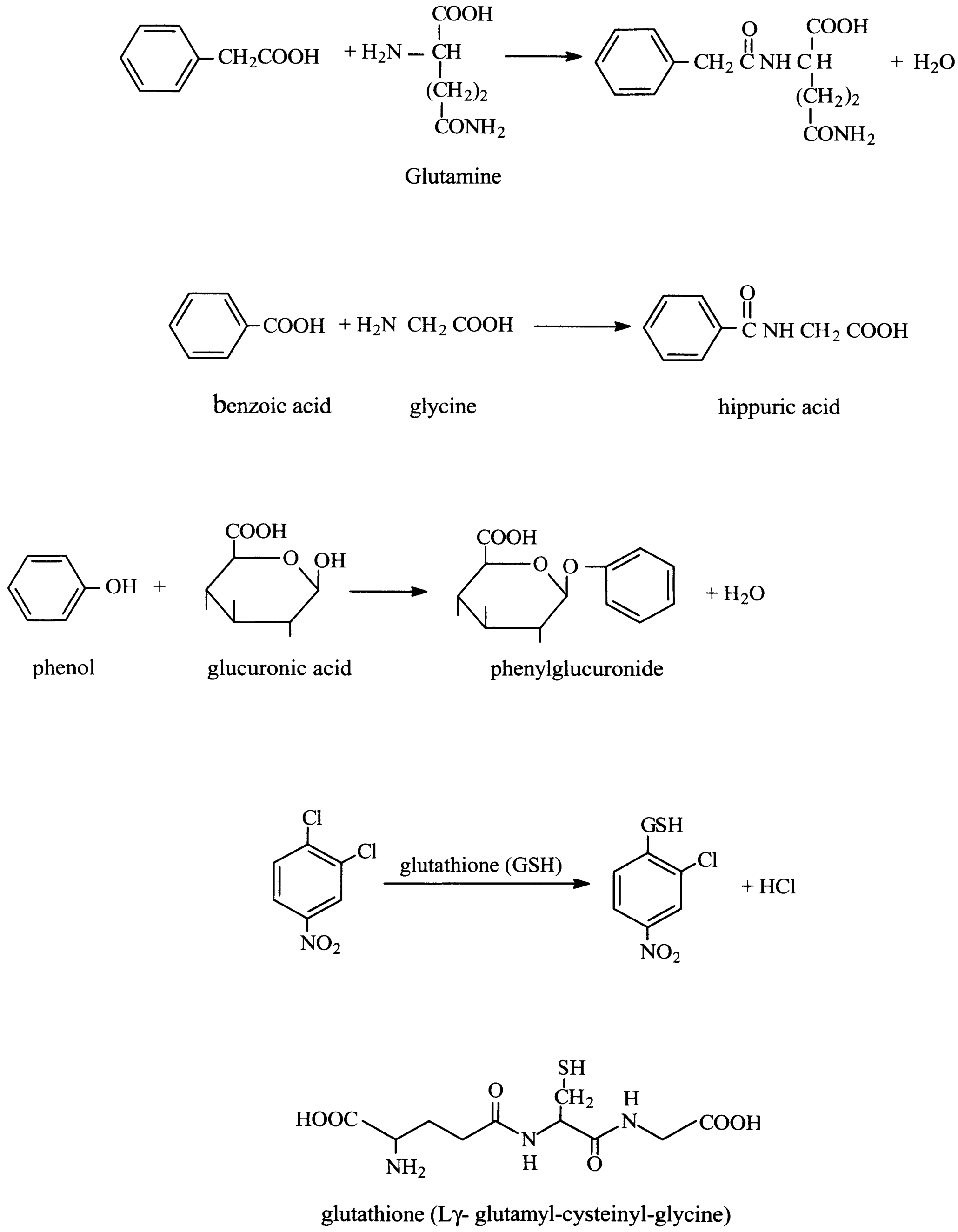


FIGURE 9.29. Examples of Phase II biotransformation reactions.

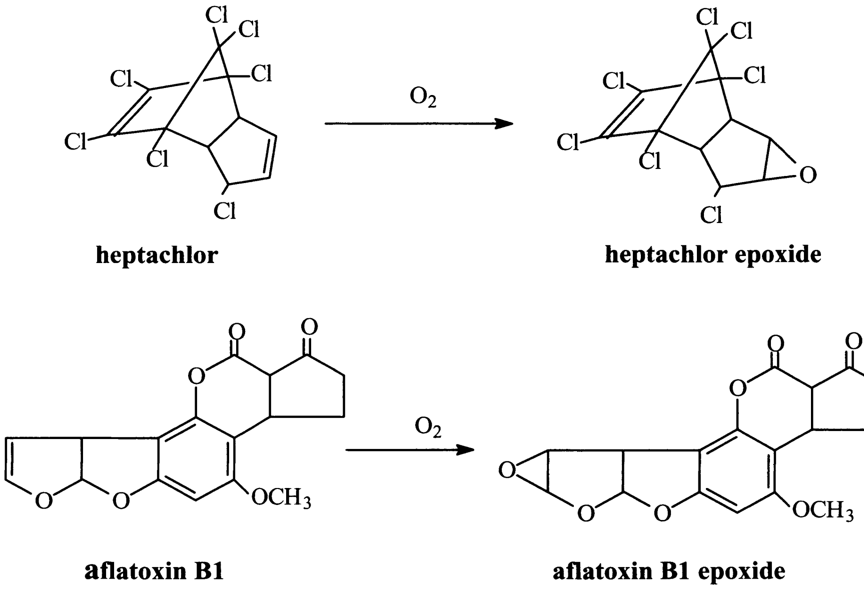


FIGURE 9.30. Biotransformation products more toxic than the absorbed compounds.

Table 9.6. In other cases, toxic effects occur at multiple sites (i.e., *systemic toxicity*).

There are several types of *systemic toxicity*. These are described below.

1.1 *Genotoxicity*

Genetic toxicity results from DNA damage and altered genetic expression. This process is known as *mutagenesis*. The genetic change is called *mutation* and the agent causing the change is a *mutagen*. There are three types of genetic changes:

- Gene mutation—change in the base sequence of DNA
- Chromosome aberration—changes in chromosome structure
- Aneuploidy/polyploidy—decrease/increase in the number of chromosomes

If the mutation occurs in a germ cell, the effect is heritable. If the mutation occurs in a somatic cell, it can cause altered growth (e.g., cancer) or cell death (e.g., teratogenesis).

TABLE 9.5. Types of interactions related to toxicity among chemical substances

Interaction	Example
Additivity The response to the combination of two or more toxicants is the sum of the expected individual responses.	Chlorinated insecticides as well as halogenated solvents produce liver toxicity. The hepatotoxicity of an insecticide formulation containing both substances is equivalent to the sum of the hepatotoxicity of each.
Antagonism Exposure to a substance results in the reduction of the effect produced by the toxicant.	Carbon monoxide poisoning is treated with O_2 that displaces the CO from hemoglobin receptors. Antidotes function by antagonizing the toxicity of a poison.
Potentiation Exposure to certain substances causes an increase in the effect of the toxicant alone.	Hepatotoxicity of CCl_4 is greatly enhanced by the presence of isopropanol. This can occur in the workplace.
Synergism Simultaneous exposure to two toxicants produces a dramatic increase in their effects.	Exposure to cigarette smoke and radon results in a significantly greater risk for lung cancer than the sum of their individual risks.

TABLE 9.6. Organ-specific toxic effects

Type of toxicity	Site of effect	Examples of effects
Blood/cardiovascular toxicity	Cells in circulating blood, bone marrow, and heart	• Hypoxia due to binding of CO to hemoglobin thus preventing dioxygen transport • Decrease in circulating leukocytes due to chloramphenicol damage to bone marrow cells • Leukemia due to benzene damage of bone marrow cells • Arteriosclerosis due to cholesterol accumulation in arteries and veins
Dermal toxicity	Direct contact or internal distribution to the skin	• Effects range from mild irritation to severe changes, such as corrosivity, hypersensitivity, and skin cancer. • Dermal irritation due to exposure of skin to gasoline • Dermal corrosion due to exposure of skin to NaOH • Dermal hypersensitivity due to exposure of skin to poison ivy • Skin cancer due to ingestion of As or exposure of skin to UV light
Ocular toxicity	Cornea and conjunctiva	• Acids and strong alkalis may cause severe corneal corrosion • Corticosteroids may cause cataracts • Methanol (i.e., wood alcohol) may damage the optic nerve
Hepatotoxicity	Liver, bile duct, and gall bladder. The liver is particularly susceptible to xenobiotics due to its large blood supply and its role in metabolism	• Steatosis (lipid accumulation in hepatocytes) • Chemical hepatitis (inflammation of the liver) • Hepatic necrosis (death of the hepatocytes) • Hepatic cancer (cancer of the liver) • Hepatic cirrhosis (chronic fibrosis) • Hypersensitivity (immune reaction resulting in hepatic necrosis)
Immunotoxicity	The normal function of the immune system is to recognize and defend against foreign invaders. This is brought about by the production of cells that enclose and destroy the invaders or by antibodies that inactivate foreign material	• Hypersensitivity (allergy and autoimmunity) • Immunodeficiency, and uncontrolled proliferation (leukemia and lymphoma) • Contact dermatitis due to exposure to poison ivy • Systemic lupus erythematosis in workers exposed to hydrazine • Immunosuppression by cocaine • Leukemia induced by benzene • Leukemia induced by ^{90}Sr or ^{137}Cs
Nephrotoxicity	Kidneys are highly susceptible to toxicants for two reasons: A high volume of blood flows through them, and they filtrate large amounts of toxins which can concentrate in the kidney tubules	• Decreased ability to excrete body wastes • Inability to maintain body fluid and electrolyte balance • Decreased synthesis of essential hormones (e.g., erythropoietin)
Neurotoxicity	Cells of the central nervous system, CNS (brain and spinal cord) and the peripheral nervous system (nerves outside the CNS)	• Neuronopathies (neuron injury) • Axonopathies (axon injury) • Demyelination (loss of axon insulation) • Interference with neurotransmission
Reproductive toxicity	Male or female reproductive system	• Decreased libido and impotence • Infertility • Interrupted pregnancy (abortion, fetal death, premature delivery) • Infant death or childhood morbidity • Altered sex ratio and multiple births • Chromosome abnormalities and birth defects • Childhood cancer
Respiratory toxicity	Upper respiratory system (nose, pharynx, larynx, and trachea) and the lower respiratory system (bronchi, bronchioles, and lung alveoli)	• Pulmonary irritation • Asthma/bronchitis • Emphysema • Allergic alveolitis • Fibrotic lung disease • Lung cancer

TABLE 9.7. Selected key substances and their toxic effects

	Mutations	Carcinogenic effects	Birth defects	Still births	Nervous disorders	Liver disease	Kidney disease	Lung disease
Benzene	X	X	X	X				
Dichlorobenzene	X			X	X	X		
Chloroform	X	X	X		X			
Carbon tetrachloride	X		X	X	X	X		
Vinyl chloride	X	X			X	X		X
Tetrachloroethylene		X			X	X	X	
Heptachlor	X	X		X	X	X		
PCBs	X	X	X	X	X	X		
Tetrachlorodibenzodioxin	X	X	X	X	X	X		
Toluene	X		X	X				
Xylene			X	X	X			
Pb					X			
Hg			X		X			

1.1.1 Carcinogenicity

Carcinogenicity is a complex multistage process of abnormal cell growth and differentiation that can lead to cancer. At least two stages are recognized: *initiation* in which a normal cell undergoes irreversible changes, and *promotion* in which initiated cells are stimulated to progress to cancer. Chemicals can act as initiators or promoters.

A *tumor* (neoplasm) is an uncontrolled growth of cells. *Malignant* tumors (cancer) invade adjacent tissues or migrate to distant sites (metastasis). They are difficult to treat and may cause death. The initial neoplastic transformation results from the mutation of the cellular genes that control normal cell growth. This transformation may involve loss of suppressor genes responsible for restricting abnormal cell growth.

1.1.2 Developmental toxicity

The toxic effects that occur from fertilization until sexual maturation to an adult can be grouped as *developmental effects*, with the following subcategories:

- *Reproductive effects* are adverse effects associated with the process of reproduction, starting from the production of germ cells via fertilization, implantation, and development of the embryo to fetal growth, and ending with birth.
- *Teratogenicity* specifically refers to the subcategory of pathological effects after the implantation of the embryo and up to the first 3 months of pregnancy in humans, where major tissues and organs differentiate and develop, and major malformations may result.
- *Fetotoxicity* represents disturbances in the later stages of pregnancy.
- *Postnatal* development is another period of concern because the rapid growth of a child makes it more susceptible than the adult body to some toxic agents.

The main toxic effects of selected key substances are listed in Table 9.7.

9.3 Human Health Risk Assessment

Assessing the toxicity of specific chemicals is a complex and uncertain undertaking due not only to the number of variables that affect the toxicity of a particular chemical, but also to the great variety of target organs and tissues that exist. This is specially true when it is the toxicity to humans that is under investigation.

For decades, risk assessors have essentially considered the effects on humans from exposure to individual substances. Standardized approaches have been developed along with research to improve this methodology and its reliability. The increased complexity of risk assessments and the numerous organizations performing them have led to the use of varied risk assessment concepts. Two main concepts—*risk* and *hazard*—were used earlier in different ways, creating confusion to the regulators and the public. To facilitate consistency, the National Academy of Sciences (NAS) recommended key definitions in

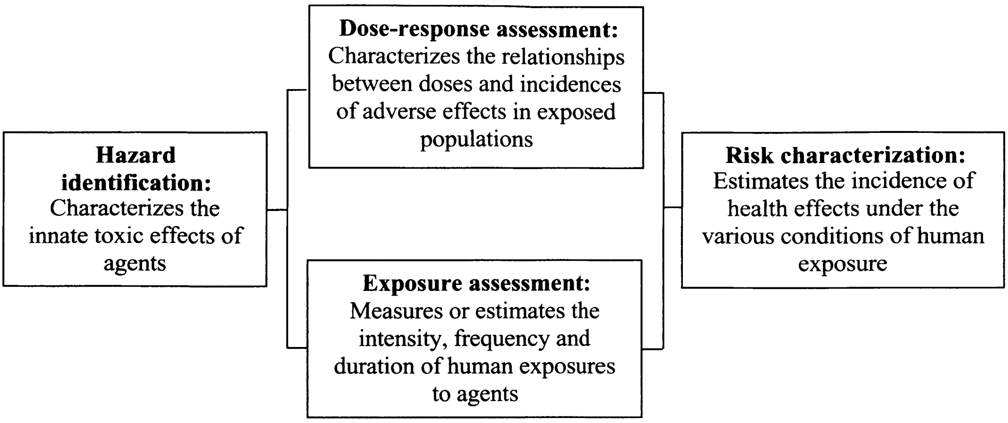


FIGURE 9.31. The NAS risk assessment process.

1983, including the main principles of risk assessment and risk management as follows:

- *Hazard* is the capability of a substance to cause an adverse effect.
- *Risk* is the probability that the hazard will occur under specific exposure conditions.
- *Risk assessment* is the estimation of the probability that an adverse effect will result from a defined exposure. It is the process by which hazard, exposure, and risk are determined.
- *Risk management* is the process of weighing policy alternatives and selecting the most appropriate regulatory actions based on the results of risk assessment and social, economic, and political concerns.

The *risk assessment* process was organized by NAS into four primary activities, as shown in Figure 9.31.

9.3.1 Hazard Identification

In this initial step, the potential for a xenobiotic to induce any type of toxic hazard is evaluated. Information is gathered and analyzed in a *weight-of-evidence approach.* This usually consists of:

- human epidemiology data
- animal bioassay data
- supporting data

Human epidemiology data are the most desirable of the three and are given the highest priority because they avoid the concern for species differences in the toxic response. Unfortunately, reliable epidemiology studies are seldom available, and typically contain incomplete and unreliable exposure histories. For this reason, it is uncommon for risk assessors to construct a reliable dose–response relationship for toxic effects based on epidemiology studies. More often, studies in humans only provide qualitative evidence of a causal relationship.

In practice, *animal bioassay data* are generally the primary data used in risk assessments. Animal studies are well-controlled with known exposures, and they are carried out with detailed, careful clinical and pathological examinations. The use of laboratory animals to determine potential toxic effects in humans is a necessary and accepted procedure. It is a recognized fact that effects in laboratory animals are usually similar to those observed in humans at comparable dose levels. Exceptions are primarily attributable to differences in the pharmacokinetics and metabolism of the xenobiotics.

The simplest and most commonly applied toxicity test is the single-exposure study, with death as the ultimate criterion of toxicity. It consists in administering a single dose to a limited number of animals and determining the LD_{50}. This test for acute toxicity was developed largely in response to concerns about the most highly exposed groups, mainly workers. While such values provide a measure of the amount needed to kill rodents, they cannot be extrapolated to estimate how much of the material would kill 50% of the humans exposed to it. However, they are useful in predicting relative toxicity in humans in addition to giving clues about toxic effects that might appear in long-term tests.

Subacute or subchronic assays assess the effects of daily exposures of an animal population to a toxicant over approximately 10% of the animal's lifetime. In rats, this corresponds to about 3 months. Careful study of the animals—including examination of all body tissues and fluids—reveals the dose at which toxic effects begin to occur at several endpoints, such as organ dysfunction, behavioral changes, or alterations in levels of normal body fluid components. The highest dose at which none of the animals show toxic effects is called *NOAEL* (i.e., no observable adverse effect). Other doses include *LOEL* (lowest observed effect level), the lowest dose for which effects were expressed; and *LOAEL* (lowest observed adverse effect level), a stricter version of LOEL that addresses only adverse effects. In these tests several species are tested and the most sensitive one is selected as a human surrogate. See Figure 9.32.

Testing for long-term chronic effects has evolved as a response concerning the general population. The best developed chronic test to date is the rodent carcinogenesis bioassay. Here, groups of rats are exposed every day to a particular chemical at the same dose for a lifetime. During the course of the study and at the end, the animals are examined for tumors, and the incidence at each dose is recorded. Generally, two or three doses are used to establish a dose–response relationship for cancer. The studies are performed with very high doses compared to the NOAEL, but lower doses than in the LD_{50}. The highest dose used is called the *maximum tolerated dose (MTD)* and can be defined as the level of exposure that will not shorten the lifetime of the animal due to toxic effects other than cancer.

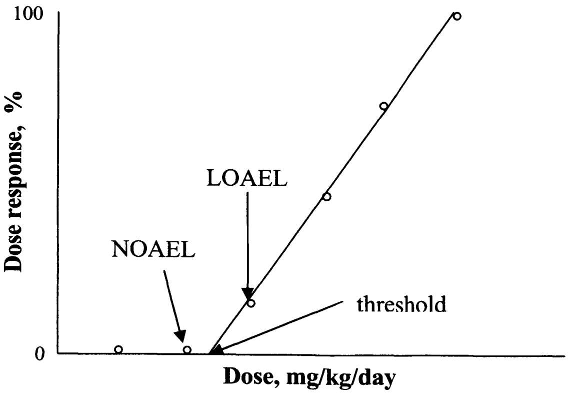


FIGURE 9.32. Dose–response relationship for non-carcinogenic effects.

Supporting data derived from cell and biochemical studies may help the risk assessor make meaningful predictions of the likely human response. For example, a chemical is often tested with both human and animal cells to study its ability to produce cytotoxicity, mutations, and DNA damage. The cell studies can help identify the mechanism by which a substance has produced an effect in the animal bioassay. In addition, species differences may be revealed and taken into account.

A chemical's toxicity may be predicted based on its similarity in structure to that of a chemical whose toxicity is known. This is called the *structure-activity relationship (SAR)*. The value of SAR in risk assessment is limited because of exceptions to the predicted toxicity.

Based on these results, one or more toxic hazards may be identified (e.g., cancer, birth defects, chronic toxicity, and neurotoxicity). A *primary hazard of concern* is one in which there is a serious health consequence (e.g., cancer) that can occur at lower dosages than other serious toxic effects. The primary hazard of concern is chosen for the dose-response assessment.

9.3.2 Dose–Response Assessment

The dose–response assessment phase measures the hazards, which were identified in the hazard evaluation phase. It determines the relationship between dose and incidence of effects in humans. Two major extrapolations are normally required: the first is from high experimental doses to low environmental doses, and the second is from animal to human doses.

The procedures used to extrapolate from high to low doses are different for the assessment of carcinogenic effects and non-carcinogenic effects. *Non-carcinogenic effects* include all the toxicological responses other than the induction of tumors. The toxic endpoints of non-carcinogenic agents vary widely, as do mechanisms by which they cause the toxic effect. Toxicants may combine with cell membranes, displace elements that are important for performing normal cell activity, or affect enzymes. Non-carcinogenic effects are considered to have dose thresholds below which the effect does not occur. The lowest dose with an effect in animal or human studies is divided by *safety factors* to provide a margin of safety. *Carcinogenic effects* are not considered to have a threshold, and mathematical models generally provide estimates of carcinogenic risk at very low dose levels.

9.3.2.1 Non-carcinogenic Risk Assessment

Historically speaking, the *acceptable daily intake (ADI)* procedure has been used to calculate permissible chronic exposure levels for humans, based on non-carcinogenic effects. The ADI is the amount of a chemical to which a person can be exposed each day for a long time (usually for a lifetime) without suffering harmful effects. It is determined by applying safety factors that account for the uncertainty in the data, to the highest dose used in human or animal studies which has been shown not to cause toxicity (i.e., the NOAEL).

The U.S. Environmental Protection Agency (EPA) has slightly modified the ADI approach and it calculates a *reference dose (RfD)* as the acceptable safety level for chronic non-carcinogenic and developmental effects. Similarly the ATSDR (Agency for Toxic Substances and Disease Registry) calculates *minimal risk levels (MRLs)* for non-cancer endpoints.

The *critical toxic effect* used in the calculation of an ADI, RfD, or MRL is the serious adverse effect which occurs at the lowest exposure level. It may range from lethality to minor toxic effects. Humans are assumed to be as sensitive as animal species unless evidence indicates otherwise.

In determining the ADIs, RfDs, or MRLs, one divides the NOAEL by safety factors (i.e., *uncertainty factors*) in order to provide a safety margin for allowable human exposure.

$$\mathrm{ADI}_{(\text{human dose})} = \frac{\mathrm{NOAEL}_{(\text{experimental dose})}}{\text{Safety factors}} \tag{9.3}$$

The *uncertainty factors* or *safety factors* used to derive an ADI or RfD are given in Table 9.8.

TABLE 9.8. Uncertainty or safety factors

10 ×	human variability
10 ×	extrapolation from animals to humans
10 ×	use of less-than-chronic data
10 ×	use of LOAEL instead of NOAEL
0.1–1.0 ×	modifying factor

The modifying factor is used only in deriving EPA Reference Doses. A modifying factor of 0.1–10 allows risk assessors to use scientific judgment in upgrading or downgrading the total uncertainty factor based on the reliability and quality of the data. For example, if a particularly good study is the basis for the risk assessment, a modifying factor of <1 may be used. If a poor study is used, a factor of >1 can be incorporated to compensate for the uncertainty associated with the quality of the study.

The general formula for deriving the RfD is:

$$\mathrm{RfD} = \frac{\text{NOAEL or LOAEL}}{\text{Safety factors}} \tag{9.4}$$

The more uncertain or unreliable the data becomes, the higher the total uncertainty factor that needs to be applied. For example, if data from a high quality epidemiologic study are available and the NOAEL is 50 mg/kg/day, a simple factor of only 10 is used to account for intra-human variability:

$$\mathrm{RfD} = \frac{50\ \mathrm{mg/kg/day}}{10} = 5\ \mathrm{mg/kg/day} \tag{9.5}$$

If data are more uncertain or unreliable, as if only LAOEL from an animal subchronic study is available, the uncertainty factors are 10 for human variability, 10 for an animal study, 10 for less than chronic exposure, and 10 for use of an LOAEL instead of a NOAEL.

$$\mathrm{RfD} = \frac{50\ \mathrm{mg/kg/day}}{10 \times 10 \times 10 \times 10} = 0.005\ \mathrm{mg/kg/day} \tag{9.6}$$

In addition to chronic effects, RfDs can also be derived for other long-term toxic effects, including developmental toxicity.

ATSDR derives *minimal risk levels (MRLs)* for non-cancer toxicity effects (e.g., birth defects or liver damage). The MRL is defined as an estimate of daily human exposure to a substance that is likely to be without an appreciable risk of adverse effects over a specified duration of exposure. For inhalation or oral routes, MRLs are derived for acute (14 days or less), intermediate (15–364 days), and chronic (365 days or more) durations of exposures. The method used to derive MRLs is a modification in the RfD methodology of the EPA. The primary modification is that the uncertainty factors of 10 may be lower, even down to 2 or 1, based on scientific judgment. These uncertainty factors are applied for human variability, interspecies variability (extrapolation from animals to humans), and use of a LOAEL instead of NOAEL. As in the case of RfDs, the product of uncertainty factors multiplied together is divided into the NOAEL or LOAEL to derive the MRL.

Risk assessments are also conducted to derive permissible exposure levels for acute or short-term exposures to chemicals. *Health Advisories* (*HAs*) are determined for chemicals in drinking water. They are the allowable human exposures for 1 day, 10 days, longer term, and lifetime durations. The method used to calculate HAs is similar to that of the RfD methodology using uncertainty factors. Data are being developed from toxicity studies with durations appropriate to the HA.

For occupational exposures, *Permissible Exposure Levels* (*PELs*), *Threshold Limit Values* (*TLVs*), and *NIOSH Recommended Exposure Levels* (*RELs*) are developed. They represent dose levels that will not produce adverse health effects from repeated daily exposures in the workplace. The method used to derive them is conceptually the same. Safety factors are used to derive the PELs, TLVs, and RELs.

Animal doses must be converted into human dose equivalents. The *human dose equivalent* is based on the assumption that different species are equally sensitive to the effects of a substance per unit of body weight or body surface area.

Historically, The U.S. Federal Drug Administration (FDA) used a ratio of body weights of humans to animals in order to calculate the human dose equivalent. EPA has used a ratio of surface areas of humans to animals for the same purpose. The animal dose was multiplied by the ratio of human to animal body weight raised to the 2/3rd power (to convert from body weight to surface area). FDA and EPA have agreed to use body weight raised to the 3/4th power to calculate human dose equivalents in the future.

9.3.2.2 Cancer Risk Assessment

In order to determine the cancer incidence at the level of concern for humans, one must mathematically manipulate the high-dose data to calculate a low-dose value. There is no scientific consensus regarding the mechanism of cancer production, and thus no general agreement as to the mathematical procedure that should be used to make the extrapolation. Depending on the assumptions, a variety of curves could be drawn and several values could be determined. The calculated dosage corresponding to a particular cancer incidence could vary by several orders of magnitude.

Cancer risk assessment involves two steps. The first step is a qualitative evaluation of all epidemiology studies, animal bioassay data, and biological activity (e.g., mutagenicity). The substance is classified as to the carcinogenic risk to humans based on the weight of evidence. If the evidence is sufficient, the substance may be classified as a definite, probable, or possible human carcinogen.

The second step is to quantify the risk for those substances classified as definite or probable human carcinogens. Mathematical models are used to extrapolate from the high experimental doses to the lower environmental doses.

The two primary cancer classification schemes are those of the EPA and the International Agency for Research on Cancer (IARC). The EPA and IARC classification systems are quite similar.

The EPA's cancer assessment procedures have been used by several federal and state agencies. The Agency for Toxic Substances and Disease Registry (ATSDR) relies on EPA's carcinogen assessments. A substance is assigned to one of six categories as shown in Table 9.9.

The basis for *sufficient human evidence* is an epidemiology study that clearly demonstrates a causal

TABLE 9.9. Carcinogenic categories

• Group A	Human carcinogen	Sufficient human evidence for causal association between exposure and cancer
• Group B1	Probable human carcinogen	Limited evidence in humans
• Group B2	Probable human carcinogen	Inadequate evidence in humans. Sufficient evidence in animals
• Group C	Possible human carcinogen	Limited evidence in animals. Inadequate evidence in animals
• Group D	Not classifiable as a human carcinogen	At least two adequate animal tests, or both epidemiology and animal studies which are negative.
• Group E	No evidence of carcinogenicity in humans	

relationship between exposure to the substance and cancer in humans. The data are determined as *limited evidence in humans* if there are alternative explanations for the observed effect. The data are considered as *inadequate evidence in humans* if no satisfactory epidemiology studies exist.

An increase in cancer appearing in more than one species or strain of laboratory animals or in more than one experiment is considered *sufficient evidence in animals*. Data from a single experiment can also be considered sufficient animal evidence if there is a high incidence or an unusual type of tumor induced. However, a carcinogenic response in only one species, strain, or study is normally considered as only *limited evidence in animals*.

When an agent is classified as a human or probable human carcinogen, it is then subjected to a *quantitative risk assessment*. For those designated as *possible human carcinogen*, the risk assessor can determine on a case-by-case basis whether a quantitative risk assessment is warranted.

The key risk assessment parameter derived from the EPA carcinogen risk assessment is the *cancer slope factor*, which is a toxicity value that quantitatively defines the relationship between dose and response. The cancer slope factor is a plausible upper-bound estimate of the probability that an individual will develop cancer if exposed to a chemical for a lifetime of 70 years. The cancer slope factor is expressed as mg/kg/day. See Figure 9.33.

Mathematical models are used to extrapolate from animal bioassay or epidemiology data to predict low dose risk. Most models assume linearity with a zero threshold dose.

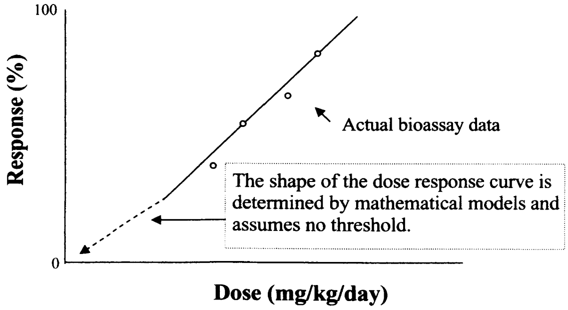


FIGURE 9.33. Dose–response relationship for carcinogen effects.

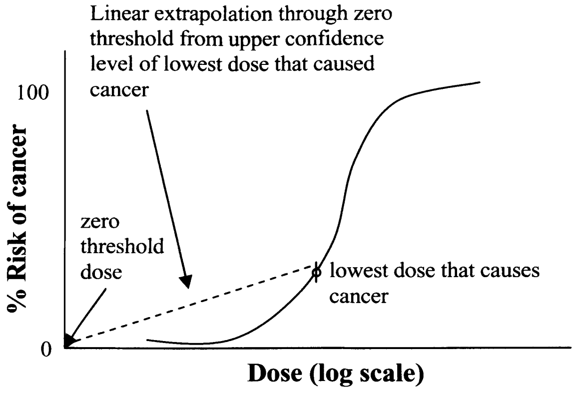


FIGURE 9.34. Extrapolation in the LMS model.

The EPA uses the *linearized multistage model* (*LMS*)—illustrated in Figure 9.34—to conduct its cancer risk assessments. It yields a cancer slope factor, known as the *q1* (pronounced Ql-star)*, which can be used to predict cancer risk at a specific dose. The LMS assumes a linear extrapolation with a zero dose threshold from the upper confidence level of the lowest dose that produced cancer in an animal test or in a human epidemiology study.

Other models that have been used for cancer assessments include:

- *One-hit model*, which is a very conservative model. It assumes that there is a single stage for cancer and that one molecular event induces a cell transformation.
- *Multi-hit model* is a non-conservative model, as it assumes that several interactions are needed before a cell can be transformed.
- *Physiologically-based pharmacokinetic model* (*PB-PK*) incorporates pharmacokinetics and mechanistic data into the extrapolation process. PB-PK models are relatively new and are being used when biological data are available. They measure the absorption of a foreign substance, its distribution, metabolism, tissue compartmentalization, and elimination. All of these biological parameters are used to derive the target dose and comparable human doses.

The values proposed by the different cancer-risk assessment models may vary by several orders of magnitude. For example, the estimated drinking water concentrations for chlordane that will cause a lifetime risk of one cancer death in a million persons are 0.03 μg/L for the one-hit model, 2 μg/L for the multi-hit model, and 0.07 μg/L for the linearized multistage model.

The last step in risk assessment consists in expressing the risk in terms of allowable exposure to a contaminated source. Risk is expressed in terms of the concentration of the substance in the environment where human contact occurs. For example, the unit risk in air is risk per mg/m^3 whereas the unit risk in drinking water is risk per mg/L.

For carcinogens, the media risk estimates are calculated dividing cancer slope factors by 70 kg (i.e., the average weight of an adult person) and multiplying by 20 m^3/day (i.e., the average inhalation rate) or by 2 liters/day (i.e., the average water consumption rate), depending on the source medium.

9.3.3 Exposure Assessment

Exposure assessment is a key phase in the risk assessment process since without an exposure route even the most toxic chemical does not present a threat. All potential exposure pathways are carefully considered. Contaminant releases, their movement and fate in the environment, and the exposed populations are analyzed.

Exposure assessment includes three steps:

- Characterization of the exposure setting (e.g., point source)
- Identification of exposure pathways (e.g., groundwater)
- Quantification of the exposure (e.g., μg/L water)

The main variables in the exposure assessment are:

- Exposed populations (general public or selected groups)
- Types of substances (pharmaceuticals, occupational chemicals, or environmental pollutants)
- Single substance or mixture of substances
- Duration of exposure (brief, intermittent, or protracted)
- Pathways and media (ingestion, inhalation, and dermal exposure)

All possible types of exposure are considered in order to assess the toxicity and risk that might occur due to these variables.

The risk assessor first looks at the physical environment and the potentially exposed populations. The physical environment assessment may include considerations of climate, vegetation, soil type, groundwater, and surface water characteristics. Also considered are populations that may be exposed as the result of chemicals which migrate from the site of pollution. Subpopulations may be at greater risk because they are at a higher level of exposure or because they have increased sensitivity (e.g., infants, elderly people, pregnant women, and those with chronic illness). These factors are integrated with data containing sources, releases, and routes of the pollutants so as to determine the important exposure pathways. Exposure pathways usually include groundwater, surface water, air, soil, food, or breast-milk.

Because actual exposure measurements are often unavailable, exposure models may be used. For example, chemical emission and air dispersion models are used in air quality studies to predict the air concentrations for down-wind residents. Residential wells located down-gradient from a site may not currently show signs of contamination, but they may become contaminated in the future as chemicals in the groundwater migrate to the well site. In these situations, groundwater transport models may estimate the period of time that chemicals of potential concern will take to reach the wells.

9.3.4 Risk Characterization

This final stage in the risk assessment process involves prediction of the frequency and severity of effects in exposed populations. The conclusions reached concerning hazard identification and exposure assessment are integrated to yield the probability of effects likely to occur in humans exposed under similar conditions.

Because most risk assessments include major uncertainties, it is important that biological and statistical uncertainties be described in the risk characterization. The assessment should identify the components of the risk assessment process that involve the greatest degree of uncertainty.

Non-carcinogenic risk is normally characterized in terms of a *hazard index* defined by the ratio of the estimated intake dose from exposure to the reference dose (RfD). Reference doses depend on the exposure route and may be used with its exposure data. The hazard index is calculated as follows:

$$\text{Hazard index} = \frac{\text{chronic daily intake (mg/kg} \cdot \text{day)/RfD}}{\text{(mg/kg} \cdot \text{day)}} \quad (9.7)$$

If the acceptable level of intake is deemed to be equal to the reference dose, then a hazard index smaller than unity is acceptable.

The *carcinogenic risk* may be defined as the chronic daily intake dose (as developed in the exposure assessment) multiplied by the carcinogenic slope factor (as selected by the toxicity assessment). The product is the probability of developing cancer during lifetime from exposure to this chemical.

$$\begin{aligned}&\text{Carcinogenic risk} = \\ &\quad \text{chronic daily intake (mg/kg} \cdot \text{day)} \\ &\quad \times \text{carcinogen slope factor (kg} \cdot \text{day/mg)}\end{aligned} \quad (9.8)$$

For example, an increase of a 10^{-6} factor in cancer risk represents an increased lifetime risk of 1 in 1,000,000 for developing cancer.

Risk assessments may be conducted for individual chemicals or for complex mixtures of chemicals. In the case of complex mixtures such as hazardous waste sites, the process of risk assessment itself becomes quite complex. This complexity results from simultaneous exposure to many substances with the potential for numerous chemical and biological interactions, exposure through multiple media and pathways, and exposure to a wide range of target organisms with different susceptibilities (e.g., infants, adults, humans, animals, organisms).

In some complex risk assessments (e.g., for hazardous waste sites), risk characterization must consider multiple chemical exposures and multiple exposure pathways. Simultaneous *exposure to several chemicals*, each at a subthreshold level, can often cause adverse effects by the simple summation of injuries.

The assumption of dose additivity is most acceptable when substances induce the same toxic effect by the same mechanism. When available, information on mechanisms of action and chemical interactions is considered and this is useful in deriving risk assessments in a more scientific manner. Individuals are often exposed to substances through more than one exposure pathway (e.g., drinking contaminated water or inhaling contaminated dust). In such situations, total exposure will usually equal the sum of the exposures through all pathways.

9.3.5 Risk Management

Risk management decisions follow the identification and quantification of risk, and they are determined by risk assessments. During the regulatory process, risk managers may request that additional risk assessments be conducted to justify the risk management decisions—the risk assessment and risk management processes are therefore intimately related.

The history of risk management reveals that the risk management options which are selected do influence the risk assessments that are performed. They are not independent. The fundamental aim of risk management is the reduction of exposure, because toxicity to humans is an inherent (and unchangeable) property of each chemical. Examples of exposure reduction include:

- In the workplace
  + Modifications in the engineering or chemistry of an industrial process
  + Utilization of personal protection equipment by a worker (e.g., a respirator and impermeable gloves)
- In the general environment
  + Enforcement of the requirements for treating effluents before they leave the manufacturing facilities
  + Proscription of certain methods for waste disposal of toxic products
  + Removal of the population from the source of exposure. This is a rather drastic and undesirable measure

In some cases zero exposure is necessary in order to ban the production and/or use of a given chemical. This occurs most often with pesticides such as DDT, dieldrin, and 2,4,5-T, as well as with other type of substances such as PCBs. The risk management of toxic chemicals is performed in the United States, for example, by the federal government under a large number of acts, as exemplified in Table 9.10.

Although the coverage and complexity of the diverse ranges of legislation have increased dramatically in the last few decades, there are relatively few substances for which quantitative, enforceable federal standards have been established.

TABLE 9.10. Examples of major U.S. legislation dealing with the regulation of toxic substances

Legislation	Type of regulations
Clear Air Act	Air pollution standards
Comprehensive Environmental Response, Compensation and Liability Act	Remediation of hazardous waste sites
Dangerous Cargo Act	Regulation of water shipment of hazardous materials
Federal Coal Mining Safety & Health Act	Mine health and safety standards
Federal Food Drug & Cosmetic Act	Regulation of drugs, food additives and cosmetics
Federal Insecticide, Fungicide & Rodent Act	Pesticide regulation
Federal Water Pollution Control Act	Effluent and water quality standards
Hazardous Materials Transport Act	Regulation of transport of hazardous materials
Occupational Safety and Health Act	Occupational health and health standards
Safe Drinking Water Act	Drinking water standards
Toxic Substance Control Act	Hazardous substance regulations

Exposure standards and guidelines

Exposure standards and guidelines are developed by governments to protect their citizens from harmful substances and activities that can cause serious health problems.

Standards are legal acceptable exposure levels or controls issued as the result of congressional or executive mandate. They result from formal rulemaking and are legally enforceable. Violators are subject to punishment, including fines and imprisonment.

Guidelines recommend maximum exposure levels that are voluntary and not legally enforceable. A guideline may be developed by regulatory and non-regulatory agencies, or by a professional society.

Exposure standards and guidelines are the products of risk management decisions. Risk assessments provide regulatory agencies with estimates of the number of persons that can be potentially harmed under specific exposure conditions. Regulatory agencies then propose exposure standards and guidelines that will protect the public from unacceptable risk.

Exposure standards and guidelines usually provide numerical exposure levels for various media (e.g., food, consumer products, water, and air) that cannot be exceeded. Alternatively, these standards may be preventive measures for reducing exposure (e.g., labeling, special ventilation, protective clothing and equipment, and medical monitoring).

Federal and state regulatory agencies have the power to issue permissible exposure standards and guidelines. They include the following categories:

- Consumer product exposure standards and guidelines
- Environmental exposure standards and guidelines
- Occupational exposure standards and guidelines

A number of databases document RfDs, AIDs, and other toxicological data for both non-carcinogenic and carcinogenic substances. Some of these are accessible as computerized databases maintained by government agencies.

A few examples are:

- Integrated Risk Information System (IRIS), the EPA's preferred source of toxicity information for hazardous wastes
- Health Effects Assessment Summary Tables (HEAST)
- Toxicological profiles prepared by the US Agency for Toxic Substances and Disease Registry
- The International Programme on Chemical Safety (IPCS), Environmental Health Criteria, published by the U.N. Food and Agriculture Organization (FAO)

9.4 Ecotoxicology

It was after World War II that increasing concern regarding the impact of toxic discharges on the environment allowed toxicology to expand from the study of the impact on humans to that of the impact on the environment. This became known as *environmental toxicology* or *ecotoxicology*. It represented a huge jump from laboratory toxicity studies using primitive test methods (often referred to as "*one fish-in-a-jar*" or "*one rat-in-a-cage*"),

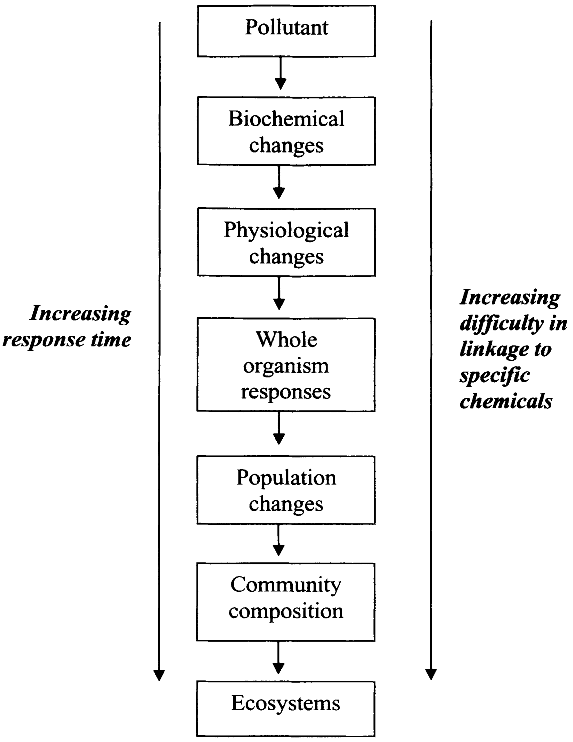


FIGURE 9.35. Relationship between responses at different organizational levels.

to studies in a complex and multivariate environment. Ecotoxicology developed from the need to measure and predict the impact of pollutants on populations, communities, and whole ecosystems rather than on individuals. Ecotoxicology represents a molecule-to-ecosystem approach, as can be seen in Figure 9.35.

The principles of exposure, absorption, metabolism, and manifestation used in the study of humans are also germane to ecotoxicology. Although the specific steps can vary widely, the pharmacokinetic fundamentals remain the same. The concepts of *structural affinity* and *chemical activity* are likewise important to ecotoxicology. Nevertheless, the application of these principles and fundamentals to diverse populations of *feral* (i.e., non-domesticated) species interacting as communities in natural systems, presents important challenges in decision-making as to the management of hazardous wastes.

As discussed in Chapter 8, pollutants may enter ecosystems as the consequence of human activity in the following ways:

- Unintended release in the course of human activities (e.g., nuclear incidents, mining operations, shipwrecks, and fires)
- Disposal of wastes (e.g., sewage and industrial effluents)
- Deliberate application of biocides (e.g., for pest control)

9.4.1 Methods of Ecotoxicology

The origin of testing dates back to pre-World War II investigations on the cause of fish kills. The pursuit of an optimal test organism has led to the testing of a wide variety of species ranging from primary producers (e.g., algae), to invertebrates (e.g., water fleas), to ultimate food chain predators (e.g., largemouth bass). Although standard toxicity test methods have been established for numerous species, scientific agreement is lacking on which species is the most sensitive to a contaminant and/or is representative of community structures.

The concept of the *most sensitive species* relates the results of toxicity tests to the "real world". In this way, certain species in a particular community are assessed as being "most sensitive" to pollutants; the results of tests on single species in artificial situations are then extrapolated to predict the effects of pollutants on whole communities or ecosystems. The logic here is that if a pollutant is non-toxic to the "most sensitive" species, then it will be safe for the rest of the community. There are, however, some questions about the usefulness of extrapolating from simple, highly artificial, single-species toxicity tests to complex, multivariate ecosystems.

Some of the ecotoxicological tests designed for monitoring changes at the subcellular, cellular, and organism levels resemble those developed for estimating toxicity in humans. In many cases, however, evaluation at the organism and suborganism level does not reveal the *extent* of a toxic effect on an ecosystem. For example, the measurement of contaminant levels in edible fish tissue is an excellent indicator of individual exposure, but it does not convey information about the possible loss of a food source in an aquatic food chain.

Ecotoxicological test methods attempt to bridge the information gaps between measurable subcellular effects and changes in the structure and function of an ecosystem. Such testing encounters increasing complexity with ascending levels of organization:

population, community, and ecosystem. The testing and evaluation of toxic effects can also fail because of interactions among chemicals released into the environment. Industrial environmental releases seldom consist of an individual chemical compound but are rather a complex mixture of chemicals. In fact, the toxicities of only relatively few of the multitude of chemicals released to the environment are understood; besides, there is minimal information with which to discern the effects of a complex *mélange* of hazardous effluents and emissions released from active facilities and contaminated sites.

These and other complicating factors may frustrate the practice of ecotoxicology. Nevertheless, well-founded approaches have been developed for evaluating toxic effects, providing reliable data for hazardous waste management decision-making. These approaches are discussed below.

9.4.1.1 Toxic Endpoints

The selection and design of an appropriate test method first requires specification of the *toxic effect* or *endpoint* to be evaluated. In ecotoxicological evaluations this is often accomplished by using two distinct, but complementary, types of endpoints: assessment and measurement. *Assessment endpoints* are ecological characteristics which, if found to be significantly affected, indicate a need for mitigating action. For example, the potential effects of a discharge to surface water on the survival and abundance of a population of native trouts presents an assessment endpoint of ecological and recreational value.

To be useful, an assessment endpoint must be measurable. Therefore, one selects a *measurement endpoint* that provides a quantitative expression related to the assessment endpoint. For the example above, the measurement endpoint may qualify the frequency of mortality within the trout population, using either toxicity tests or field monitoring as to changes in the abundance of species relative to the discharge location and dilution. The toxicity endpoints of chemicals to birds include clutch size, shell thickness, hatchability of eggs, embryiotoxicology, and viability of chicks. In the case of plants, most of the work has been done to assess the effects of metals that can be accumulated by plants known as *metallophytes*. Some metallophytes are able to grow naturally on metal-contaminated soils. A number of techniques quantify metal tolerance in plants whose endpoints include seedling survival biomass, shoot growth, and root growth, with respect to the performance of non-tolerant plants.

Assessment and measurement endpoints used in ecological evaluations at hazardous waste sites include for example:

- The number of species (or species diversity) for a community
- The extinction, abundance, yield or massive mortality of a population
- The productive capability for an ecosystem

9.4.1.2 Bioassays

To evaluate the hazards associated with chemical exposure of non-humans, ecotoxicologists have historically relied on the contamination of short-term and long-term bioassays. A *bioassay* is a technique by which organisms, biological systems or biological processes are used to measure the effects of chemical exposure.

In the context of hazardous waste management, bioassays may be defined as the laboratory exposure of organisms to field-collected environmental samples for the purpose of identifying actual or potential toxic effects on resident species. A bioassay typically involves laboratory testing in soils, sediments, or waste samples using a standard array of test organisms under controlled conditions. A simple example consists in pumping contaminated surface water through a tank containing juvenile trout.

Nevertheless, simulating exposure and interpreting its effects on communities and ecosystems is far more demanding than measuring exposure and effects on populations of individuals exposed in laboratory systems.

Laboratory simulation of ecosystems has been attempted. *Microcosms* have been used to imitate ecosystem structure and function on a reduced scale in the laboratory. For example, terrariums are common microcosms used as surrogates of simplified terrestrial ecosystems. In order to reduce the difficulty presented by the scale used and diminish the uncertainty in data extrapolation, ecotoxicologists have developed macro model systems (known as *mesocosms*) as isolated portions or replications of natural settings. Microcosms and mesocosms are often used to evaluate the fate, transport, and effects of new chemicals seeking registration.

9.4.2 Ecotoxicity Determination

There are many different ways to measure toxicity.

9.4.2.1 *Short-Time Toxicity Tests*

Short-time or acute toxicity tests are used to evaluate severe effects from exposures spanning relatively short periods of time. The standard test for measuring acute lethality is designed to produce a 50% lethal response in a test organism after a 96-hour exposure. As in the case of an LD_{50}, an LC_{50} is used to measure lethality via inhalation or exposure in an aqueous solution. The 96-hr LC_{50} is recognized as the standard.

Short-term toxicity tests used to determine doses associated with sublethal responses provide an *effective concentration* (EC_{50}). For some organisms (e.g., invertebrates) death is not easily discernible; therefore the 96-h EC_{50} is cited to reflect endpoints such as immobilization or loss of equilibrium, which are considered surrogates of lethality.

When tests are performed on terrestrial animals, it is common to apply single (measured) doses orally, topically (i.e., applied to the skin or cuticle), or by injection into tissues or body fluids. There can be very large differences among groups of organisms and among species in their susceptibility to the toxic action of chemicals. The *selective toxicity ratio (SER)* is expressed in terms of the median lethal dose, and is important for the differentiation between beneficial organisms and pests:

$$\mathrm{SER} = \frac{\mathrm{LD}_{50} \text{ for species A}}{\mathrm{LD}_{50} \text{ for species B}} \tag{9.9}$$

Some SER examples are given in Table 9.11.

Acute toxicity tests can answer numerous questions about waste management such as the toxicity of an individual chemical, mixture of chemicals, leachate, or other concentrated waste streams. Tests can also be used to locate toxic "hot spots" at waste sites, and to evaluate the effectiveness of waste treatment technologies. Selecting the proper organism, exposure system, and boundary conditions is important for producing meaningful reports.

TABLE 9.11. Examples of selective toxicity ratios

	Acute oral LD_{50} (mg/kg)		
Compound	Rats	Birds	SER
Malathion	1650	685	2.4
DDT	400	923	0.43
Dieldrin	40	91	0.75

9.4.2.2 *Long-Term Toxicity Tests*

Long-term toxicity tests (commonly referred to as *chronic toxicity tests*) are used to evaluate whether the extended laboratory exposure to a chemical will adversely affect individuals, species, or populations. These terms may measure effects on development, homeostasis, growth, and reproductive potential to establish the *lowest observed level (LOEL)*, which represents the lowest concentration associated with a measurable effect, and the *non-observed effect level (NOEL)*, which denotes a concentration that did not produce a measurable effect.

Chronic toxicity usually provides a more sensitive measurement of toxicity. To develop acceptable exposure concentrations (e.g., water quality standards), ecotoxicologists use a subcategory of chronic toxicity tests referred to as *life-cycle tests.* These tests evaluate the responses of individuals from a species over a complete life cycle to evaluate effects on their survival, growth, and reproduction. For example, a life cycle test for freshwater fish may include exposures of embryos and juvenile fish (at various stages of maturation) and adults, continuing through the reproduction and hatching of the next generation. In selecting the administration route of chemicals in toxicity testing, the major routes of natural uptake require consideration.

With aquatic organisms the direct uptake from water is a route of major importance (e.g., uptake across the gills of a fish or across the permeable skin of amphibia), but uptake may also occur from food during its passage through the alimentary system. Testing with aquatic organisms (e.g., fish like *Daphnia* and *Gammarus pulex*) usually involves continuous exposure to defined concentrations rather than the administration of single doses. Sediments represent an important source of pollutants to aquatic organisms. Lipophilic organic pollutants and some metals are strongly retained by sediments in which they have long residence times. The toxicity of chemicals associated with sediments is difficult to assess but meaningful tests are actively pursued.

It may seem that testing with terrestrial animals is simpler than with aquatic animals, as only one route of exposure (i.e., via the gut) needs consideration.

Although this is the case with widely utilized tests using rats and mice, this is certainly not so with more modern tests using invertebrates in which exposure via the external medium (i.e., air or soil) is also important. Two ecotoxicological tests using earthworms and bees are in widespread use for testing the effects of chemicals upon representative terrestrial invertebrates. Nevertheless, springtails are used to measure effects on reproduction—mainly through contact poisoning of the adults, their eggs, or the juveniles that hatch from the eggs. The most widely used organisms for the development of ecotoxicological tests are algae, earthworms, springtails, honeybees, *Daphnia*, and other fish and birds.

Apart from toxicity tests involving the use of live animals, there are other ways of evaluating the toxic properties of chemicals that stem from an understanding of their mode of action. For example, the *Ames test* aids in the identification of substances that act as carcinogens or mutagens in mammals. Also, the study of the relationship between structure and toxicity (i.e., *quantitative structure-activity relationships* or *QSARs*) can provide support for the identification of toxic substances. These approaches will become more viable as molecular mechanisms of toxicity become better known, and they can lead to an understanding of the molecular characteristics that cause a chemical to interact adversely with cellular macromolecules.

Results from short- and long-term toxicity tests are often used to

- Establish water quality criteria
- Estimate the killing or knock-down power of pesticides
- Calculate permit limitations for effluent discharge
- Project the potential impacts of catastrophic spills and chemical accidents
- Understand the actual and potential effects of hazardous waste disposal and cleanup

The fact that chemicals can be so selective makes it difficult to extrapolate toxicity data from one species to another. For practical reasons, it is possible to perform toxicity tests only on a very limited number of species. Multiple-species tests represent a more sophisticated approach to ecotoxicity testing than do single species tests, but they are at an early stage of development.

Matters can still become more complicated when considering the pollution that actually exists in the environment. For example, sewage, factory, and pulp mill effluents released into surface waters often contain complex mixtures of pollutants. The same happens in contaminated sediments and soils, where the situation can become more complex by the presence of highly persistent lipophilic compounds with long biological half-lives. Although toxicity is usually additive, there is the possibility of potentiation or inhibition (see Table 9.5).

9.4.3 Bioconcentration, Bioaccumulation, and Biomagnification

Some pollutants are assimilated by organisms to a greater extent than others, and, if they are lipophilic, they may accumulate. Measures of exposure to chemicals which bioaccumulate in tissue are easily accomplished through an analysis of tissue residues. In the absence of tissue residues, empirical constants are often derived and used by ecotoxicologists to predict bioaccumulation; examples include the *octanol—water partition coefficient*, which approximates a chemical's behavior between the lipid and water phase (see Section 8.3), the *bioconcentration factor (BFC)*, and the *bioaccumulation factor (BAC)*. These last two are defined as follows:

$$\mathrm{BCF} = \frac{\text{conc. of the chemical in the organism}}{\text{conc. of the chemical in the ambient environment}} \tag{9.10}$$

$$\mathrm{BAC} = \frac{\text{conc. of the chemical in the organism}}{\text{conc. of the chemical in food or ingested water}} \tag{9.11}$$

Bioconcentration factors are important in aquatic ecotoxicology, where the ambient medium is a major source of organic pollutants. Bioaccumulation factors are critical in terrestrial ecotoxicology, where food (or in some cases ingested water) is a major source of organic pollutants.

The tissue concentration of a persistent lipophilic pollutant with a long biological half-life that bioaccumulates and/or bioconcentrates, can increase as the chemical moves up through trophic levels in the food chain in a process known as *biomagnification*. This concentration can reach a very high level in vertebrate predators at the top of food chains. Examples of such pollutants include organochloride insecticides (e.g., dieldrin and DDT), many PCBs, dioxins, methyl mercury, and tributyltins. Water-soluble and readily-biodegradable compounds usually do

TABLE 9.12. Examples of biomarkers

Biomarker	Pollutant	Organizational level
Inhibition of ALAD (see Text)	Pb	Organ
Induction of metallothionein	Cd	Organ
DNA and hemoglobin adducts	PAHs	Organ
Eggshell thinning	DDT, DDE	Individual animal, population
Inhibition of AchE (acetylcholine esterase)	Organophosphorous and carbamate pesticides	Organ, individual animal
Induction of monooxygenases	Polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds (OCs)	Organ, population
Feminization of embryos	Estrogenic chemicals	Organism, population
Anticoagulant clotting proteins	Rodenticides	Organism, population
Imposex in dog whelks (see text)	Tributyl tin	Organism, population

not cause problems of persistence and bioaccumulation.

Tissue residues alone do not convey information about biological responses to chemical exposure. Furthermore, measuring tissue residues is not feasible with chemicals that do not readily bioaccumulate, or with complex mixtures that require time and cost-intensive analyses that may not identify all toxic chemicals. In such cases, other indirect measures may be preferable for indicating a biological response to a toxicologically significant exposure (i.e., a *biomarker*, see below).

9.4.4 Biomarkers and Bioindicators

A *biomarker* is any biological response to an environmental chemical (at the individual, cellular, or subcellular levels) that demonstrates a departure from the healthy status. Thus, biochemical, physiological, morphological, and behavioral measurements are to be considered as biomarkers. Biological responses at higher organizational levels (i.e., populations, communities, and ecosystems) are considered as *bioindicators*. The relationship between biomarkers and bioindicators is such that it is difficult to relate biochemical changes to ecological changes, and it is also difficult to relate ecological changes to specific chemical causes.

The underlying concept in biomarkers is that the selected measurement endpoints (typically comprised of biochemical and physiological responses) can provide sensitive indexes of exposure or health effects other than death. Measurements of body fluids, cells, or tissues can indicate (in cellular or subcellular terms) the relative magnitude of chemical exposure or organism response.

Biomarkers may be of two types: biomarkers of *exposure* and biomarkers of *effect*. The first indicate exposure of the organism to chemicals, but they do not give information about the degree of the toxic effect. On the other hand, the biomarkers of effect demonstrate an adverse outcome on the organism.

Biomarkers are related to different toxicants and organizational levels. Several examples are given in Table 9.12. Biomarkers range from those that are highly specific to those that are non-specific: (a) those highly specific, as the enzyme aminolevulinic acid dehydratase (ALAD), which catalyzes a reaction involved in heme synthesis and is very sensitive to inhibition by inorganic lead; (b) those non-specific, as effects in the immune system that can be caused by a wide variety of pollutants.

Another common biomarker for trace metal exposure is the metal–binding protein *metallothionein*, which regulates normal zinc and copper metabolism and provides a mechanism for metal detoxification. Changes in metallothionein activity provide a sensitive marker of trace metal exposure.

One of the most successful biomarker assays is the measurement of "imposex" in dog whelks (*Nucella lapillus*, which have brightly-colored shells). This phenomenon is caused by tributyl tins (TBTs), widely used as antifouling coatings in boats (see Section 12.3.2). TBTs impose male characteristics on females, leading to a reduction in reproductive performance and local extinction of dog whelk populations in the most contaminated sites.

9.4.5 In Situ Monitoring

Numerous factors influence the bioavailability of chemicals to organisms: temperature fluctuations, interactions with other pollutants, soil and sediment types, rainfall characteristics, pH, and salinity. This makes it difficult to accurately predict the extent to which chemical residues are assimilated by animals and plants, as well as their biological effects in the field. Consequently, many researchers have used in situ biological monitoring to gather such information.

There are four main approaches to in situ biological monitoring of pollution:

(a) Corroborating the presence or absence of species at a site, or composition changes in the species (i.e., "community effects").
(b) Measuring concentrations of pollutants in organisms collected in the field.
(c) Assessing the effects of pollutants on organisms and relating them to concentrations in those organisms and other biotic and abiotic indicators.
(d) Detecting generally different strains of species which have evolved resistance in response to a pollutant.

9.4.6 Ecological Risk Assessment

The introduction of chemicals into an ecosystem may provide a direct hazard to individual organisms, or it may affect their ability to reproduce. These perturbations can impinge on the overall structure and function of an ecosystem or its components.

The current approaches for estimating risks to the environment are included in the ecological risk assessment. They are designed to evaluate the nature, magnitude, and transience or permanence of potential ecological effects. Somewhat similar to the four-stage process for human health risk assessment is the ecological risk assessment, consisting of the four interrelated tasks discussed below.

9.4.6.1 Characterization of the Baseline Ecology and Identification of Potential Receptor Populations

A synopsis of the prevailing ecology offers an overview of the system diversity and identifies potential sensitive subpopulations and any threatened or endangered species. It is worthwhile to select indicator species, which may represent important commercial and/or recreational populations, or sensitive, endangered species present near the affected area.

9.4.6.2 Ecological Toxicity Assessment

This is a qualitative and quantitative evaluation of the potential adverse effects from the possible exposure of the chemical of concern. It involves a summary of ecotoxicity data for chemicals present in a sensitive ecosystem, identifying relevant indexes of toxicity against which potential exposure concentrations can be compared in the risk characterization.

9.4.6.3 Evaluation of Potential Exposures

This process measures the intensity, frequency, and duration of exposure to an agent. More precisely, it evaluates the potential exposure to each chemical of concern by the potential receptor populations or indicator species that are biotic components of any ecosystems in the site which may be affected. Two important components of an exposure assessment are: (a) an exposure pathway analysis, and (b) the estimation of exposure point concentrations. To evaluate potential exposures, one requires concentrations of the chemicals of concern in the exposure media (e.g., surface water or sediments).

9.4.6.4 Risk Characterization

This task integrates information from the other three tasks. The risks to potential receptor populations that inhabit and/or use the affected ecosystems are represented with quantitative indexes and a qualitative discussion regarding the possibility for adverse effects. This qualitative method of characterization may not provide a definitive answer regarding potential risks, but it does provide a basis for professional judgment concerning the likelihood of adverse effects and yields important insights needed for further evaluation. Finally, the limitations and uncertainties inherent to ecological risk assessment must be discussed so as to provide a proper perspective when using risk characterization results in decision-making.

9.4.7 Risk Assessment

Toxicity data obtained by the testing procedures described above are eventually used to make hazard and risk assessments. Risk assessment depends on two issues: (a) the toxicity of a compound, expressed in terms of concentration (i.e., EC_{50}, LC_{50}, NOEL), and (b) the anticipated exposure of an organism to the same chemical, expressed in the same units of concentration in the water, food, or soil to which the organism is exposed.

Calculations are performed to obtain values for the *predicted environmental concentration (PEC)* and the *predicted non-effect environmental concentration (PNEC)*. Calculations of PEC are based on known release rates and dilution factors in the environment. To estimate PNEC, one divides the LC_{50} or EC_{50} for the most sensitive species tested in the laboratory by an arbitrary safety factor (often 1000). This allows room for the great uncertainty in extrapolating from laboratory toxicity data for one species to expected field toxicity for other species.

$$\frac{\text{PEC}}{\text{PNEC}} = \text{risk quotient} \qquad (9.12)$$

If this value is much smaller than unity, the risk is low. If it is unity or above, there is a substantial risk. These calculations only provide rough estimates of risk, and thus the environmental exposure must be considered as well. Such considerations strengthen the case for developing new strategies using biomarkers for risk assessment. Biomarker assays can provide measures of exposure (and sometimes of toxic effects) under actual field conditions.

Field studies encompass a wide variety of activities. In theory, the study of the effects of chemicals on individuals, populations, and communities in the field directly addresses the basic issues of ecotoxicology. The overriding problem in field studies is the very limited opportunity to control variables such as temperature, rainfall, water and air movements, and the mitigation by animals, all of which can influence the effects of environmental chemicals. The use of biomarkers to measure responses to a chemical in individual organisms can provide a causal link between exposure to the chemical and a change at the population level (i.e., population decline, decline in reproductive success, or increased mortality rate). Many field studies do not involve the controlled release of chemicals, but rather the investigation of an ongoing pollution problem. When residues of chemicals are detected, they may be related to biomarker responses that such chemicals are known to cause. In turn, these responses can be related to population changes.

Model populations or communities can be established in the laboratory or in the field which they simulate, but they do not exactly reproduce the real situation. They can be used to run controlled experiments with adequate replication and can demonstrate the effects of chemicals on ecological processes such as the carbon and nitrogen cycles discussed in Chapter 7.

The greatest importance of ecotoxicology resides in the study of the manifestation of damaging effects brought about by pollution on communities of organisms and wider ecological processes. For example, a reduction in the population of earthworms in soils contaminated with metals may lead to an accumulation of undecomposed leaf litter, which would normally be converted into feces for more rapid microbial decay. Dead leaves lock up nutrients that would otherwise be returned to the soil for new plant growth. In the aquatic environment, the acidification of lakes results in a lower overall diversity, although there are a few species which can benefit from the reduced competition and reach higher population densities than in unacidified media.

Related Experiment in the Companion Book

23. Toxicity assay using bacterial growth

Additional Related Experiments/Activities

Buell, P.; Girard, J. *Laboratory Manual for Chemistry Fundamentals*, 2nd ed.; Jones and Bartlett: Boston, MA, 2002.

- Testing for toxic substances in the environment (Experiment 23).

Lieberman, M. "A Brine Shrimp Bioassay for Measuring Toxicity and Remediation of Chemicals," *Chem. Educ.* **1999**, *76*, 1689–1691.

Persinger, H. "Expanded Emphasis on Toxicology in an Environmental Chemistry and Engineering Course," *214th Am. Chem. Soc. Nat. Meet.*, Las Vegas, NV, Sept. 7–11, 1997. Chem. Ed. Division Paper # 269.

Peters, H. P. "In Search for Opportunities to Raise Environmental Risk Literacy," *Toxicol. Environ. Chem.* **1993**, *40* (1–4), 289–300.

Pyatt, F. B. "An Introductory Appraisal of Some Effects of Copper and Lead Salts on 'Polycelis' spp," *Environ. Educ. Info.* **1991**, *10(1)*, 25–36.

Tomboulian, P.; Parrot, K. "Chemical Education for Toxic Substance Control," *J. Chem. Educ.* **1997**, *74*, 1434–1436.

References and Further Reading

Calabrese, E. J.; Baldwin, L. A. "Toxicology Rethinks its Central Belief," *Nature* **2003**, *421*, 491–492.

Cannon, J. G.; Burton, R. A.; Wood, S. G.; Owen, N. L. "Naturally Occurring Fish Poisons from Plants," *J. Chem. Educ.* **2004**, *81*, 1457–1461.

Cox, D. R. "Regression Models and Life Tables," *Royal Stat. Society, Ser. B* **1972**, *34*, 187–202.

Frome, E. L.; Kutner, M. K.; Beauchamp, J. "Regression Analysis of Poisson-Distributed Data," *J. Am. Stat. Assoc.* **1973**, *68*, 935–940.

IUPAC "Glossary of Terms Used in Toxicokinetics," *Pure Appl. Chem.* **2004**, *76*, 1033–1082. http://www.iupac.org/reports/provisional/abstract06/duffus_300906.html

Kamrin, M. A. *Toxicology: A Primer on Toxicology Principles and Applications*; Lewis Publishers: Boca Raton, FL. 1988.

Lee, C. M. "The Influence of Aluminum Speciation on Fish," Environmental Chemistry Library. NSF-Clemson University. 2002. http://www.ces.clemson.edu/ecl/labs/general/index.html

United States National Library of Medicine. Toxicology Tutorials; http://www.sis.nlm.nih.gob/enviro/ toxtutor.html

United States National Library of Medicine. Toxnet: Toxicology Data Network. http://toxnet.nlm.nih.gov/

University of Adelaide, Australia. "Data on the Environmental and Toxicological Effects of Chemical Substances"; http://www.adelaide.edu.au/library/guide/sci/Chemistry/env.html

Walker, C. H.; Hopkin, S. P.; Sibly, R. M.; Pea, D. B. *Principles of Ecotoxicology.* 2nd ed.; Taylor & Francis: London, 2001.

Yu, M.-H. "Environmental Toxicology: Impacts of Environmental Toxicants on Living Systems," Lewis Publishers: Boca Raton, FL, 2001.

Zakrezawski, S. F. *Principles of Environmental Toxicology*; American Chemical Society: Washington, DC, 1991.

Zimpleman, J. M. "Dioxin, not Doomsday," *J. Chem. Educ.* **1999**, *76*, 1662–1666.

10

Physicochemical and Physical Treatment of Pollutants and Wastes

Interest in the treatment of pollutants and wastes is not new. For example, the summary report of the papers presented at the Division of Water, Sewage and Sanitation Chemistry at the American Chemical Society National Meeting nearly a century ago (in 1925), stated:

> "Probably the greatest interest was shown in connection with the papers concerned with the treatment and disposal of industrial wastes. The proper disposal of such wastes is becoming of increasing importance, and there is no doubt but that many developments may be expected along this line in the near future."

In the same vein—as early as 1902—the U.S. Massachusetts Legislature passed an act directing the State Board of Health to "prohibit the discharge of sewage... or every other substance which may be injurious to public health or may tend to create a nuisance or to obstruct the flow of water, including all waste or refuse from any factory or other establishment where persons are employed, unless the owner thereof shall use the best practicable and reasonably avoidable means to render such waste or refuse harmless."

The emphasis of this rule on water pollution was visionary. In fact, at present approximately 75% of the hazardous wastes generated in the United States that are treated undergo *aqueous* treatment, another 10% undergo land disposal or deep-well injection, and the rest are incinerated, given various other treatments, or are either illegally dumped or stored untreated.

Numerous processes exist for the treatment of gaseous, liquid, and solid pollutants. In this chapter we give an overview of several key *principles* for pollutant treatment. Unlike previous chapters, we deal here with such processes not according to their *sphere of action* (i.e., atmosphere, hydrosphere, lithosphere, or biosphere) but according to the *physicochemical principle* involved.

10.1 Physicochemical Processes

These treatments manipulate selected physicochemical properties of pollutants in such a way that they are either rendered less harmful (or even virtually harmless in some cases) or else removed from the target medium. They are based on redox, acid–base, complexation, electrochemical, solubility, and catalytic principles, as discussed below.

Note that the success of some of these technologies based on delivery of the remediation material to the target medium often depends on finding favorable conditions for the *transfer* of the material. An example of the difficulties that may be encountered is the use of potassium permanganate, which can yield solid MnO_2 that (unfortunately) generates soil plugging and results in poor contact of the oxidizing agent with the target contaminants. This may also bring about the formation of channels that would render the technique inefficient.

10.1.1 Redox Processes

Key environmental properties as toxicity, mobility, and (bio)availability of many polluting species depend on the oxidation state of their elements. For example, as discussed in Section 6.3.1, it is well known that the chromate ion (where chromium is in a +6 oxidation state) is very toxic, whereas chromium (+3) is much less dangerous and even necessary for human life as a trace element. On the other hand, the high oxidation state of arsenic (+5) is relatively innocuous, while its low oxidation state (+3) is highly toxic. Thus, by changing oxidation states, redox processes have long been used to decrease toxicity and/or reactivity, to induce precipitation, change physical state, and increase stability. Processes discussed below include the following examples: chemical oxidation and incineration, chemical oxidants and disinfectants (chlorine, hypochlorite, chloramines, chlorine dioxide, ozone, hydrogen peroxide, permanganate, ferrate), incineration, wet oxidation (WO), advanced oxidation processes (AOP), photoassisted processes (homogeneous photolysis, hydrogen peroxide decomposition, ozone decomposition, heterogeneous photolysis, photocatalysis, electrochemically-assisted photocatalysis), the Fenton reaction, chemical reduction (sulfur-based reducing agents, nitrogen-based reducing agents, carbon-based reducing agents, metal-based reducing agents, and other reducing agents).

A key parameter for understanding these processes is the standard reduction potential, discussed in Chapter 2. Some values are given in Table 10.1.

TABLE 10.1. Redox potentials of some chemical oxidants, reductants, and radical species of interest in waste treatment and/or disinfection processes.

Species	Standard Potential, V vs. SHE
F_2/F^-	2.90*
$^\bullet OH/H_2O$	2.72
$HFeO_4^-/Fe_2O_3$	2.09
$O_3/O_2,H_2O$	2.07
H_2O_2/H_2O	1.78
MnO_4^-/MnO_2	1.68
$HO_2^\bullet/H_2O$	1.66
Cl_2/Cl^-	1.36
$ClO_2/HClO_2$	1.28
$O_2^{\bullet -}/H_2O$	0.65**
$SO_4^{2-}/SO_2 \cdot xH_2O$	0.17
Fe^{2+}/Fe	−0.45
NH_2NH_2/N_2	−1.16
BO_3^-/BH_4^+	−1.24
$e^-_{(aq)}/H^\bullet,OH^-$	−2.93
Li^+/Li	−3.04*

* F_2 and Li are included here for comparison purposes only.
** At pH = 14.

As discussed in Chapter 2, the standard (reduction) potentials are given at a pH of 0. Some redox couples have a constant value regardless of pH, but the potential of other couples varies with this parameter. The Pourbaix diagram of each system (see Section 2.3.4) determines the variations of the different equilibria involved as a function of pH.

10.1.1.1 Chemical Oxidation and Incineration

Oxidation is frequently used for the destruction of organic pollutants, for changing oxidation states of metallic ions to modify target properties, for inducing abnormal redox processes in microorganisms so as to deactivate them, and so forth. Incineration is an extreme oxidation at high temperature that is used when oxidations under milder conditions are ineffective. The main oxidants are presented in this section, although intense research on many others is under way. Since dioxygen is by far the most abundant oxidant available on Earth, it is presented separately from the others discussed below.

Dioxygen is normally used under atmospheric conditions, although high temperatures and pressures are required in special cases (see, for example, points b and c below). Aerobic biological treatment requires the presence of dioxygen for the microorganisms involved to effectively degrade wastes (see Chapter 11). In addition, some metal ions show preferential precipitation in different oxidation states. For example, $Fe(OH)_2$ is much more soluble than $Fe(OH)_3$ at the pH values normally found in environmental settings (i.e., non-extreme values). Thus, if one desires to remove Fe^{2+} from water, it is advisable to oxidize it to Fe^{3+} and then raise the pH of the solution as needed to form the insoluble hydroxide.

In spite of the high standard potential of the O_2/H_2O redox couple ($E^0 = 1.23$ V), oxidation of pollutants by atmospheric dioxygen is usually slow. This unfortunate effect may be explained with two facts:

- The reduction of dioxygen to water (concomitant with the oxidation of other species) is a $4e^-$ process, and it is virtually impossible to have the four electrons transferred simultaneously without the formation of intermediates (like $O_2^{\bullet -}$ and H_2O_2).
- The electronic configuration of the dioxygen molecule contains two unpaired electrons,

whereas most organic species do not contain unpaired electrons. Thus, there is a quantum-mechanical difficulty for electron transfer to start with. In fact, direct oxygenation of *organic* pollutants frequently requires the radical intermediate $O_2^{\bullet -}$, whose production can be favored by the addition of selected redox mediators (e.g., metal ions like Fe^{2+} and Mn^{2+}) because, like dioxygen, they possess unpaired electrons.

a. Chemical Oxidants, Chemical Disinfection

In addition to dioxygen, many other chemical oxidants are used for water and waste treatment purposes. Not surprisingly, they also tend to be powerful microorganism deactivators (and thus good disinfectants) because they may induce abnormal redox processes in cells that kill or deactivate them (or else prevent their reproduction) by the following possible mechanisms: attack or alteration of the cell wall, of the cell contents (nucleic acids, protoplasm), or of the cell functions and processes (protein synthesis, redox processes, enzymatic activity).

Waterborne microorganisms are largely responsible for the transmission of diseases such as cholera, typhoid, dysentery, muscular paralysis (e.g., poliomyelitis), infectious hepatitis, gastroenteritis, giardiasis, cryptosporidiosis, and so forth. In a drinking-water potabilization procedure not *all* the microorganisms present in water need to be killed (*sterilization*), but only those *disease-related (disinfection)*. Water disinfection can be achieved by chemical, physical, or mechanical action. Agents that provide chemical action for such purposes include:

- Halogens and derivatives (Cl_2, Br_2, I_2, HClO, ClO^-, ClO_2, HBrO, HIO, polyiodide anion exchange resins, chloramines, etc.)
- Oxygenated and highly oxidized compounds (ozone, hydrogen peroxide, phenols, alcohols, persulfate, percarbonate, permanganate, peracetic acid, etc.)
- Others (metal ions such as Ag^+ and Cu^{2+}, dyes, quaternary ammonium compounds, strong acids and bases, enzymes, etc.)

The main oxidants and disinfectants will now be described. Because the treatment they are given for each of these two roles is difficult to separate, they are dealt with together in this section, in greater detail than the other chemicals described in this chapter.

a.1 Chlorine, Hypochlorite and Chloramines

Adding chlorine to water yields the following disproportionation equilibrium:

$$Cl_{2(g)} + H_2O_{(l)} \rightleftarrows HClO + Cl^- + H^+ \qquad K = 4 \times 10^{-14} \tag{10.1a}$$

Chlorine is used for the oxidative transformation of some pollutants into innocuous species. For example, toxic cyanides can be rendered harmless by oxidation with hypochlorous acid as follows:

$$2NaCN + 5HClO \rightleftarrows 2CO_{2(g)} + N_{2(g)} + H_2O_{(l)} + 3HCl + 2NaCl \tag{10.1b}$$

In addition, the low cost and high potency of chlorine as a water disinfectant has promoted its use since the mid-19th century, and it is still the main water disinfectant used worldwide. Unfortunately, it can produce several disinfection by-products (or DBPs) including harmful halogenated organics (mainly trihalomethanes, THM, and haloacetic acids, HAA) from reactions with natural or anthropogenic organic matter. Furthermore, chlorine does not have enough residual action to avoid bacterial plaque re-growth and, consequently, it promotes corrosion in many pipelines. Nevertheless, chlorine will remain the principal disinfectant for years to come.

The dosage required for a chlorination application varies according to the specific purpose and the composition of the water to be treated. For example, the maximum recommended dosage (in mg/L, or ppm) for the reduction of BOD is 2, whereas that for the disinfection of a primary effluent is 20, and for the oxidation of the supernatant obtained in a water-treatment digester (see Section 11.1) can be as high as 140.

A. Formation of chloramines

In wastewaters, NH_3 originates from the enzymatic attack of nitrogen-containing molecules (e.g., urea and proteins). The hypochlorous acid can then react stepwise with ammonia so as to produce the three chloramines (i.e., mono-, di-, and trichloramine):

$$NH_{3(g)} + HClO \rightarrow NH_2Cl + H_2O_{(l)} \tag{10.2}$$

$$NH_2Cl + HClO \rightarrow NHCl_2 + H_2O_{(l)} \tag{10.3}$$

$$NHCl_2 + HClO \rightarrow NCl_3 + H_2O_{(l)} \tag{10.4}$$

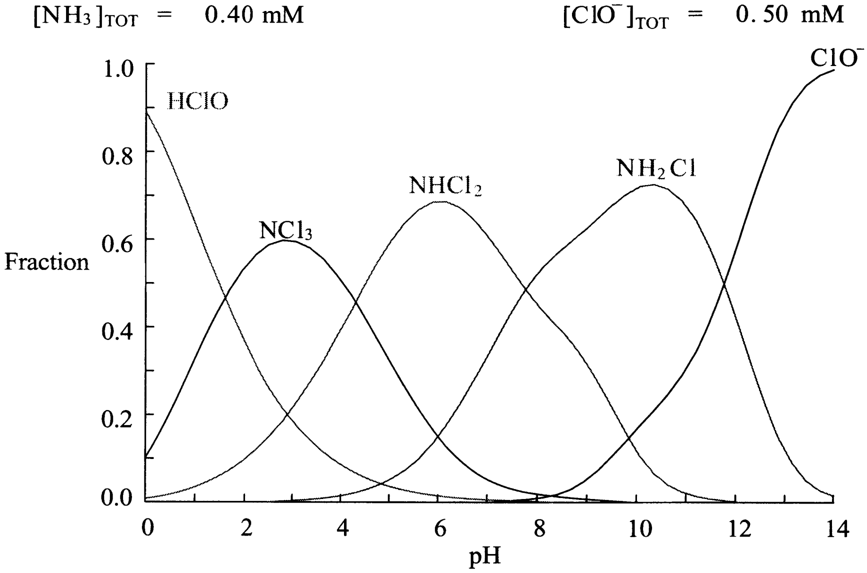


FIGURE 10.1. Chloramine distribution with pH.

Chloramines have been known since the beginning of the 19th century, and used in water treatment since the beginning of the 20th century. They have the general formula $NH_{3-x}\ Cl_x$ ($x = 0$–3). Under normal conditions, monochloramine (NH_2Cl) is the predominant chloramine in aqueous solutions.

Chloramines can be viewed as chlorine-releasing substances. Even though NH_2Cl has the same oxidizing capacity as free chlorine (in terms of the capacity for electron removal), it is less reactive and a weaker disinfectant, allowing a longer residual effect.

Many water treatment plants throughout the world have adopted the use of chloramines in addition to (or instead of) chlorine to prevent the deterioration of water-quality during passage of the liquid through distribution systems, because water may take from a few minutes to several days to reach all the points of a system. At present, approximately one-third of the water-treatment facilities in the U.S. serving cities >10,000 people use chloramination for that purpose. This produces biologically stable water, which does not promote bacterial growth. Besides, coliform re-growth decreases dramatically.

As stated above, chloramines are produced in solution when Cl_2 or ClO^- reacts with NH_3 or NH_4^+. Monochloramine is produced in aqueous solution by a fast reaction between HClO and NH_3 (99% complete in <1 min). For water treatment, it is normally produced by mixing chlorinated water (or a NaClO solution) and a solution of ammonia or ammonium chloride, at a chlorine to nitrogen (from NH_4^+ or NH_3) weight ratio between 4:1 and 5:1. Higher ratios produce dichloramine, whereas lower ratios yield an excess of NH_3. A typical chloramine species distribution diagram as a function of pH is shown in Figure 10.1. (Not all of these curves are simple monotonics due to the complexity of the equilibria involved).

Other advantages in the use of chloramines are:

- They have longer lasting action than chlorine (they may take weeks to disappear).
- There is reduced pipeline corrosion.
- Monochloramine has a higher taste and odor threshold than chlorine.
- Chloramines may be combined with other agents for special effects (e.g., with chlorine dioxide for further biofilm control and DBP reduction, and with ozone to prevent nitrification).

Challenges and disadvantages associated with the use of chloramines include the following:

- They require greater contact times than chlorine.
- Because chlorine is needed to produce the chloramines, higher chlorine doses are required to treat the same amount of water.

- Chloramination by-products such as cyanogen chloride, nitriles, aldehydes, and some halogenated compounds may form. Organic chloramines of unknown disinfecting strength may also form.
- Chloramines are dangerous for consumption when they go directly into the bloodstream. (Fortunately, normal digestive processes deactivate them). Kidney dialysis patients and fish owners need to take special care when using chloraminated water, since chloramines go through the dialysis membranes and the fish gills. Addition of ascorbic acid, or removal by granulated activated carbon (GAC), prevent this problem.
- Monochloramine promotes Pb dissolution and this may lead to increased Pb levels in drinking water.
- Chloramines may decay as a result of (i) reaction with reducing materials, (ii) hydrolysis, and (iii) disproportionation as follows.

(i) Reaction with reducing materials. The presence of reducing materials (e.g., natural organic matter, NOM) promotes chloramine decay with the concomitant ammonia production and its introduction into the water system, which may lead to nitrification. The half-reaction for monochloramine reduction can be generalized as

$$NH_2Cl + H^+ + 2e^- \rightleftarrows NH_{3(g)} + Cl^- \qquad (10.5)$$

By application of LeChatelier's principle, one can see that reaction 10.5 is favored at lower pH. The reaction of NH_2Cl with NOM can be interpreted as *chloramine demand* exerted by NOM oxidation, and written as follows:

$$NH_2Cl + NOM \rightleftarrows NH_4^+ + Cl^- + \text{oxidized products} \qquad (10.6)$$

Iron-based materials (e.g., pipe deposits, corrosion products) also promote chloramine disappearance by reacting with it to release ammonia as follows:

$$2Fe(II)_{(s)} + NH_2Cl + 6H_2O_{(l)} \rightleftarrows 2Fe(OH)_{3(s)} + NH_{3(g)} + Cl^- + 5H^+ \qquad (10.7)$$

Additionally, these iron materials may protect ammonia-oxidizing bacteria (AOB) from inactivation, which produces water nitrification that in turn promotes chloramine destruction. Numerical indicators for nitrification prevention, which are based on the [total Cl_2/free NH_3] ratio, aid in the control of such a phenomenon.

(ii) Hydrolysis. Hydrolysis of monochloramine is slow and produces small amounts of HClO:

$$NH_2Cl + H_2O_{(l)} \rightleftarrows NH_{3(g)} + HClO \qquad (10.8a)$$

The acid thus produced favors the disproportionation reaction described below (see c). Trichloramine also hydrolyzes (at pH >7):

$$NCl_3 + H_2O_{(l)} \rightleftarrows NHCl_2 + HClO \qquad (10.8b)$$

(iii) Monochloramine disproportionation:

$$2NH_2Cl + H^+ \rightleftarrows NH_4^+ + NHCl_2 \qquad (10.9)$$

The dichloramine thus formed decomposes rapidly. The reaction rate decreases with pH.

B. *Available chlorine (or chlorine residual)*

In addition to ammonia, organic compounds present may also react with HClO but at a much slower rate. Therefore, in the following discussion we will consider that any chlorine added to the water under discussion reacts mainly with these nitrogenated species in the form of HClO (recall eq. 10.1a). This acid may ionize as follows:

$$HClO \rightleftarrows ClO^- + H^+ \quad K_a = 2.7 \times 10^{-8} (\text{at } 20°C) \qquad (10.10)$$

The Frost diagram for chlorine species (see Experiment 19) shows that Cl^- is the most stable species of this system in water. Accordingly, Cl_2, HClO, and ClO^- each require $2e^-$ in order to be converted into Cl^- and, in this sense, the three will be taken as equivalents in the following equations, assuming that the final product in the three cases is the chloride ion. The *free available chlorine* (or *free chlorine residual*) can thus be understood as the sum of the concentrations of Cl_2, HClO, and ClO^-:

$$\text{Free available chlorine} = [Cl_2] + [HClO] + [ClO^-] \qquad (10.11a)$$

Chloramines have an oxidizing capacity of their own. In fact, assuming that the products are NH_3 and Cl^-, one has:

$$NH_2Cl + H^+ + 2e^- \rightleftarrows NH_{3(g)} + Cl^- \qquad (10.11b)$$

$$NHCl_2 + 2H^+ + 4e^- \rightleftarrows NH_{3(g)} + 2Cl^- \qquad (10.11c)$$

$$NCl_3 + 3H^+ + 6e^- \rightleftarrows NH_{3(g)} + 3Cl^- \qquad (10.11d)$$

Therefore, one can say that chloramines produce a *combined available chlorine* (or *combined chlorine residual*). Here, each chloramine must be proportionally taken into account according to the factor with which they take $2e^-$ as follows:

$$\begin{aligned}&\text{Combined available chlorine}\\&= [NH_2Cl] + 2[NHCl_2] + 3[NCl_3]\\&= \left(\sum_{x=0}^{2}[(3-x)]NH_xCl_{3-x}\right) \qquad (10.11e)\end{aligned}$$

Then, after the process of disinfection, and after the reactions with reduced organic and inorganic matter (including NH_3) take place, the *total available chlorine* (or *total chlorine residual*) is given by the sum of the *free available chlorine* and the *combined available chlorine*:

$$\begin{aligned}&\text{Total available chlorine}\\&= [Cl_2] + [HClO] + [ClO^-]\\&\quad + \left(\sum_{x=0}^{2}(3-x)NH_xCl_{3-x}\right) \qquad (10.11f)\end{aligned}$$

(The concentrations of Cl_2 and of NCl_3 are usually negligible).

Interestingly, after the stoichiometric formation of $NHCl_2$ from NH_2Cl, dichloramine decomposes as a result of the activation produced by the two highly electronegative chlorine atoms towards nucleophilic attack by water. Such an attack yields an unstable intermediate, (NOH)*, which is a key player in subsequent reactions:

$$NHCl_2 + H_2O_{(l)} \rightarrow (NOH)^* + 2Cl^- + 2H^+ \qquad (10.12)$$

$$NH_2Cl + (NOH)^* \rightarrow N_{2(g)} + H_2O_{(l)} + Cl^- + H^+ \qquad (10.13)$$

$$NHCl_2 + (NOH)^* \rightarrow N_{2(g)} + HClO + Cl^- + H^+ \qquad (10.14)$$

This reaction sequence brings about a decrease in the *total available chlorine*, because part of the chlorine content is transformed into Cl^-. In addition, the ammonia-nitrogen is oxidized to N_2. The global reaction resulting from this sequence is:

$$2NH_{3(g)} + 3HClO \rightarrow N_{2(g)} + 3H_2O_{(l)} + 3Cl^- + 3H^+ \qquad (10.15)$$

(See Example 10.1)

From this discussion, we can outline a plot of the total available (or residual) chlorine as a function of added chlorine. As chlorine is added, it attacks microorganisms and reacts with all the readily oxidizable substances present (i.e., DOM and inorganic substances such as sulfides, and low-valent metal ions such as Mn^{2+} and Fe^{2+}) until completion. This region of the plot is labeled "immediate chlorine demand". See Figure 10.2. Adding more chlorine

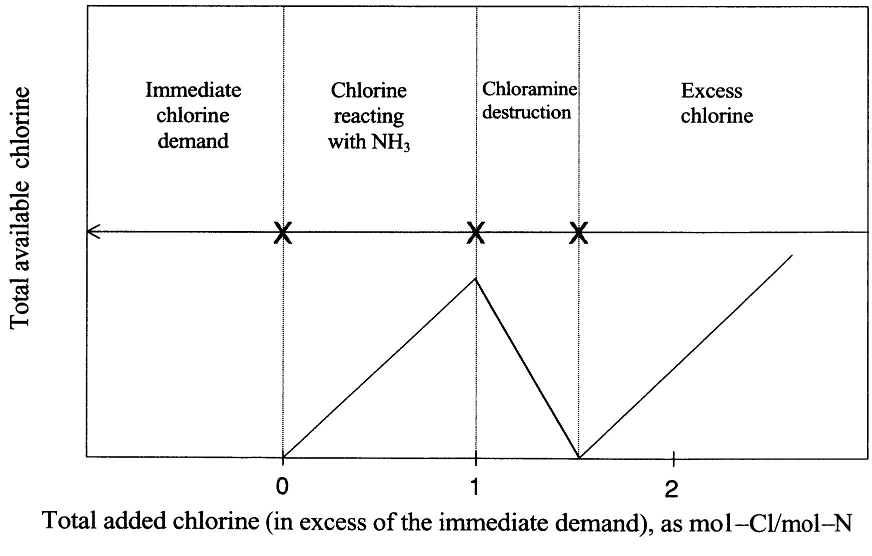


FIGURE 10.2. Idealized *total available chlorine* curve (or *breakpoint chlorination* curve).

Example 10.1 Deduce equation 10.15 from the reactions written so far in the present chapter.

Answer

We can apply the Hess Law: because the molecular N_2 in eq. 10.15 only appears in eqs. 10.13 and 10.14 (as a product), we can add them (each multiplied by one half). *Note: Physical states are omitted for simplicity.*

$$\frac{1}{2}[NH_2Cl + (NOH)^* \rightarrow N_2 + H_2O + Cl^- + H^+] \qquad (10.13)$$

$$\frac{1}{2}[NHCl_2 + (NOH)^* \rightarrow N_2 + HClO + Cl^- + H^+] \qquad (10.14)$$

$$\frac{1}{2}NH_2Cl + \frac{1}{2}NHCl_2 + (NOH)^* \rightarrow N_2 + \frac{1}{2}HClO + \frac{1}{2}H_2O + Cl^- + H^+$$

Then, we note that the $(NOH)^*$ intermediate must disappear from the equation because it does not appear in eq. 10.15. To this end, we add this last equation to eq. 10.12 as follows:

$$\frac{1}{2}NH_2Cl + \frac{1}{2}NHCl_2 + (NOH)^* \rightarrow N_2 + \frac{1}{2}HClO + \frac{1}{2}H_2O + Cl^- + H^+$$

$$NHCl_2 + H_2O \rightarrow (NOH)^* + 2Cl^- + 2H^+ \qquad (10.12)$$

$$\frac{1}{2}NH_2Cl + \frac{3}{2}NHCl_2 + (NOH)^* + H_2O \rightarrow N_2 + \frac{1}{2}HClO + \frac{1}{2}H_2O + 3Cl^- + 3H^+ + (NOH)^*$$

By canceling and uniting terms, we obtain

$$\frac{1}{2}NH_2Cl + \frac{3}{2}NHCl_2 + \frac{1}{2}H_2O \rightarrow N_2 + \frac{1}{2}HClO + 3Cl^- + 3H^+$$

Now we note that we need an equation with $2NH_3$ as the reactant, and then we must eliminate $^1/_2NH_2Cl$ and $\frac{3}{2}NHCl_2$ from the reactant side. We achieve the first objective by adding eq. 10.2 twice to the above equation:

$$\frac{1}{2}NH_2Cl + \frac{3}{2}NHCl_2 + \frac{1}{2}H_2O \rightarrow N_2 + \frac{1}{2}HClO + 3Cl^- + 3H^+$$

$$2[NH_3 + HClO \rightarrow NH_2Cl + H_2O] \qquad (10.2)$$

$$\frac{1}{2}NH_2Cl + \frac{3}{2}NHCl_2 + \frac{1}{2}H_2O + 2NH_3 + 2HClO \rightarrow N_2 + \frac{1}{2}HClO + 3Cl^- + 3H^+ + 2NH_2Cl + 2H_2O(10.3)$$

This can be simplified as:

$$\frac{3}{2}NHCl_2 + 2NH_3 + \frac{3}{2}HClO \rightarrow N_2 + \frac{3}{2}NH_2Cl + \frac{3}{2}H_2O + 3Cl^- + 3H^+$$

Because we now need to remove $NHCl_2$ as the reagent and NH_2Cl as the product, we add this equation to eq. 10.3 (multiplied by 3/2) and obtain:

$$\frac{3}{2}NHCl_2 + 2NH_3 + \frac{3}{2}HClO \rightarrow N_2 + \frac{3}{2}NH_2Cl + \frac{3}{2}H_2O + 3Cl^- + 3H^+$$

$$\frac{3}{2}[NH_2Cl + HClO \rightarrow NHCl_2 + H_2O] \qquad (10.3)$$

$$\frac{3}{2}NHCl_2 + 2NH_3 + \frac{3}{2}HClO + \frac{3}{2}NH_2Cl + \frac{3}{2}HClO \rightarrow N_2 + \frac{3}{2}NH_2Cl + \frac{3}{2}H_2O + 3Cl^- + 3H^+ + \frac{3}{2}NHCl_2 + \frac{3}{2}H_2O$$

and simplifying one has eq. 10.15:

$$2NH_3 + 3HClO \rightarrow N_2 + 3H_2O + 3Cl^- + 3H^+ \qquad (10.15)$$

results in oxidation of ammonia—N, until all of it becomes NH_2Cl in a 1:1 mole ratio (reaction 10.2). Then further addition of chlorine produces $NHCl_2$ (reaction 10.3), which in turn starts producing the reactive intermediate, NOH* (reaction 10.12). Consequently, the chloramine concentration decreases due to reactions 10.12–10.14 with a concomitant reduction in the total available chlorine. If the chloramine content is completely lost, the total available chlorine only appears as the free available chlorine. Then, equation 10.15 signals that at a chlorine-to-ammonia ratio of 3:2 (i.e., 1.5) all of the free available chlorine will be consumed. This is called the *breakpoint*, and the resulting curve (sketched in Figure 10.2) is called the *breakpoint chlorination curve*. After this point, any extra chlorine added (labeled as "excess chlorine") remains unreacted.

In practice, the breakpoint often occurs after the 1.5 mole ratio due to overoxidation of NH_3 to NO_3^-, which requires many more electrons from the available chlorine than its oxidation to $NHCl_2$ (i.e., $4e^-$ vs $8e^-$).

a2. Chlorine Dioxide A chlorine-based alternative to chlorine itself is chlorine dioxide, ClO_2 (also called chlorine peroxide), which is now in use at major water treatment facilities. This synthetic yellowish-green gas with a chlorine-like odor, under appropriate conditions, can act as an extremely effective biocide, disinfectant, and oxidizer. It is active against some chlorine-resistant pathogens. Its oxidizing and disinfecting properties remain essentially constant over a wide pH range (from 4 to 10).

Chlorine dioxide disinfection by-products (DBPs) are substantially fewer than those produced by chlorine. This is so, given that ClO_2 is unable to react with unsaturated bonds in NOM due to its different reaction mechanism: ClO_2 directly oxidizes organic matter by electrophilic abstraction rather than by the substitution and oxidation pathway of chlorine. The use of ClO_2 considerably decreases the formation of trihalomethanes and haloacetic acids, and it does not react with ammonia to produce chloramines. Concentrations of its organic by-products are sometimes a function of pH and are typically in the ppt (parts-per-trillion) range, whereas chlorine disinfection characteristically produces concentrations in the ppb (parts-per-billion) range or sometimes higher. The normal inorganic DBPs of ClO_2 are ClO_2^- and Cl^-, and under special conditions, also ClO_3^- and ClO_4^-.

Other applications include

- Pulp, paper, textile and flour bleaching
- Chemosterilization of surfaces and antiseptic applications (topical sterilization, dental and medical devices)
- Color removal and oxidation of organics and inorganics
- Decontamination connected with anthrax (terrorist attacks on U.S. offices involving anthrax have been dealt with ClO_2)
- Use also as deodorant, sanitizer, and the like

The economic perspective of chorine dioxide is promising because it costs about 80% less than the chemicals typically used for bleaching, and it constitutes only about 1% of the selling price of the products for which it is used. Because its thermodynamic instability makes ClO_2 unsuitable for transportation or storage, on-site production is usually necessary. Its geometric and electronic structures are best explained by a V-shaped, paramagnetic molecule ($\cdot O{=}Cl{=}O \leftrightarrow O{=}Cl{=}O\cdot$) that can act as a Lewis acid (in the sense that it can receive an electron to complete the oxygen's octet).

Chlorine dioxide can be produced in many different ways, mainly through the reduction of Cl(V) or the oxidation of Cl(III). The mechanistic details are seldom simple and the products are generally not pure. For this reason, the following equations in aqueous solution are only indicative of the main reactions:

(A) Chemical reduction of Cl(V)

$$ClO_3^- + {}^1/_2H_2O_{2(l)} + H^+ \rightarrow ClO_{2(g)} + {}^1/_2O_{2(g)} + H_2O_{(l)} \tag{10.16a}$$

(B) Chemical oxidation of Cl(III)

$$ClO_2^- + {}^1/_2Cl_{2(g)} \rightarrow ClO_{2(g)} + Cl^- \tag{10.16b}$$

(C) Disproportionation of Cl(III)

$${}^5/_4HClO_2 \xrightarrow{cat.} ClO_{2(g)} + {}^1/_2H_2O_{(l)} + {}^1/_4Cl^- + {}^1/_4H^+ \tag{10.16c}$$

(Note that reaction 10.16b is a *double* disproportionation, and reaction 10.16c is a *simple* disproportionation.)

Light (especially UV) is known to facilitate ClO_2 gas decomposition into Cl_2 and O_2; this is why its production is preferably conducted in the dark or in very subdued light.

a.3 Ozone Ozone is one of the most powerful oxidants and disinfectants. It has been used in drinking water treatment in Europe for over a century. It has become increasingly popular because of other uses and advantages as an environmentally clean oxidant/disinfectant in water treatment and in several new processes in chemical and pulp industries. Examples include:

- Decomposition of a wide variety of hazardous organic and inorganic chemical wastes (e.g., phenols, pesticides, detergents, cyanides)
- Sterilization of surfaces, potable water, municipal wastes, and specialty waters
- Precipitation of some undesirable heavy metal ions as oxides and hydroxides (e.g., iron, manganese)
- Bleaching in aqueous systems
- Control of slime formation
- Control of odor in sewage treatment and in manufacturing industries
- Removal of taste in drinking water
- Chemical synthesis

Advantages of using ozone instead of chlorine:

- Ozone is a stronger oxidizing agent.
- It kills bacteria more rapidly and it also destroys viruses.
- Ozone leaves fewer potentially harmful residues.
- The action of ozone is less pH-sensitive.
- Ozone can be used in combination with UV light or hydrogen peroxide to produce free radicals during the oxidation of wastes.
- Excess ozone decomposes into oxygen and hydroxyl radicals.
- Ozone does not impart any odor or taste to water.

Challenges encountered when using ozone:

- Its transportation is potentially hazardous.
- The cost of ozone-generating equipment is relatively high.
- It has a short decomposition time.
- Its solubility in water is limited.
- Its highly oxidizing power promotes strong interaction with surrounding materials (frequently leading to degradation).
- Ozone is explosive when concentrated (either as a liquid or gas), or when dissolved in solvents or absorbed into gels.
- Its oxidizing action is non-selective.
- Scavengers present in water (e.g., HCO_3^-, S^{2-}, NO_2^-, Br^-) decrease ozone's effectiveness due to their reaction with $^\bullet OH$ radicals, which are essential intermediates in the mechanism for ozone action.
- Excess ozone must be destroyed because it is a highly irritating and toxic gas. Fortunately, as discussed earlier, its decomposition product is pure dioxygen which can be recycled for ozone production.

The main techniques used for the production of ozone are *corona discharge, UV irradiation*, and *electrolysis.*

A. *Corona discharge* (silent electric discharge process)

Air or oxygen is passed through an intense, high voltage (approximately 4,000–12,000 V), high-frequency alternating current field. The discharge process forms ozone:

$$\frac{3}{2}\,O_{2(g)} \rightleftarrows O_{3(g)} \tag{10.17}$$

with a typical concentration range of 2.5 and 7.5 % by weight, depending on the use of air or oxygen, respectively when produced without mechanical refrigeration. This is by far the most common way of producing commercial ozone.

B. *UV irradiation*

Ozone produced by the UV-irradiation of air has a concentration in the range of a few thousand parts per million. This method is used for the production of small amounts of ozone.

C. *Electrochemical process* The reactions involved in the electrolytic production of ozone are:

Anode: $3H_2O_{(l)} \rightleftarrows O_{3(g)} + 6H^+ + 6e^- \quad E^0 = -\ 1.51\ V$ (10.18a)

Cathode: $6H^+ + 6e^- \rightleftarrows 3H_{2(g)} \quad E^0 = 0\ V$ (10.18b)

Overall: $3H_2O_{(l)} \rightleftarrows O_{3(g)} + 3H_{2(g)} \quad E^0 = -1.51\ V$ (10.18c)

Dioxygen is also evolved at the anode. An alternative cathodic reaction is the reduction of dioxygen using oxygen depolarized cathodes. Here, the anodic reaction is the same as above, while the cathodic reaction is:

$$O_{2(g)} + 4H^+ + 4e^- \rightleftarrows 2H_2O_{(l)} \quad E^0 = +1.23\text{ V} \tag{10.19a}$$

This renders the following overall reaction:

$$\tfrac{3}{2}O_{2(g)} \rightleftarrows O_{3(g)} \quad E^0 = -0.28\text{ V} \tag{10.19b}$$

Therefore, this last approach requires a much smaller potential than that in which hydrogen reduction is the cathodic process. In addition, the overall reaction is equal to the transformation of oxygen into ozone. Although this process requires a more sophisticated cathode, it significantly reduces power consumption and thus represents a promising approach. Solid polymer electrolytes can facilitate the process even more.

a.4 Hydrogen Peroxide Hydrogen peroxide is a colorless liquid used in the environmental field (including water treatment) both as an oxidizing and as a reducing agent, depending on the redox potential of the pollutant to be treated. For example, it oxidizes many toxic organics (e.g., formaldehyde) and reduces some inorganics (e.g., Cr^{6+} species) to less harmful species like CO_2 and Cr^{3+}, respectively. Its well-known thermodynamic instability (see the corresponding Frost diagram in Chapter 2) would appear to be a major drawback for its usage. However, its spontaneous decomposition is very slow in the absence of light and of transition metal ions that catalyze it, yielding $O_2 + H_2O$. Such a decomposition can be violent if the initial solution is concentrated (>65%), and it becomes more important at higher pH values. The addition of metal-complexing agents is a common practice to prevent this spontaneous decomposition. The use of H_2O_2 in advanced oxidation processes is discussed later (see Section 10.1.1.2).

a.5 Permanganate The high oxidation state of Mn in MnO_4^- (i.e., +7) makes permanganate a very good oxidizer for many organic and inorganic compounds. The corresponding standard potentials are given below for different pH conditions.

Highly acidic solutions:

$$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O_{(l)} \quad E^0 = 1.51V \tag{10.20a}$$

Moderately acidic solutions:

$$MnO_4^- + 4H^+ + 3e^- \rightleftarrows MnO_{2(s)} + 2H_2O_{(l)} \quad E^0 = 1.68V \tag{10.20b}$$

Alkaline solutions:

$$MnO_4^- + 2H_2O_{(l)} + 3e^- \rightleftarrows MnO_{2(s)} + 4OH^- \quad E^0 = 0.60V \tag{10.20c}$$

As such, it is used in water treatment to control taste and odors, remove color, and control biological growth. It promotes the removal of iron and manganese species by rendering them insoluble through oxidation:

$$3Fe^{2+} + MnO_4^- + 7H_2O_{(l)} \rightarrow 3Fe(OH)_{3(s)} + MnO_{2(s)} + 5H^+ \tag{10.21a}$$

$$3Mn^{2+} + 2MnO_4^- + 2H_2O_{(l)} \rightarrow 5MnO_{2(s)} + 4H^+ \tag{10.21b}$$

Permanganate can be used indirectly to decrease the formation of some DBPs by oxidizing their organic precursors and by reducing the need for other disinfectants, in spite of being a poor disinfectant itself. It has a unique affinity for oxidizing carbon–carbon double bonds in halogenated organic compounds; the final oxidation products are carbon dioxide, chloride salts, and manganese dioxide.

The EPA has summarized the most positive and negative aspects of using potassium permanganate as a disinfection method for drinking water. Many of these apply to other uses as well. Because of the wide variation in systems as well as in water parameters and conditions, some of these aspects may not apply to a particular system.

Advantages

- It oxidizes iron and manganese.
- It oxidizes odor and taste-causing compounds.
- It is easy to transport, store, and apply.
- It is useful in controlling the formation of some DBPs.
- Its use has little impact on other treatment processes.
- It is effective against certain viruses.

Disadvantages

- It involves long contact times.
- It can turn water a pink color.
- It is toxic and irritating to skin and mucous membranes.
- No byproducts are generated when preparing the feed solution.
- The solid can cause serious eye injury, it is a skin and inhalation irritant, and it can be fatal if swallowed.
- Over-dosing is dangerous and may cause health problems.

a.6 Ferrate A highly oxidized iron species called ferrate (FeO_4^{2-}) is another oxidant alternative that has been known for over a century and a half (but not studied for environmental purposes until recently). The standard potential of the Fe(VI)/Fe(III) couple in acidic or basic media is as follows:

$$FeO_4^{2-} + 8H^+ + 3e^- \rightleftarrows Fe^{3+} + 4H_2O_{(l)} \quad E^0 = +2.20\ \text{V} \qquad (10.22a)$$

$$FeO_4^{2-} + 4H_2O_{(l)} + 3e^- \rightleftarrows Fe(OH)_{3(s)} + 5OH^- \quad E^0 = +0.72\ \text{V} \qquad (10.22b)$$

Besides the high standard potential of ferrate, iron is normally innocuous to the environment. An added advantage in the use of ferrate for remediation applications is that $Fe(OH)_3$, a well-known coagulating–flocculating agent capable of removing a large variety of pollutants, is normally the reaction product of ferrate in neutral or alkaline conditions. Ferrate can destroy harmful organic and inorganic species. It can also be used for biofouling control and for the removal of other pollutants such as metals, nonmetals, and radionuclides. Thus, ferrate has been proposed as a multipurpose wastewater chemical for coagulation, disinfection, and oxidation.

Ferrate is a tetrahedral ion, where all the Fe–O bonds are equivalent and covalent. It can be prepared either chemically or electrochemically. In the chemical synthesis, a strong alkaline solution of hypochlorite oxidizes Fe(III):

$$2Fe^{3+} + 3ClO^- + 10OH^- \rightarrow 2FeO_4^{2-} + 3Cl^- + 5H_2O_{(l)} \qquad (10.23)$$

In the electrochemical synthesis, elemental iron is oxidized anodically to Fe(VI) in strongly alkaline solutions, because ferrate is unstable in acidic and weakly alkaline solutions. This anodic oxidation of Fe involves a rather complicated mechanism. For simplicity, the overall reaction (i.e., anodic + cathodic) for the production of ferrate may be represented as follows:

$$Fe_{(s)} + 2OH^- + 2H_2O_{(l)} \xrightarrow{\text{electrolysis}} FeO_4^{2-} + 3H_{2(g)} \qquad (10.24)$$

The instability of ferrate in acidic aqueous solutions is unfortunate, because it is a stronger oxidant upon protonation. The source of such instability is its capacity for oxidizing water as follows:

$$4FeO_4^{2-} + 10H_2O_{(l)} \rightarrow 4Fe(OH)_{3(s)} + 3O_{2(g)} + 8OH^- \qquad (10.25)$$

Ferrate is fairly stable in strongly alkaline media, as can be deduced from the application of LeChatelier's principle to this equation. This is the reason for its preparation in concentrated NaOH or KOH solutions. The region of stability of ferrate ions appears at high potentials and high pH values in the corresponding Fe–Pourbaix diagram.

Other strong oxidants (e.g., persulfate, percarbonate, peracetic acid, xenon tetroxide) can also be used for specific applications, but they are not discussed here. We will now discuss oxidations at high temperatures.

b. Incineration

Only a small percentage (in the low single-digit range) of the hazardous wastes produced in the United States is burned in special incinerators that include kilns, boilers, and industrial furnaces. Temperatures vary widely from approximately 700 to 1500°C. Incineration has several advantages, including the relative technical simplicity and safety of the process, the highly efficient destruction of organic compounds, and the self-generation of heat during the waste combustion process. However, the deleterious effects seem to overshadow this bright side. These effects include the production of highly toxic cyclic compounds as furans and dioxins (resulting from the combustion of chlorinated organics—see their structures in Figure 10.3), and the emission of particles and vapors of relatively low-melting point toxic substances (containing Hg, Cd, Pb, As, Be, Cr).

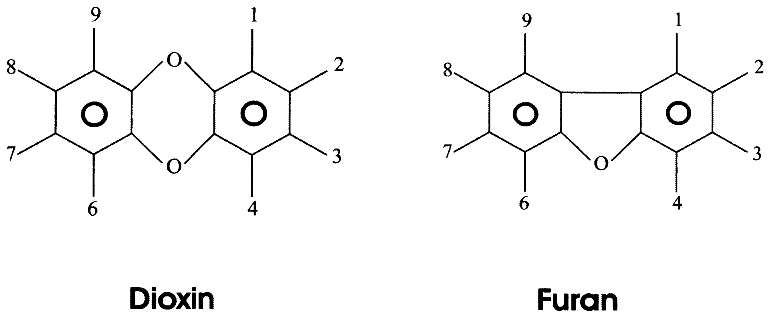


FIGURE 10.3. Chemical structures of key highly toxic cyclic halogenated compounds.

In dioxins or furans each of the positions numbered 1–4, and 6–9 can be substituted with a halogen atom, typically chlorine, an organic radical, or a hydrogen atom.

Ways to mitigate the emission of pollutants from incinerators include the capture of particulates by installing filters and systems to quickly quench hot exiting gases in order to decrease dioxin formation, and the use of sensors to constantly monitor the emitted gases so as to obtain timely feedback for the control of the pertinent process parameters.

In spite of these efforts, it is unlikely that public perception about incinerators will shift toward a more assenting view, and thus the difficulties to be met in situating incinerators prefigure a problematical future for them. U.S. EPA strategies in this regard emphasize less reliance on this technique and greater confidence in the minimization of waste generation. This last subject is discussed in Chapter 12.

c. Wet Oxidation (WO)

As discussed in Section 3.2, the rates of most chemical reactions increase with temperature. Also, more oxygen can dissolve at higher pressures. To take advantage of both phenomena and increase the rate of pollutant oxidation with dioxygen, water is heated in a pressurized reactor (on the order of 20–200 atm) until it reaches 150–320°C. This pressure maintains water as a liquid at this temperature and favors a high oxygen concentration. Such conditions are often used for the total or partial combustion of organic sludge and wastes—the technique is called *wet oxidation process (WO)*. The temperature limit is set at the point above which water can no longer exist as a liquid, regardless of the pressure (i.e., its *critical point*); such high temperatures favor high reaction rates. WO is considered a clean process.

Some *large organic* molecules are not completely oxidized; they typically yield low-molecular weight organic acids and other products. Direct oxygenation of *inorganic* pollutants can also be performed. For example, highly toxic sulfides can be oxidized with dioxygen to the less toxic $S_2O_3^{2-}$, SO_3^{2-}, or SO_4^{2-} ions. An additional advantage of WO is its ability to treat large amounts of effluents, especially when pollutant concentrations are not high enough to be incinerated but are too high to undergo biotreatment.

An obvious disadvantage is the high energy requirement for attaining process conditions. Lower operation costs and safety risks can be achieved with more moderate conditions by adding selected catalysts (*catalytic wet oxidation*).

Organic pollutants can be oxidized in an aqueous medium above the critical point of water (T_c = 374°C, P_c = 218 atm), whereby the solubility of the organics and of the oxidizing gas is higher than that under normal conditions. This is called *supercritical water oxidation (SCWO)*. A more thorough discussion of supercritical fluids is given in Section 12.3.8.

Other thermal treatments do not involve oxidation and they can be conceptualized as physical treatments (e.g., thermal desorption and plasma arc). However, they fall outside the scope of this book. A different approach that does not require such harsh conditions involves the production of one of the most powerful oxidants: the $^{\bullet}$OH radical, highly effective in oxidizing pollutants. Such processes are called *advanced oxidation processes*, and are discussed below.

10.1.1.2 Advanced Oxidation Processes (AOP)

The term AOP refers to a group of processes whose common characteristic is their use of •OH radicals to destroy complex organic compounds, not oxidized biologically, into simpler end products. The hydroxyl radical (•OH), a non-selective oxidizing radical with a very high standard potential (approximately 3 V), is capable of oxidizing virtually any existing organic (and many inorganic) species and of destroying bacteria. Ultrasound and photochemistry can also produce such radicals—they are presented later in this chapter (Sections 10.6.3.3, and 10.6.3.4). Key AOPs are now discussed.

a. Photoassisted Processes

As discussed in Chapter 3, irradiation of a chemical species with light of sufficient energy may result in its direct or indirect (mediated) transformation into a product (or products). Even though direct photolysis of a pollutant can in principle be used for this purpose, in practice it is rarely applied. The electromagnetic radiation of choice is UV, although higher energy is also used (e.g., for water disinfection), but this falls outside the scope of the present book. Two main photoassisted strategies are currently in use: homogeneous and heterogeneous photolysis.

a.1 Homogeneous Photolysis A substance that upon irradiation produces reactive radicals capable of transforming pollutants into less harmful species is placed in the same medium as the target pollutant (both in the same phase), and the mixture is irradiated. Reactive radicals of interest include •OH, $^\bullet O_2^-$, $HO_2^\bullet$, and $e^-_{(aq)}$. (Note that aquated electrons are powerful *reductants*).

For example, H_2O_2 and O_3 produce the powerful oxidant •OH upon irradiation with UV light as follows:

(A) Hydrogen peroxide decomposition

This photodecomposition is written as

$$H_2O_2 + h\nu \rightleftarrows 2^\bullet OH \qquad (10.26)$$

The maximum yield is obtained at intermediate H_2O_2 concentrations, because the back reaction becomes increasingly important at high concentrations of the •OH radicals produced. Likewise, at high H_2O_2 concentrations, the •OH radicals are consumed by a reaction with H_2O_2:

$$H_2O_2 + {}^\bullet OH \rightleftarrows H_2O_{(l)} + HO_2^\bullet \qquad (10.27)$$

A drawback for this photogeneration of •OH is that H_2O_2 absorbs solar radiation weakly and thus radical formation is slow. Such a disadvantage is probably offset by the low cost of H_2O_2, its relatively simple handling requirements, and the environmental compatibility of its decomposition products.

(B) Ozone decomposition

Ozone is decomposed by UV light as shown in Figure 10.4.

This ozone-mediated pathway for the production of •OH is about twice as expensive as that using H_2O_2—it can only compete with the latter when the photolysis of H_2O_2 becomes inefficient (as in opaque waters). In fact, processes that combine H_2O_2, O_3, and UV are now more commonly used because of their high efficiency.

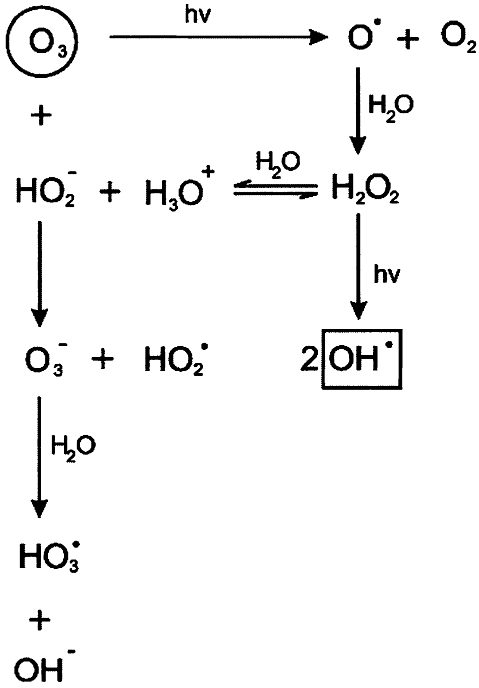


FIGURE 10.4. Ozone photolysis.

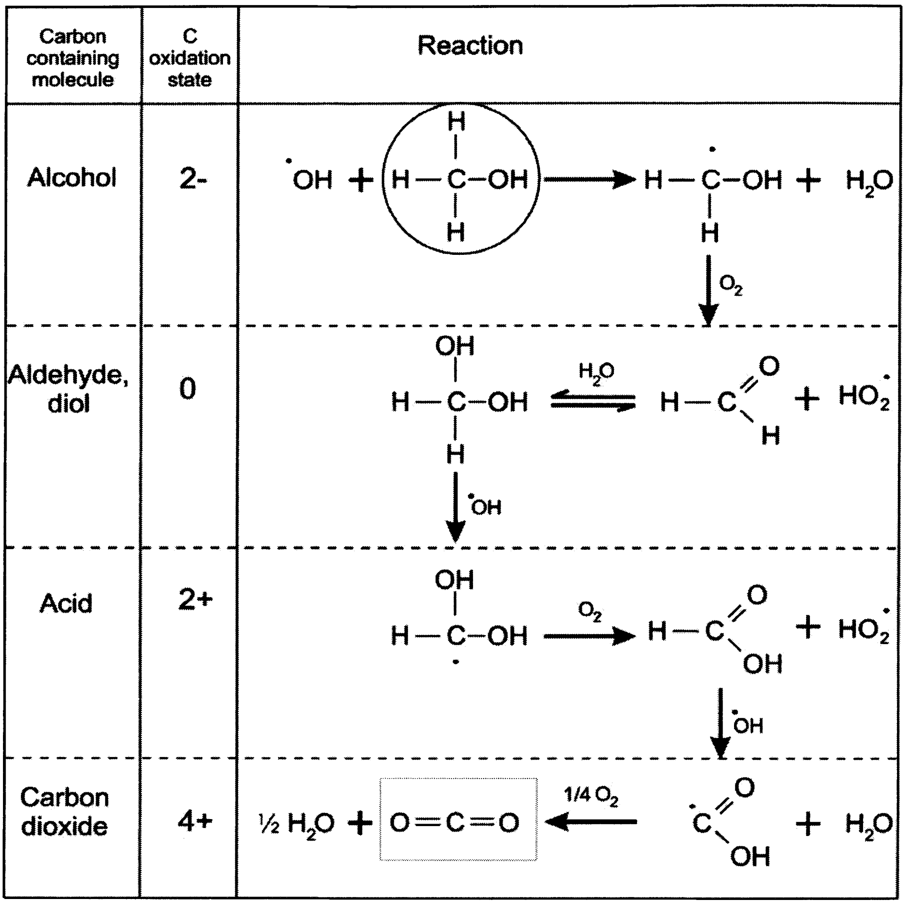


FIGURE 10.5. Hydrogen abstraction from methanol by •OH radicals. (Adapted from Rajeshwar, 1997.)

The •OH radicals predominantly react with nonaromatic organics through a hydrogen abstraction mechanism, exemplified with methanol in Figure 10.5. The final oxidation product is normally CO_2.

Even though aquated electrons $e^-_{(aq)}$ are powerful reducing agents (see Table 10.1 and Section 10.1.1.3), they can also produce •OH as follows:

$$[Fe(CN)_6]^{4-} + h\nu \rightleftarrows [Fe(CN)_6]^{3-} + e^-_{(aq)} \quad (10.28)$$

$$e^-_{(aq)} + N_2O_{(g)} + H^+ \rightleftarrows N_{2(g)} + {}^\bullet OH \quad (10.29)$$

This case is an excellent introduction to a key question: Is it better to oxidize or to reduce an undesirable substance? There is no single answer because the selection of a given treatment depends not only on the redox potentials involved, but also on costs, environmental compatibility of the products, reaction yields, the chemical and physical conditions required, the degree of development and availability of a given technique, and so on. Another criterion involves the rates of the different processes. For instance, the (bimolecular) rate constant for the reaction of phenol, C_6H_5OH, with •OH is about 300 times *higher* than that with $e^-_{(aq)}$, whereas the rate for the reaction of chloroform (trichloromethane), $CHCl_3$, with •OH is some 6000 times *lower* than that with $e^-_{(aq)}$.

Unfortunately, scavengers may considerably reduce the desired effect of radicals for waste treatment. For example, the main natural scavengers of •OH are the HCO_3^- and CO_3^{2-} ions as well as the humic acids. Their scavenging efficiency for •OH can be quite high; for example, in a dilute bicarbonate solution (e.g., 15 mM), 98% of the photogenerated •OH are scavenged by HCO_3^-.

a.2 Heterogeneous Photolysis

(A) Photocatalysis

Light with supraband gap energy absorbed by a semiconducting particle (e.g., TiO_2) can excite an electron from its valence band to the conduction band. This process also creates a positive *hole* in the valence band, which is an oxidizer and may react with adjacent oxygenated species to produce $^{\bullet}OH$ radicals. At the same time, the excited electron is capable of directly or indirectly reducing species in contact with the semiconductor. Such phenomena are electrochemical in nature—they are under intense study for application in the environmental remediation arena where they are globally called *photocatalysis*.

Owing to its low cost, non-toxicity, extreme stability, wide availability, and other advantages (see discussion below), TiO_2 is the semiconductor of choice for environmental applications. The main application is the mineralization of toxic organic pollutants in air, water, or soil matrices (i.e., their conversion into small, non-toxic inorganic molecules as CO_2, H_2O, HCl). In some cases it has been used for the reduction and removal of metal ions from aqueous solutions (e.g., $Cu^{2+}{}_{(aq)} \rightarrow Cu^{+} - TiO_{2(s)}$). In very few cases, both the anodic and cathodic reactions have been advantageously utilized (e.g., to remove a metal ion and to oxidize an organic molecule).

Additional advantages of using TiO_2 for pollutant treatment include:

- Its band gap energy (approximately 3.2 eV for the anatase phase) is appropriate for excitation with near-UV light (approximately 388 nm) provided by the Sun or by artificial sources.
- Surface modification and metal ion doping can widen its absorption spectrum.
- A large number of pollutants can be almost completely mineralized.
- The reaction rates can be relatively high if large photocatalyst surfaces are used.
- Because it acts as a catalyst, TiO_2 is largely unaffected and can normally be recycled.

Challenges include the following:

- There is a mismatch with the solar spectrum, because only a small portion (i.e., near-UV light) can be used by the semiconductor.
- When TiO_2 is used as a powder, a separation step must be integrated after pollutant treatment.
- Owing to its insolubility, TiO_2 tends to precipitate out of its suspensions, and as a result extra energy has to be supplied in order to keep it in suspension (typically by mechanical agitation, liquid movement, or gas sparging).
- The target polluted media frequently contain substances that produce light scattering and optical absorption, thus preventing part of the excitation light from reaching its goal.
- Some of the electrons and holes produced by the absorption of supraband gap energy can recombine and become useless for photocatalysis.
- The quantum yield for the TiO_2/UV process is typically low.
- Intermediates may form that are more toxic than the parent compound.

Clever schemes have been devised to face such challenges:

- The walls of a photochemical reaction vessel are covered with chemically or physically deposited TiO_2. Alternatively, TiO_2 can be immobilized on other inert substrates (e.g., sand). Such an approach obviates the need for the separation step mentioned earlier.
- Dye molecules can be adsorbed at the TiO_2 surface to capture *visible* light and then transfer energy to the semiconductor (photosensitization) so as to produce the desired photocatalytic events.
- Photocatalytic rates, which are limited by the cathodic reaction rate, can be increased using supported catalysts (e.g., Pt, Pd, Ag, Cu) that speed-up electron transfer.
- Electron–hole recombination rates can be lowered by modifying TiO_2 with metal ions (e.g., Ag^{+}) capable of trapping photogenerated electrons, or by applying a small potential bias to an electrode coated with TiO_2 (see below).

(B) Electrochemically-assisted photocatalysis

As discussed above, photocatalytic processes are electrochemical in nature. A clever enhancement approach involves the application of a judiciously selected potential bias to a semiconductor electrode. The potential promotes a better charge-separation, thus decreasing the electron–hole recombination and increasing the yield of the target processes. This approach is called *electrochemically* *assisted photocatalysis*, or *photoelectrocatalysis*. Here, an externally applied potential drives selected charge carriers out of the semiconductor into the counter (auxiliary) electrode (i.e., the photogenerated electrons from a photoanode, made of an n-type semiconductor—or the photogenerated holes from a photocathode, made of a p-type semiconductor). This allows the majority carriers (i.e., holes in the photoanodes and electrons in the photocathodes) to effect their attack on the target pollutant without recombining with the minority carriers. Complete mineralization of many organic compounds has been achieved in this manner. Even though this approach is still in the developmental stage, its future in the waste treatment arena looks promising.

b. The Fenton Reaction

At the end of the 19th century, in Cambridge, H. J. H. Fenton discovered that if a small amount of Fe^{2+} were added to a solution of H_2O_2, the resulting mixture could oxidize a considerable number of organic substances in acid solution within a short period of time. The combination of $Fe^{2+} + H_2O_2$ (usually at $pH < 3$) is thus called *Fenton reagent*. At least 50 different metal ions were tested for the oxidation of organics under similar conditions, and none was even close to the oxidation yield obtained with Fe^{2+} salts. The reaction occurs as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \qquad (10.30)$$

The reaction mechanism was first proposed by Haber and Weiss. The reactions involved in the oxidation of organics with Fenton's reagent can be quite complicated and will not be discussed here; for example, the oxidation of phenol entails some 24 possible intermediate reactions!

Although not discovered by Fenton, it was later established that Fe^{3+} species can also oxidize many organics in the cases indicated below.

(b.1) Hydrogen peroxide reduces Fe^{3+} to Fe^{2+} (reaction 10.31), which may react with more H_2O_2 to form Fenton's reagent (reaction 10.30):

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \qquad (10.31)$$

This is called the *Fenton-like* or *Fenton-type* reaction.

(b.2) In the presence of light, photoredox reactions of Fe^{3+} species yield the necessary Fe^{2+} to produce Fenton's reagent with H_2O_2 (reaction 10.32). This is termed *photo-Fenton* or *photoassisted Fenton* reaction:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^\bullet OH \qquad (10.32)$$

$$Fe^{3+}L_n + h\nu \rightarrow Fe^{2+} + \text{products} \qquad (10.33)$$

where L is a complexing agent (e.g., oxalate, citrate, and humic acid derivatives).

(b.3) Facultative anaerobic Fe(III)-reducing bacteria can also generate Fe(II) for this purpose.

Interestingly, H_2O_2 is also generated in aqueous solutions on the surface of an illuminated semiconductor (e.g., ZnO), which in turn can form Fenton's reagent with artificially added Fe^{2+}. Likewise, active species (mainly radicals), resulting from the photosensitization of humic acids, generate H_2O_2. Electrogenerated H_2O_2 can be successfully utilized with Fe^{2+} salts as well, to produce Fenton's reagent and degrade organics that resist direct electron transfer at an electrified interface (see Section 10.1.4).

Recent discoveries include other metal ion systems capable of producing ${}^\bullet OH$ in a Fenton-like fashion [e.g., Co(II)/organic acid/H_2O_2, and Cu(II)/organic acid/H_2O_2].

Fenton's reaction is used for environmental remediation in view of certain advantages:

- Natural sources of iron can be used to produce Fenton's reaction, and the products of their reactions are typically environmentally friendly.
- H_2O_2 and its decomposition products are also environmentally friendly.
- Dilute H_2O_2, Fe species, and their mixtures are relatively easy to handle.
- Costs involved are low and the reactants are readily available.
- At circumneutral pH (i.e., pH near 7), a Fe^{3+} precipitate forms. It is capable of adsorbing or coprecipitating aqueous toxic species such as As^{3+}, thereby facilitating their removal from the aqueous phase.

Several challenges must be faced in order to take full advantage of Fenton's reactions:

- The concentration requirement for Fe^{2+} is high (nearly stoichiometric).
- Fe^{2+} reacts with ${}^\bullet OH$, thus competing for this radical with the very same target compounds that one is trying to destroy.
- Low pH values are required since the OH^- ions produced (see reaction 10.30) are capable of

yielding an undesirable precipitate of ferric hydroxide. This may necessitate an additional acidification step.

Many *in situ* soil and groundwater Fenton remediation processes have been commercialized, including the treatment of gasoline, waste oil, perchloroethylene, chlorophenols, explosives and munitions, chlorinated hydrocarbons, and nitrification inhibitors.

10.1.1.3 Chemical Reduction

Chemical reduction of pollutants is often aimed at a double target: decreasing their toxicity and removing them through phase change for disposal or recovery. For example, toxic metal ions from industrial effluents can often be precipitated by reduction to their elemental state (i.e., oxidation state = 0). The most common reducing agents for pollutant-treatment applications include sulfur-, nitrogen-, oxygen-, and metal-based reagents as exemplified below.

a. Sulfur-based Reducing Agents

(a.1) Sulfur dioxide and sulfite ions

Gaseous sulfur dioxide is dissolved in water for use as a reducing agent. Its standard potential (in acidic solution) is given by the equation

$$SO_4^{2-} + 4H^+ + (x-2)H_2O_{(l)} + 2e^- \rightleftarrows SO_2 \cdot xH_2O \qquad E^0 = +0.17\ \text{V} \qquad (10.34)$$

In basic solution it changes to

$$SO_4^{2-} + H_2O_{(l)} + 2e^- \rightleftarrows SO_3^{2-} + 2OH^- \qquad E^0 = -0.93\ \text{V} \qquad (10.35)$$

Sulfur dioxide is commonly applied for the removal of free and combined chlorine (e.g., in the vicinity of a 1.5:1 mol ratio); this reaction yields Cl^- and SO_4^{2-} ions. Bisulfites are sometimes used for a similar purpose.

Another typical application is the reduction of toxic Cr(VI) to Cr(III). If carried out in an aqueous basic solution, this last species precipitates in the presence of OH^- (this facilitates its removal):

$$2CrO_4^{2-} + 5H_2O_{(l)} + 3SO_3^{2-} \rightleftarrows 2Cr(OH)_{3(s)} + 3SO_4^{2-} + 4OH^- \qquad (10.36)$$

In addition, SO_2 is used for reducing excess chlorine in water-disinfection procedures.

(a.2) Dithionite

The $S_2O_4^{2-}$ ion (dithionite, also called hydrosulfite or hyposulfite) is used for reducing some metal ions to their corresponding elemental state, which facilitates their removal from aqueous solutions:

$$S_2O_4^{2-} + M^{n+} \rightarrow M^0_{(s)} + \text{sulfur species} \qquad (10.37)$$

(a.3) Sulfide

Gaseous H_2S can remediate certain redox-sensitive pollutants by reduction, often with concomitant immobilization resulting from the production of insoluble materials. For example, H_2S is pumped in vadose zone sediments/soils to reduce and immobilize toxic chromates:

$$2CrO_4^{2-} + 3H_2S_{(g)} + 2H_2O_{(l)} \rightleftarrows 2Cr(OH)_{3(s)} + 3S^0_{(s)} + 4OH^- \qquad (10.38)$$

This technique is called *in situ gas reduction* (*ISGR*) which is easier and cheaper to apply than other treatments such as liquid phase extraction or excavation.

(a.4) Thiosulfate

Its reducing power can dehalogenate toxic organics as follows:

$$R\text{–}X + S_2O_3^{2-} \rightarrow R\text{–}S_2O_3^- + X^- \qquad (10.39a)$$

or with di- or polyhalogenated species:

$$X\text{–}R\text{–}X + S_2O_3^{2-} \rightarrow X\text{–}R\text{–}S_2O_3^- + X^- \qquad (10.39b)$$

Thiosulfate acts as a nucleophile in these S_N2 reactions, whereby toxicity is greatly reduced (or even eliminated).

b. Nitrogen-based Reducing Agents

(b.1) Hydrazine

Hydrazine, NH_2NH_2, is a powerful reducing agent ($E^0 = -1.16$ V); in addition, its nitrogenated reaction product is the harmless and environmentally safe N_2. A disadvantage is that NH_2NH_2 is toxic (possibly carcinogenic). Consequently, it is used primarily in closed circuits.

(b.2) Hydroxylamine

Hydroxylamine (NH_2OH) and some of its derivatives have been used for example in the reduction of mercury species, nitrogen oxides, aqueous chlorine or bromine, and hexavalent chromium (see Jackson, 1993):

$$2(NH_2OH)_2 + H_2SO_4 + Na_2Cr_2O_7 + 2NaOH \rightleftarrows Cr_2O_{3(s)} + 2Na_2SO_4 + 9H_2O_{(l)} + N_{2(g)} + N_2O_{(g)} \quad (10.40)$$

An additional use involves the extraction of metals from soil samples and the selective reduction of actinides to separate them from uranium.

c. Carbon-based Reducing Agents

c.1 Activated carbon (activated charcoal)

This form of carbon offers a two-fold advantage: its large surface area is ideal to adsorb pollutants, and its redox potential is sufficiently low so as to reduce several metal ions to less-toxic oxidation states. For example, it can reduce chromate ions to Cr^{3+}, where CO_2 is produced as a byproduct. Examples of its use as an adsorbent are given in Section 10.2.1.

(c.2) Aldehydes

Aldehydes are typically good reducing agents (e.g., the classical qualitative tests for aldehydes involve the production of elemental metallic deposits by reduction). Unfortunately, they increase the carbon content of the treated solution, which poses a serious restriction to their widespread use.

d. Metal-based Reducing Agents

(d.1) Zero-valent metals (ZVM)

Metals with substantially negative standard potentials (M_1) yet relatively unreactive toward water, have long been used to recover valuable metal ions (M_2) from spent solutions:

$$M_{1(s)} + M_2^{n+} \rightleftarrows M_1^{n+} + M_{2(s)} \quad (10.41)$$

This process is called *cementation*. For example, Cu^{2+} ions in industrial waste solutions are recovered as Cu^0 metal by the addition of scrap iron or steel.

Zero-valent metals, ZVM (most commonly Fe), are used for the construction of barriers to the diffusion of reducible pollutants in underground reservoirs and currents. For example, elemental Fe "walls" are used downstream so as to prevent chromate-containing waters from polluting groundwater by operating the desired reduction to Cr^{3+}. Likewise, ZVM are used in the dehalogenation of toxic halogenated organics; in general, the fewer the number of halogen atoms attached to an aromatic ring, the lower the toxicity of the aromatic compound. Other *reductates* include some anions (e.g., $NO_3{}^-$ and anionic dyes) and neutral species (e.g., organic ketones, explosives and solvents).

(d.2) Ferrous ion

The $Fe^{3+/2+}$ couple has an $E^0 = +0.77$ V, which makes Fe^{2+} a moderate reducing agent. Fe(II) can either be added as a salt, or produced electrochemically using an Fe anode. A case in point is its widespread use for chromate reduction:

$$CrO_4^{2-} + 3Fe^{2+} + 4H_2O_{(l)} + 4OH^- \rightleftarrows Cr(OH)_{3(s)} + 3Fe(OH)_{3(s)} \quad (10.42)$$

A further example involves the reduction of perchlorate ions that impede proper iodine uptake by the thyroid:

$$ClO_4^- + 8Fe^{2+} + 8H^+ \rightleftarrows Cl^- + 8Fe^{3+} + 4H_2O_{(l)} \quad (10.43)$$

Fe(II) adsorbed onto natural oxides is also a good reducing agent. For example, it reduces CCl_4 to CO or to $CHCl_3$.

e. Other Reducing Agents

(e.1) Hydrogen peroxide

Even though it is commonly regarded as an oxidant, hydrogen peroxide can also be used as a reducing agent for powerful oxidants as in the recovery of spent catalysts.

(e.2) Molecular hydrogen

The chemical reduction of polluting CO_2 to produce methanol is a long-sought process. Molecular hydrogen can do the trick:

$$CO_{2(g)} + 3H_{2(g)} \rightleftarrows CH_3OH_{(g)} + H_2O_{(g)} \quad (10.44a)$$

Unfortunately, the high temperature required promotes a loss in product selectivity, and consequently, CO becomes the predominant product:

$$CO_{2(g)} + H_{2(g)} \rightleftarrows CO_{(g)} + H_2O_{(g)} \quad (10.44b)$$

Catalysts can solve the problem, with the additional benefit of considerably reducing energy consumption and yielding a methanol product free of hydrocarbons and ketones.

(e.3) Borohydrides

The most common borohydride used for reduction is $NaBH_4$. Its E^0 is very negative (-1.24 V).

A drawback in its use is the introduction of boron species to the treated water. Moreover, its high cost is often prohibitive.

(e.4) Solvated electrons

They are under study for the chemical dehalogenation of herbicides, insecticides, PCBs, chemical warfare agents and residues, and the like. Solvated electrons are produced when alkali (e.g., Na) or alkaline earth (e.g., Ca) metals dissolve in solvents such as NH_3, amines and ethers. Anhydrous ammonia is often the solvent of choice because it is easily recycled, and the solvated electrons exhibit a long half-life in it (approximately 300 h). Quite the opposite, the half-life of the electrons in pure water is in the order of 100 milliseconds, which hampers their use in aqueous media.

10.1.2 Precipitation/Immobilization, Acid–Base/Hydrolysis, and Ion-Exchange Processes

10.1.2.1 Chemical Precipitation/Metal Immobilization

Metal ions are generally recovered or removed from aqueous discharges by selective precipitation of their insoluble compounds. One of the most popular precipitating agents is the OH^- ion. The addition of commercial bases to wastewaters so as to precipitate and remove insoluble metal hydroxides is a common practice for water treatment. This is a relatively simple operation, and the reagents used (typically lime and soda ash) are inexpensive, safe, and readily available. The approximate relative cost of the commercial bases $Ca(OH)_2$, Na_2CO_3 and NaOH is 1:3:5, respectively.

Disadvantages of this practice include:

- Cost and space requirements of the equipment involved (i.e., clarifier and filters)
- Considerable start-up time to come to equilibrium
- Extensive operator attention
- Temperature changes that may cause major hydraulic disruptions
- Need for water re-acidification in order to comply with discharge guidelines
- Metals capable of forming amphoteric hydroxides produce stable hydroxo-complexes that prevent metal removal

The low solubility of many sulfides and carbonates is also used to remove undesirable metal ions. Phosphates can be precipitated out by forming their insoluble Al(III), Fe(III), or Ca(II) salts with alum, iron salts, and lime, respectively, as shown in equations 10.45a–c.

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightleftarrows Ca_{10}(PO_4)_6(OH)_{2(s)} \qquad (10.45a)$$

$$Al^{3+} + H_nPO_4^{(3-n)-} \rightleftarrows AlPO_{4(s)} + nH^+ \qquad (10.45b)$$

$$Fe^{3+} + H_nPO_4^{(3-n)-} \rightleftarrows FePO_{4(s)} + nH^+ \qquad (10.45c)$$

In the same manner of metal ion removal, *water softening* entails the elimination of Ca(II) and Mg(II) ions. A common practice involves adding soda ash and sodium hydroxide to produce the corresponding insoluble carbonates of Ca and Mg that precipitate out of the solution.

Chemical coagulation is of paramount importance in water treatment. This consists in adding to the water to be treated, multivalent-metal ions (mainly salts of Fe^{3+} or Al^{3+}) that hydrolyze due to their acid character (see Section 2.2.1), followed by rapid stirring of the water. These multivalent ions can react with species that cause water alkalinity and form gelatinous hydroxide gels. Furthermore, charged particulates (e.g., colloids) combine with such ions and produce charge neutralization that allows particles to cluster. Coagulation is very effective in removing pollutants of colloidal size and larger, as well as color-causing organic compounds.

Challenges faced when using chemical salts as coagulants include the relatively high cost of the chemicals involved, the management of the resulting sludge (i.e., its bulkiness and the need for dewatering and disposal), and residual pollutant concentration.

Polymeric forms of the coagulants (e.g., polyaluminum chloride) are rather useful because they require lower alkalinity consumption and the concomitant lower production of sludge. Once the colloids are destabilized, slow stirring can also help them merge and form relatively large aggregates called *flocs* (hence the name *flocculation*) that are separated from water by settlement and filtration. In some cases, these *flocs* can be attached to purposefully generated gas bubbles and separated by flotation.

Metal immobilization in soils can be accomplished by increasing their retention in the soil matrix, which decreases their mass transfer rates.

Here, metal ions are either retained by the soil components or rendered insoluble by induced precipitation reactions. This general approach includes:

- *In situ* chemical-aided precipitation in the form of insoluble sulfides, carbonates, phosphates, hydroxides
- Formation of metal complexes to increase interactions with soil components
- Physical entrapment in the immobile water surrounding soil pores
- Incorporation into the crystalline structure of clays and metal oxides

Also gaining acceptance as alternative routes for immobilizing metals are processes such as soil vitrification, and the addition of cement-like (pozzolonic) agents whereby undesirable soil components are entrapped in a vitrified matrix. Vitrification of radioactive waste materials is currently being used as well. Examples of vitrifying media include borosilicate glasses and iron phosphates. Whether a specific vitrification process is chemical or physical in nature is not always clear. Table 10.2 lists the main selection criteria for this application.

These techniques may have some negative impact due to the possible concomitant fixation of essential nutrients. In addition, the polluting metals may slowly leach out as a result of chemical or biological activity.

10.1.2.2 *Acid–Base/Hydrolysis Processes*

a. *Neutralization.* Excess acidity or basicity in an aqueous stream may, for example, affect microorganisms, plant growth in soils, natural and anthropogenic water processes, exchange with the atmosphere, metal ion mobility, and materials attack, including corrosion.

Owing to its low cost and wide availability, sulfuric acid is the main neutralizer for basic solutions. The most important base for neutralizing acidic wastes is calcium hydroxide (or calcium oxide), although its low solubility sometimes poses a problem. This can be circumvented by the use of sodium hydroxide (albeit at a higher cost, as discussed in the previous section). Owing to the chemical and mechanical simplicity of these neutralization operations, highly automated systems can be employed. Such pH adjustment operations are normally performed prior to other water treatment steps.

TABLE 10.2. Selection criteria in vitrification processes

Criterion or parameter	Desirable situation	Comments
Cost of raw materials	Low	Typical raw materials are phosphates, borosilicates, oxides (preferably industrial wastes).
Maximum waste loadings	High	Chemical incompatibility may limit loading.
Physical and chemical durability	High	Hydration, chemical attack, fracturing, inhomogeneous crystallization may occur.
Material release	Low	Leaching may result from physical or chemical phenomena.
Melting temperature	Low	Lower temperatures save costs, increase safety.
Melting time	Short	Shorter times save costs, increase safety.
Additives required	None	Additives may be needed for chemical or physical reasons.
Flexibility of atomic structure	High	This flexibility should accommodate ions of widely different size and charge.
Corrosion ability	Low	Target materials must not attack the equipment/materials used for their melting.

b. *Alkaline hydrolysis* (i.e., hydrolysis under alkaline conditions) is used for example to detoxify cyanide-containing wastes

$$\text{R-CN} + 2\text{H}_2\text{O}_{(l)} \rightleftarrows \text{NH}_{3(g)} + \text{R-COOH} \qquad (10.46)$$

and to destroy nitro-explosives.

10.1.2.3 *Ion Exchange*

Ion exchange is widely used for the selective separation/removal of metal ions from an aqueous medium either for environmental clean-up, for the removal of undesirable components, or for metal recovery. Other species that have been treated include nitrate, ammonia, and silicate. This process is normally based on the use of polymeric resins (typically styrene/divinylbenzene polymer backbones) that have chemically active groups attached to them. Sulfonic or carboxylate groups are regularly used for the removal of cations, and quaternary ammonium groups are used for the removal of anions.

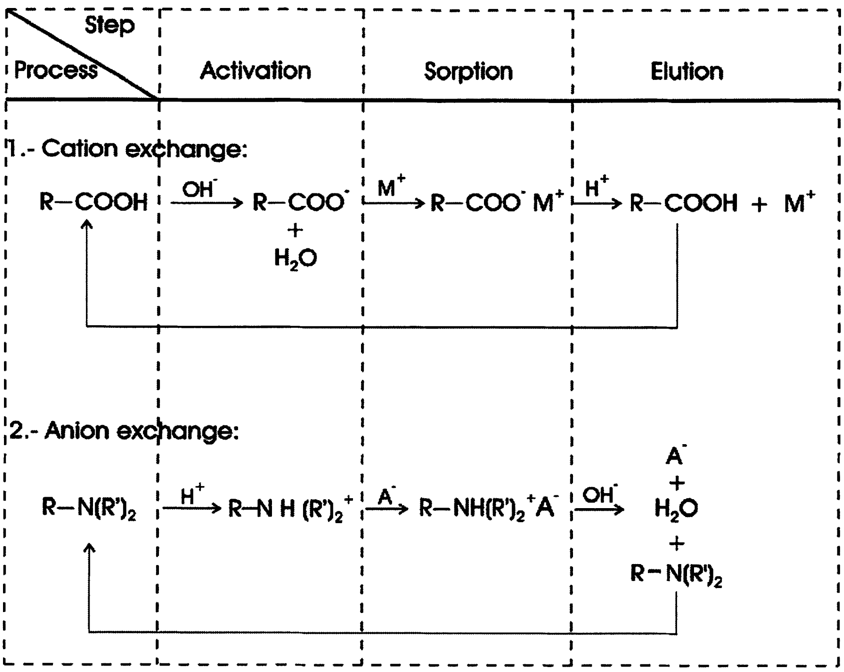


FIGURE 10.6. Typical ion exchange processes.

Naturally-occurring inorganic zeolites are also used for this purpose.

The first step consists in removing the target ions (*sorption*). This is followed by regenerating the ion exchange material through the release of the absorbed ions (*elution*), which are then replaced by protons or sodium ions (*cation exchange*), or by hydroxyl ions (*anion exchange*). Finally, the oppositely charged ions from water are partitioned into the ion exchange material so as to make it ready to reinitiate the cycle (*activation or regeneration*). See Figure 10.6.

Chelate ion exchangers are based on the selective complex formation between a metal ion and a chelating ligand anchored onto the resin's polymeric structure.

Desirable performance characteristics of an ion exchange resin include high reactivity toward the target metal ions, high capacity, stability and selectivity, improved ion access to the exchange sites, and fast exchange kinetics. A typical performance parameter that is used for assessing an ion exchange operation is the *distribution coefficient* , K_d (also called *dry-weight distribution ratio, D*) given in mL/g, which gives the concentration of the target cation exchanged onto the resin as compared to the concentration left in the solution. It is defined as

$$\begin{aligned} K_d &= [(C_0 - C_f)/m](V/C_f) \\ &= [(C_0 - C_f)/C_f](V/m) \qquad (10.47) \end{aligned}$$

where C_0 and C_f are, respectively, the initial and final (or equilibrium) activities (or concentrations, if sufficiently dilute) of the target metal ion, m is the mass of the ion exchanger, and V is the total solution volume.

Disadvantages of the ion exchange processes are:

- Large amounts of wastes may be generated at the elution and regeneration steps.
- Strongly acidic solutions obstruct exchange with the acid exchange sites of typical cation exchange resins.
- Strongly basic anion exchange resins are sensitive to organic matter (particularly humic substances), with attendant decreases in their ion exchange capacity, pH, and active depth, as well as with increases in the amount of water required for the washing operation, and in the conductivity of the final solution.

Recent developments in the ion exchange field include the following:

(a) Certain ion exchange resins display a noticeable temperature dependence in their selectivity toward different ions. Therefore, by varying temperature, the equilibrium constant of the ion exchange reaction of one metal ion with the resin (or the equilibrium constant of its complex formation in solution) varies differently from that of the other metal ions present, and thus a more selective separation can be achieved. For example, some alkali-earth metal ions can be separated using this principle.

(b) Specialty ion exchange resins can be designed knowing the bonding data between special functional groups and the target metal ion. For example, diphosphonic acid groups show much improved metal retention compared with the traditional sulfonic acid groups for divalent ions of Mn, Co, Cu, Zn, Cd, Pb, and Ni.

(c) Inorganic ion exchangers (e.g., titanosilicates and aluminosilicates as the zeolites) have high thermal, chemical, and radiation stability. They can also have high capacity and selectivity for many monovalent and divalent metal ions. An added advantage is that they may be "tailor-made" by altering their structures during synthesis (e.g., substituting different metal ions into their framework structures, which modifies their effective cavity diameters). Such ion exchangers are used with non-specific point pollutants (e.g., to prevent heavy metal-laden groundwater runoff due to storm erosion), as well as in point-of-use treatments (e.g., to remove radioactive isotopes from wastes and groundwater).

10.1.3 Complexation Processes

Ligands can form complexes with many metal ion pollutants, helping to transform them into less dangerous species or to transfer them from a given phase into another phase where pollutants become less problematic. If the ligand is the pollutant, the same principles apply. We will now examine examples of complexation with gas, liquid, and solid pollutants.

10.1.3.1 Gaseous Pollutants

Complex formation removes gaseous pollutants when they can be used as ligands for a specific metal ion, typically in aqueous solution. The complex thus formed can be chemically or electrochemically oxidized or reduced, whereby the pollutant (ligand) is destroyed so as to produce less harmful species; then the metal ion is ready to reinitiate the cycle.

10.1.3.2 Aqueous Pollutants

a. Metal Separation by Polymeric Ligand Exchange (PLE)

As mentioned above, many anionic ligands are trace contaminants in water and wastewater streams or bodies. Some metal ions can be anchored onto polymeric ion exchange resins to sorb (and thus remove) ligands. This sorption affinity can be substantially enhanced by appropriately modifying the interfacial chemistry of the ion exchanger, as shown in the following reaction scheme:

$$\equiv\mathrm{RL}'\text{—}\mathrm{M}^{n+}_{(s)} + \mathrm{L}^{n-}_{(aq)} \rightarrow \equiv\mathrm{RL}'\text{—}\mathrm{M}^{n+}\text{—}\mathrm{L}^{n-}_{(s)} \qquad (10.48)$$

where $\equiv$RL$'$ is the stationary (electrically neutral) polymer ion exchanger, and M^{n+} is the metal ion selected on the basis of its capacity to bind the desired polluting anion, L^{n-}. Such a scheme has the extra advantage of being manageable for efficient regeneration with inexpensive raw materials (e.g., brine).

b. Dendrimers

While traditional chelating agents and macrocycles can typically bind only one metal ion per molecule, a new class of highly branched polymers called *dendrimers* can bind more than one hundredfold metal ions per unit of dendrimer. These dendrimers have controlled composition and architecture consisting of a core, interior branch units, and terminal branch units. They can serve as high capacity nanoscale containers for toxic metal ions through the covalent attachment of ligand atoms (e.g., nitrogen) to flexible chains. The *extent of binding* (*EOB*) is defined as the number of moles of a given metal ion (with a concentration of M_b) bound per mole of dendrimer:

$$\mathrm{EOB} = M_b / C_d \qquad (10.49)$$

where C_d is the concentration of dendrimer in solution, in mol L^{-1}.

c. Radioactive Decontamination

Multidentate synthetic chelating agents are used for the decontamination of nuclear reactors and for nuclear waste processing, because they form stable soluble complexes with many radionuclides. Unfortunately, their joint disposal has sometimes resulted in increased radionuclide mobility, with the concomitant contamination of groundwater. An attempt to lessen this problem involves degrading the chelating agents with bacteria (see Chapter 11).

d. Metal Extraction by Complex Flotation

Metals in the aqueous phase can be removed by complexing them with ligands to form charged or uncharged complexes, and then separated by selective flotation with surfactants. For example, an aqueous metal ion (M^{n+}) reacts with a ligand (L) to form a cationic complex (ML^{n+}). Then, a surfactant is added (e.g., a long-chain organic acid, RCOOH) and the pH of the solution is controlled so as to dissociate the acid. The resulting anion binds the cationic complex, making it electrically neutral and thus propitious for flotation in the solution to be removed. The sequence of reactions is as follows:

$$M^{n+} + L \rightleftarrows ML^{n+} \quad (10.50a)$$

$$RCOOH \rightleftarrows RCOO^- + H^+ \quad (10.50b)$$

$$nRCOO^- + ML^{n+} \rightleftarrows [ML(RCOO)_n] \quad (10.50c)$$

This approach is used to remove traces of toxic heavy metals from industrial effluents and to preconcentrate trace substances (e.g., recover valuable metals from seawater).

e. Solubilization by Selective Complexation

The most typical route for metal ion removal/recovery from polluted aqueous media is precipitation (see Section 10.2). However, in some cases the target metal ion cannot be precipitated in a pure form because other metal ions may co-precipitate. Selective complexation can then be used to promote the solubilization of either the target ions or the accompanying ions. Here, the constant for metal complexation must be greater than the solubility product. (Note that in order for this comparison to be valid, one has to be aware of the differences in the units of the constants). For example, one can recover Ag from spent photographic solutions by raising the pH of the solution in the presence of a ligand that complexes other ions in the solution, but not silver. In this way, silver can be precipitated out of the solution as its hydroxide by simply raising the pH, whereas the other metallic ions remain in solution as soluble complexes.

10.1.3.3 Soil Pollutants

The main methods for the remediation of heavy metals from soils are based on three principles: (a) metal immobilization (see Section 10.2), (b) electrokinetic remediation (see Section 10.4), and (c) metal extraction from the soil matrix.

This last method involves transferring the metals into a washing solution by desorption from the soil, followed by dissolution. The main components of the washing solutions are generally chelating agents or acids, although bases, surfactants, alcohols, and other additives are also used. In the so-called *ex situ* washing, the soil is first screened to remove any debris and then vigorously mixed with the washing solution, separated by a second screening step, washed with water to remove any residual extractant, and finally returned to the ground.

The use of acid solutions (mainly hydrochloric, nitric, and sulfuric acids) offers quite high removal yields because metal ions tend to be more soluble at low pH values. A drawback is that the soil becomes acidified—this can introduce major alterations in its chemical, physical, and biological properties; in addition, carbonate-rich soils strongly interact with the acids and produce CO_2. As discussed in Chapter 3, metal complexes with natural or synthetic chelating agents tend to be soluble and stable. Then, heavy metals in soils can also be solubilized by chelation and extraction followed by an *ex situ* treatment.

The general equation for the irreversible dissolution of an insoluble metal species, $MA_{(s)}$ by complexation with $L^{y-}_{(aq)}$ is

$$MA_{(s)} + xL^{y-}_{(aq)} \rightarrow (ML_x)^{2-xy}_{(aq)} + A^{2-}_{(aq)} \quad (10.51)$$

where $L^{y-}_{(aq)}$ is an anionic or neutral ligand ($y > 0$ or $y = 0$, respectively), M is a divalent metal cation, and A is a divalent anion. See Example 10.2.

Even though the complexation approach has less impact on the soil properties than acid washing, it poses problems of its own as well. For instance, synthetic chelating agents [e.g., aminopolycarboxylic

Example 10.2 Write a balanced equation for the dissolution of barium sulfate using the smallest possible stoichiometric amount of the negatively charged ligand, H_3EDTA^-. [The resulting metal-containing species is charged (negatively), which facilitates its dissolution].

Answer

$$BaSO_{4(s)} + 3H_3EDTA^-_{(aq)} \rightarrow [Ba(H_3EDTA)_3]^-_{(aq)} + SO^{2-}_{4(aq)}$$

acids such as ethylenediaminetetraacetic (EDTA), nitrilotriacetic (NTA), and diethylenetriaminepentaacetic (DTPA)] can be difficult to degrade biologically, and may also remove essential components and nutrients from the soil that impair its use for agricultural purposes. An example is the extraction of Pb with the sodium salt of EDTA that not only removes up to 80% of the Pb initially present, but can also remove substantial amounts of Ca^{2+}. A clever approach to prevent this from happening is based on simple equilibrium (LeChatelier-type) considerations by utilizing the *calcium* salt of EDTA.

Another challenge is that polluting metal ions may be difficult to remove by alkalinization from the resulting chelate-containing washing solutions due to the intrinsic thermodynamic stability of the metal chelates (see Section 3.1.6). Electrolysis is a method that allows the recovery of both the metal ion in its elemental form and the chelating agent from the extraction solution (see Section 10.4). Ongoing research also focuses on the possibility of using natural, biodegradable chelating agents from weak organic acids and their salts (e.g., citrates), which have a lower tendency to form chelates with Ca, Mg, and Fe and thus pose a smaller impact on the final composition of the soil.

Additional applications of complexing agents include removal of mineral scales and deposits from industrial processes, oil reservoirs, and vapor generation that often become sources of in-plant production problems as well as safety concerns.

10.1.4 Electrochemical Processes

In Section 10.1 we noted that a simple electron transfer may change the toxicity of a chemical species as a result of changes in geometry, mobility, solubility, or standard potential. Such an electron transfer can often be achieved at an electrified surface (electrode); this opens a wide-ranging opportunity for the electrochemical treatment or destruction of pollutants (see Rajeshwar and Ibanez, 1997).

Electrochemistry offers a considerable degree of environmental compatibility, thermodynamic efficiency, cost economy, versatility, easiness for automation, simplicity of process conditions, and selectivity.

In spite of these advantages, there are also challenges to be faced:

(a) Electrode materials may erode, form complexes, oxidize, wear out, or inactivate.
(b) Most electrochemical processes are performed in aqueous solutions, where solvent decomposition (i.e., water oxidation/reduction) is often difficult to avoid, thereby causing concomitant energy waste.
(c) The production of gases from water decomposition ($H_2 + O_2$) may form explosive mixtures.
(d) The best electrode materials in terms of durability and inertness frequently involve precious metals or diamond.
(e) The cost of electricity in many countries/areas is considerably high.
(f) Initial capital investment may be large in some cases.
(g) The lack of knowledge or understanding of electrochemistry limits its use for this purpose.

Despite these considerations, the commercial availability of many electrochemical reactors and systems for the applications discussed below confirms their validity as competitive technologies in the environmental remediation arena.

10.1.4.1 Direct and Indirect Processes

Electrons can be transferred *directly* from an electrode to an electroactive species or vice versa. These are called *direct* processes. In other instances this is not possible because either the target species may not be electroactive (i.e., capable of receiving electrons from an electrode or donating them to one), or there may be an energy barrier that makes the reaction rate extremely slow. One can alternatively generate active species (called *mediators*) at the electrodes—these species are capable of diffusing into the solution and reacting there with the target pollutant. Such processes are called *indirect* processes. Depending on whether the mediator can be regenerated or not, the process is called *reversible* or *irreversible*, respectively.

a. Direct Oxidations

These processes are applied to *organic* compounds including phenols, aromatic amines, halogenated compounds, nitrated derivatives, fecal wastes, dyes, aldehydes, carboxylic acid anions, and others. The *inorganic* substance that has probably been the most commonly treated through the electrochemical route is cyanide; its main product is the much less toxic cyanate ion.

b. Direct Reductions

Direct reduction of *metal ions* is undoubtedly the electrochemical reduction process that has reached the highest degree of technical and commercial development. Fortunately, the concentration of these ions in aqueous streams and wastes is typically low, but this introduces an additional complication for their treatment because mass transfer becomes severely limited. To counter this, electrochemists have designed reactors that promote more turbulence and higher contact areas. Three-dimensional and moving electrodes offer promising alternatives.

The direct reduction of pollutants also includes other *inorganic* compounds such as chromates, oxychlorinated species (e.g., chlorites and chlorates) and oxynitrogenated ions (nitrates and nitrites), as well as *organic* compounds (e.g., the dehalogenation of chlorinated hydrocarbons and the reduction of organic acids to the corresponding alcohols or phenols).

c. Indirect Oxidations

Metallic species in high oxidation states are good oxidants, typically accessible by electrochemical means. Examples include Ag(II), Ce(IV), Mn(VII), Fe(VI), and insoluble metallic oxides such as Bi_2O_3, MnO_2, and CoO. Hydrogen peroxide (H_2O_2) is another oxidant that can be produced electrochemically and can be formed by the reduction of dissolved O_2 at basic pH. This can be reacted with Fe(II), which can also be produced electrochemically, to yield the powerful oxidizer $^{\bullet}OH$ radical (i.e., the *electro Fenton* process). See Section 10.1.1.2.

In addition, wastewaters containing emulsions formed with water and a dispersed immiscible liquid (e.g., in gasoline stations and oil extraction sites) can be treated with an electrical field to break up the emulsion. This produces flocculating–coagulating agents (e.g., Al^{3+}, Fe^{2+}, and Fe^{3+} hydroxides) by the anodic oxidation of suitable metal anodes, and a gas (typically hydrogen). The resulting solid is a low-density waste produced by the flotation action of the gas, which facilitates its separation from the aqueous phase. This also applies to the removal of dyes that impair the passage of light to the lower areas of aquifers, thus interfering with natural cycles.

d. Indirect Reductions

An example is the indirect reduction of toxic NO_3^- and NO_2^- at electrodes covered with metallophthalocyanines (acting as mediators), which produces NH_3, N_2, or NH_2OH.

10.1.4.2 Electrochemical Processes Based on Ion Exchange

Aqueous wastes with high salinity or high metal ion content present a double incentive for treatment, because one can prevent pollution and at the same time recover valuable materials by recycling, reusing, or recovering metals or salts. Electrodialysis has been used for this purpose. It is based on the application of an electric field to guide ion migration and concentrate solutions of waste ions through the use of selective ion membranes; this also dilutes the waste streams. A high degree of selectivity can thus be achieved. Typical examples include nitrate removal, boron elimination, desalination of brackish water, nitric acid concentration, and glycerin recovery.

10.1.4.3 Electrochemical Treatment of Gases

The electrochemical route is widely studied for the treatment of various gases, after absorption or

TABLE 10.3. Electrochemical Treatment of Various Gaseous Pollutants

Gas	Treatment	Product (s)	Comments
CO_2	Reduction	Saturated hydrocarbons (with four or fewer C atoms), ethylene, small linear alcohols, CO, formic acid, and oxalic acid	It is not yet clear whether these reactions can be made energetically and economically viable.
NO	Reduction, preceded by reactive dissolution, that forms a soluble iron chelate	N_2O, NH_2OH, NH_2NH_2, NH_3	NO is quite insoluble. The Fe chelate is regenerated and reused.
NO_2	Reduction by direct or indirect processes	N_2 or NH_3 produced by direct reduction; N_2 produced by indirect reduction with $S_2O_4^{2-}$	NO_2 is soluble.
N_2O	Electrocatalytical reduction	N_2	High current efficiencies can be achieved.
H_2S	Indirect oxidation with H_2O_2, FeO_4^{2-} or Fe^{3+}	S	Some oxidants may be electrochemically regenerated.
SO_2	Direct or indirect oxidation or reduction	SO_3, SO_4^{2-}, or S	Called Electrochemical *Flue Gas Desulfurization (FGD)*
Hydrocarbons	Oxidation by heterogeneous catalysis	CO_2 (ideally)	Used in solid-electrolyte cells
Chlorine	Chlorine oxidation of metal ions and production of chloride ions that are sent to the anodic compartment to be re-oxidized	Pure gaseous Cl_2	Initial dissolution in a metal ion solution is made. Waste and impure chlorine can be treated.

reaction in the liquid phase (remember that in order to have an electrochemical cell one must have an ion conductor or electrolyte). Examples are shown in Table 10.3.

10.1.4.4 Electrokinetic Treatment of Soils

Electric fields are used for the treatment of a wide variety of polluted soils. The technique is based on the passage of electrical current through electrodes strategically buried underground. This generates the movement of charged (and some uncharged) species as a result of three main phenomena: electrophoresis, electroosmosis, and electromigration.

Electrophoresis involves the movement of charged particles (typically colloids) under the influence of an electric field. *Electroosmosis* is the movement of the solvent (typically water) within the soil pores, owing to the formation of an electric double layer between charged surface particles and dissolved ions or solvent dipoles. The external field then attracts the solvent, which in turn drags dissolved species. *Electromigration* consists in the movement of ionic species in the liquid phase towards the oppositely charged electrode.

Electrokinetic remediation (also called electroreclamation, electrorestoration, electroremediation, electrokinetic processing, or electropotential ion transport) has been used for a variety of pollutants as organic substances (benzene, toluene, ethyl benzene, xylenes, gasoline, warfare agents, acetates, phenols, trichloroethylene, and the like), inorganic species (metallic ions of Zn, Hg, Cd, Ni, Pb, Cr, Cu, Fe, Ag, anions of As, Cl^-, NO_3^-, SO_4^{2-}, CN^-, complexes, and the like), and radioactive substances. This technique is also in use for cleaning up sludge and groundwater.

10.1.4.5 Electrochemical Production of Water Disinfectants

The main disinfectants produced by the electrochemical route can be classified according to the oxidizing element as:

a. Chlorine-based. These include Cl_2 gas, ClO^-, HClO, ClO_2.
b. Oxygen-based. These include O_3, H_2O_2, $^\bullet OH$.
c. Others. Examples include MnO_4^-, FeO_4^{2-}, ions of other transition metal ions (e.g., Cu and Ag), percarbonate, persulfate, and other halogens and derivatives (e.g., Br_2, I_2).

10.1.4.6 Hybrid Processes that Involve an Electrochemical Step for the Treatment of Aqueous Wastes

Biological processes for pollutant treatment are frequently the method of choice (see Chapter 11). However, the complexity of some wastes (e.g., refractory and/or highly toxic) necessitates other approaches such as the use of hybrid alternatives that offer the possibility for partial electrochemical degradation (e.g., the transformation of non-biodegradable material into biodegradable). This involves large savings in electricity, because—as shown in Example 10.3—in order to completely oxidize

Example 10.3

(a) Balance the following half-reaction for the electrochemical oxidation of benzene, assuming its complete mineralization into CO_2 (i.e., find the values of the stoichiometric coefficients *a, b, c, d*):

$$C_6H_6 + aH_2O \rightleftarrows bCO_2 + cH^+ + de^-$$

(b) Compare the number of electrons required above, to that required for the oxidation of one molecule of benzene to yield fumaric acid, $C_6H_6O_4$.

$$C_6H_6 + wH_2O \rightleftarrows xC_4H_6O_4 + yH^+ + ze^-$$

Answer

(a) We take one benzene molecule as the basis. The number of carbon atoms on the product side must be equal to that on the reactant side, thus $b = 6$. We then proceed to calculate the number of electrons exchanged and to balance the charges on both sides. Note: If you are more familiar with the half-reaction or the oxidation number methods, use them instead!

The oxidation state of carbon in benzene is -1, since there are six carbons and six hydrogens; likewise, its oxidation state in carbon dioxide is $+4$. Thus, one needs to remove five electrons from each carbon atom, for a total of 30 electrons ($= d$). Since the only positive species on the product side is H^+, and there are no charged species on the reactant side,

$$c = d = 30$$

Finally, we balance the oxygens:

$$2b = a = 2(6) = 12$$

the balanced equation is then

$$C_6H_6 + 12H_2O \rightleftarrows 6CO_2 + 30H^+ + 30e^-$$

This is a very large number of electrons!

(b) $C_6H_6 + wH_2O \rightleftarrows xC_4H_6O_4 + yH^+ + ze^-$
Since there are six carbon atoms on the left side, one must also have six on the right, and thus $x = 6/4 = 3/2$. With the same rationale as above, the oxidation state of carbon in fumaric acid is $+2/4 = +1/2$. Then one needs to remove an equivalent of 1.5 electrons from each carbon in benzene, i.e., $1.5 \times 6 = 9 = z$. The charge balance requires 9 protons $= y = z$, and thus there is a total of $y + 3/2(6) = 18$ hydrogens on the product side, which leads to $w = 18/2 = 9$. Then,

$$C_6H_6 + 6H_2O \rightleftarrows 3/2C_4H_6O_4 + 9H^+ + 9e^-$$

Since fumaric acid is biodegradable, benzene may be electrochemically degraded only partially to fumaric acid, which is then biodegraded. This process requires fewer electrons (30 vs 9) and thus represents a much lower cost, since biodegradation is normally the cheapest treatment alternative for organic wastes.

a molecule of benzene, for example, 30 electrons need to be removed! However, partial oxidation of this same molecule can be done to produce biodegradable molecules as fumaric, maleic, and oxalic acids. This process requires fewer electrons per molecule. Such products are then propitious for biological treatment. Other alternatives consist in hybridizing electrochemical processes with catalytical, photochemical, sonochemical, or microwave-induced processes.

10.1.5 Other Chemical Processes

10.1.5.1 Selective Dissolution in CO_2

Supercritical CO_2 is used as an inexpensive, relative innocuous substitute for many noxious solvents. These characteristics have made it attractive for remediation purposes as well. (*Supercritical fluids* are defined and discussed further in Section 11.3). In spite of its non-polar nature, CO_2 is studied for the removal of positively-charged metal ions from waste streams as follows.

The metal ions (e.g., radioactive wastes) are complexed by negatively-charged ligands and rendered neutral. Then, supercritical CO_2 selectively dissolves them; it has a critical temperature of 31.1°C and a critical pressure of 73.8 bar. Nonetheless, many extractions can be performed well below this pressure.

10.1.5.2 Extraction with Other Liquefied Gases

Liquefied gases (LG) are studied as extractants for the removal of some aqueous-phase organic contaminants such as halogenated hydrocarbons, phenols, and aromatic compounds. High removal efficiencies (greater than 90% in a single extraction stage) can be achieved for a large number of hydrophobic organic contaminants.

10.1.5.3 Extraction with Liquid Solvents (Liquid–Liquid Extraction)

Organic or metal ion pollutants that are completely soluble in a waste stream can be separated by selective dissolution in a liquid extractant (immiscible with the parent stream), from which they can be recovered at a later stage. For example, metals are usually recovered as chelates. Because the volume of the extractant is typically smaller than that of the waste stream, this can be viewed as a concentration step. The extracting medium (e.g., oils, aromatic solvents, ethers and esters, ketones, and halogenated solvents) can normally be recycled. The extraction efficiency depends on several factors, including process thermodynamics (i.e., high partition coefficients) and kinetics (i.e., high reaction and mass transfer rates). Optimization often involves multiple extraction stages.

Unfortunately, when the concentration of pollutants is high, large amounts of extractant must be used and this frequently entails additional disposal or treatment problems. Furthermore, the cleansed parent stream usually ends up with some extracting solvent that must sometimes be removed before final release into the environment. The flammability of most solvents is another drawback.

10.1.5.4 Catalytic Hydrodechlorination

In situ catalytic hydrodechlorination of chlorinated hydrocarbons in wastewater can be used for detoxification of process wastewater or groundwater contaminated with low-molecular weight chlorinated hydrocarbons such as trichloroethylene and trichloroethane. The advantage of this approach is that it consists of a single-step process which can be carried out under ambient conditions.

10.2 Physical Processes

Many physical processes for pollutant treatment and/or removal are in use. Selected processes will now be discussed. Note that some of them are actually *physicochemical* rather than purely *physical.*

10.2.1 Adsorption Processes

The use of large-surface area activated charcoal or carbon (approximatlely 500–1500 m^2/g), either as powder activated carbon (PAC) or granular activated carbon (GAC), is the most popular adsorption technique. It is a relatively simple, low-cost, and widely applicable method of pollutant removal, and the literature is replete with descriptions of applications. The GAC version is mostly used in effluents that have already received normal biological treatment but need a polishing process to remove taste, smell, chlorine, and refractory organic compounds, as well as residual amounts of inorganic compounds such as nitrogen, sulfides, and heavy metals. In addition, the carbon surface may be modified so as to adsorb specific pollutants (this type of materials is also called *getter materials*). Examples used for carbon-surface impregnation and the species that they trap include Cu(II)/ammonia vapors, NaOH/acids, and Ag^+/radioactive iodide.

In the same vein, key strategies for the selective removal of DOM (typically a mixture of acidic macromolecules ionized at circumneutral pH values; see Section 6.1.3) with activated charcoal include tailoring this by attaching species with a high affinity for DOM, and developing a positively charged basic surface. Zeolites are also common adsorbents, and their action is much more specific than that of activated carbon since zeolites capture pollutants in cages of specific sizes.

The point of breakthrough occurs when the adsorption sites in the adsorbent medium become saturated. Here, concentrations of the target contaminant in the influent and effluent become equal. Typical problems include accumulation of solids and biofouling. Both can be prevented by pre-treating the target stream and adding biocides. Activated carbon is also problematic because of surface blocking by high-molecular weight species. This effect not only blocks useful adsorption sites but may also result in the replacement of such species by others with higher affinity for carbon, which gives rise to concentration spikes in the treated effluent.

10.2.2 Incorporation of Pollutants into Solid Materials

10.2.2.1 Clay Incorporation

When Al^{3+} substitutes some Ca^{2+} ions, clay minerals develop a positive charge on their octahedral layers. Then, negatively charged pollutant anions can be incorporated into the clay so as to balance the positive charges. For example, $B(OH)_4^-$, SeO_4^{2-}, CrO_4^{2-}, and MoO_4^{2-} can be removed from wastewater in this way using hydrocalumite $[Ca_4Al_2(OH)_{12}(OH)_2 \cdot 6H_2O]$, a hydration product of ordinary Portland cement.

Similar strategies are used to ameliorate the so-called *arsenic crisis* in Bangladesh, where some half of the drinking-water wells are contaminated with arsenic leaching out of pyritic sedimentary rocks. As a result, almost a quarter of a million people have been diagnosed to date with arsenicosis. Low-cost, low-tech treatment alternatives include filtration through tubes filled with volcanic rocks that contain aluminum hydroxide, believed to bind arsenic. An alternative indirect treatment consists in the simple aeration of water, whereby iron ions contained in it precipitate as a result of the formation of insoluble iron hydroxides that scavenge arsenic. Other techniques include the addition of iron filings mixed with sand, to well water spiked with barium sulfate. Here, Fe^0 scavenges dissolved O_2, and the As species become reduced by the *zero-valent metal* (ZVM; see Section 10.1) to precipitate as arsenopyrite. An even simpler technique involves wrapping aluminum potassium sulfate (i.e., cheap alum) in a cloth and dipping the wrapped alum in water for a few seconds; after some hours, an arsenic-containing precipitate forms and this can be filtered out with a fine cloth.

10.2.2.2 Supersoaker Materials

High-surface porous silica can be coated with functionalized monolayers so as to trap metal ions from polluted water by means of groups with high affinity for them. The process is so effective that the resulting water is often drinkable; in addition, the material can be reused. One can measure its effectiveness with the distribution coefficient, K_d:

$$K_d = \frac{\text{amount of adsorbed metal/g of adsorbing material}}{\text{metal concentration left in solution}} \tag{10.52}$$

Interestingly, high-surface porous silica shows very high K_d values (on the order of 3×10^5).

10.2.2.3 Vitrification

Vitrification processes are becoming increasingly important for the incorporation of pollutants into solid materials. See Section 10.1.2.1.

10.2.3 Radiation-Based Processes

10.2.3.1 Microwave Energy

Soil samples can be irradiated with microwaves so as to partially melt some of their components, producing a vitrified mass that incorporates pollutants and renders them insoluble. (That is why this technique can only be used with non-agricultural soils). Conducting rods (e.g., graphite, iron) promote an even conduction of energy. Interestingly, dechlorination of organic materials can also be achieved in this way, as can evaporation and/or destruction of other organic pollutants.

10.2.3.2 Electron Beams

Irradiation of an air stream with electrons produces excitation of its components (e.g., N_2, O_2, and H_2O), yielding active moieties capable of oxidizing pollutants contained in it. The most common active species thus produced include atoms (N and O), molecular ions (N_2^+, O_2^+), neutral oxidizing molecules (O_3), and radicals ($^{\bullet}OH$). Consequently, this technique does not merely transfer pollutants from one phase to another, but actually transforms them into more environmentally friendly species. This method represents an economical advantage in cases such as the reduced emission of certain dioxins.

10.2.3.3 Ultrasound

Ultrasound applied to aqueous solutions creates a phenomenon called *cavitation*, which involves high pressures (up to 1000 atm) and temperatures (up to 5000 K) inside minute bubbles formed in the liquid. Useful chemical phenomena may occur as a result of radical production, such as the highly oxidizing $^{\bullet}OH$ radicals (see AOP in Section 10.1.2). Examples of use include the oxidation of pollutants such as toxic As(III) to As(V), gasoline oxygenates, cyanobacterial toxins, and carbon disulfide.

10.2.3.4 Photochemical Methods

Photochemical oxidations are traditionally linked to the AOP discussed earlier (Section 10.1.1.2), because they normally involve irradiation of a sample with UV light in the presence of H_2O_2 and/or ozone that produces $^{\bullet}OH$ radicals. Interestingly, solar radiation can also effect photochemical degradations on its own, with half-lives even on the order of a few minutes. Examples include the almost complete degradation of hormone steroids and the photooxidation of herbicides and ligands.

10.2.4 Methods Based on Magnetic Fields

10.2.4.1 Magnetic Treatment

A low-conducting medium without ferromagnetic properties cannot per se absorb magnetic-field energy. However, the sudden application of a magnetic field to a moving liquid promotes the loosening and alteration of hydrate layers and films of insoluble species, thus facilitating their coagulation and coalescence. For example, the carbonate equilibrium

$$Ca(HCO_3)_2 \rightleftarrows CaCO_{3(s)} + CO_{2(g)} + H_2O_{(l)} \tag{10.53}$$

shifts toward the formation of insoluble $CaCO_3$ owing to an increase in the number of crystallization centers in the aqueous solution under magnetic treatment. Dissolution of the extra CO_2 thus produced by this equilibrium shift promotes a pH change that can be monitored to evaluate the efficiency of this removal process. Additional effects include degassing as a result of the local dehydration of surface microbubble films, and a pressure decrease in the center of vortices caused by the coalescence and transition from dissolved molecular gases into free-bubble form. Finally, free radicals, atomic oxygen, peracids, and nitrogen-containing compounds are formed as a result of the application of magnetic fields.

10.2.4.2 Magnetic Particles

Other environmentally-oriented uses of magnetic separation involve the use of very fine particles of a magnetic compound (e.g., magnetite mineral, Fe_3O_4) that are added to the water to be treated (e.g., drinking water, industrial wastewater, domestic sewage). These particles are washed beforehand so as to remove impurities and get a point of zero charge in the circumneutral range (see Section 6.3.2). Then, with a slight acidification of the treatment medium, one obtains positively charged particles capable of adsorbing negatively charged colloidal particles. An additional advantage is that the fine magnetite particles have large surface areas.

The mixture is then passed through a pipe surrounded by permanent magnets, which makes the particles aggregate and settle to the bottom of a clarifier, carrying along a large portion of the impurities.

Unmagnetized magnetite settles slowly (approximately 1 m/h); a magnetic field, however, makes it settle much faster (approximately 100 m/h). This treatment can be enhanced by adding coagulants. In order to reuse the magnetite particles, one adds caustic soda to reverse their surface charge with the concomitant stripping-off of the attached impurities. The mixture is then passed through a series of permanent magnetic separators; the recovered magnetite is then recycled. Uses include the adsorption of organic dyes, remediation of oil-spills, and removal of metal ions.

An alternative concept, the *magnetically-assisted chemical separation*, involves the coating of magnetic particles with selective metal ion extractants in an organic polymer shell. Once the metal ions are removed from the target solution, the process can be reversed by stripping them off at a judiciously selected pH.

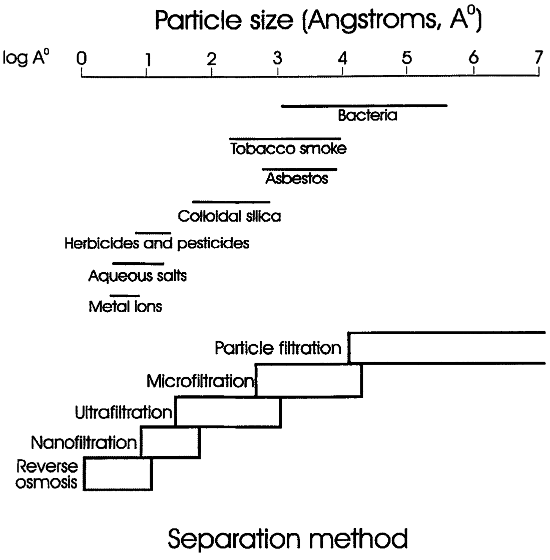


FIGURE 10.7. A simplified filtration spectrum.

10.2.5 Filtration Methods

Filtration systems separate solid or suspended pollutants from a liquid matrix by virtue of their different sizes. They can be used independently or in conjunction with other separation systems; in fact, suspended solids are commonly removed from wastewater by filtration before further treatment. Typical filtering media include sand, ceramic materials, metals, polymers, and other materials that are inert to the target liquid and to the suspended materials or solids. Fouling and plugging are often solved by backwashing. Microorganism growth on the filtering medium can be corrected by adding disinfectants to the stream before treatment. Filtration removes the residual suspended solids from secondary effluents of biological and chemical treatment processes (e.g., chemically-precipitated phosphorus). A discussion of filtration methods is more conveniently addressed in light of the so-called *filtration spectrum*. See Figure 10.7.

Surface filtration involves the removal of particulate material suspended in a liquid by mechanical sieving. This is achieved by passing the liquid through a thin layer of woven metal meshes, cloth fabrics, or a variety of synthetic materials.

Depth filtration includes several layers of filtration media, each one of different size and density. Light, coarse material lies at the top of the filter bed and media become progressively finer and denser in the lower layers. Larger suspended particles are removed by the upper layers, while smaller particles are removed in the lower layers. Particles are trapped throughout the bed, not in just the top few inches. Particles thus removed have diameters in the range of 10–10^{3} μm.

Micro-, ultra-, and nano-filtration can separate smaller particles using media with defined porous sizes (i.e., 10^{-1}–1 μm in microfiltration, 10^{-2}–10^{-1} μm in ultrafiltration, and 10^{-3}–10^{-2} μm in nanofiltration). Residual colloidal and suspended solids can be removed by microfiltration. Selected salts, most organic compounds, bacteria, protozoan cysts, oocysts and viruses are removed by nanofiltration, so that the treated water will be disinfected. This advanced filtration is used for the treatment of effluents for indirect potable reuse applications such as groundwater injection, water softening, decolorization, or removal of micropollution.

Reverse osmosis can be understood as an extreme form of filtration. Osmosis involves the migration of water from a low-concentration side to a high-concentration side across a *semipermeable* membrane that separates both solutions. Its physicochemical basis resides in the requirement to balance the chemical potentials of both sides. Here, the membrane must be permeable to the solvent but not to the dissolved contaminants to be removed (e.g., salts and high-molecular weight compounds).

On the other hand, pressure is applied in reverse osmosis to drive the solvent (water) out of the high-concentration side into the low-concentration side; this facilitates de-watering insoluble species for their removal. This process produces high-quality water and concentrated refuse. It separates and removes dissolved solids, organics, pyrogens, colloidal matter, viruses, and bacteria from water in the particle range 10^{-4}–10^{-2} μm. Reverse osmosis can remove up to 95%–99% of the total dissolved solids (TDS) and 99% of all bacteria. It is used for the obtention of drinking water from seawater and for the production of ultra pure water in various industries.

Membranes are typically made of cellulose acetate or aromatic polyamides because of their high permeability to water and low permeability to salts. They are normally produced in tubular or spiral-wound modules, which are then packed inside a reaction vessel. Their fouling can be minimized by either pretreating the influent streams or diluting them with the clean water produced.

An interesting alternative development is that of *forward osmosis*. Whereas in *reverse osmosis* a high pressure is required to oppose the natural tendency of freshwater to move across such a membrane via osmosis to dilute the seawater, in *forward osmosis* the system takes advantage of this natural tendency. Here, salt water sits on one side of the membrane, but the freshwater on the opposite side is transformed into a high-concentration solution by adding NH_3 and CO_2. Water naturally flows from the salt water to what is now the *draw solution*, which can have a solute concentration as high as 10 times that of the salt water. There is no need for an external pressure. The diluted draw solution is then heated to evaporate off the CO_2 and NH_3 for reuse, leaving behind freshwater. (See Patel-Predd, 2006).

10.2.6 Evaporation

In the field of remediation, this thermally-driven process involves a phase change from a liquid or slurry to the gaseous state in order to concentrate a target contaminant in the liquid phase and reduce the volume to be treated. The smaller the concentration of the contaminant, the less useful is this technique. Possible problems include scaling, foaming, corrosion, and salting. The high cost of heating and of heat- and corrosion-resistant equipment makes evaporation an expensive alternative. Solar evaporation is an interesting option, although the cost of land can not be overlooked.

10.2.7 Air/Steam Stripping

Dissolved pollutants can be transferred from a condensed (liquid or solid) phase into the vapor phase under the action of steam or air streams. As a mass transfer phenomenon, it is driven by a concentration gradient between the condensed and gas phases. It applies fundamentally to pollutants that show sufficiently high vapor pressures under the operating conditions. If the source phase is a liquid, Henry's law regulates the corresponding equilibrium (see Chapter 6). Steam can remove pollutants that may be difficult to remove with air. Obviously, the resulting (contaminated) gas stream or condensate must be treated before its release into the atmosphere.

Stripping units (typically packed towers, known as *air strippers*, or aeration tanks) rely heavily on high area-to-volume ratios, usually provided by polymeric or ceramic materials. The air stripper includes a spray nozzle at the top of the tower. It sprays water over the packing in the column. As the water descends, air is forced up through the column, stripping off the volatile compounds. Packing or baffles within the tower increase the surface area of the contaminated water exposed to air, and therefore maximize the degree of volatilization. The gas is then collected and cleaned. Its main applications include the removal of dissolved gases from wastewater—especially ammonia, odorous gases, and volatile organic compounds (VOCs). As with filtration, typical problems include plugging and fouling, with the concomitant loss of air or steam pressure.

10.3 Combined Treatments

The combination of methods for waste treatment often offers a wider range of possibilities and greater efficiency. As an example, microwaves are combined with photocatalysis for the treatment of oxygenated organics. Also, processes that combine H_2O_2, O_3, and UV are highly efficient. In fact, many of the processes described in this chapter can be combined among themselves to enhance their effectiveness and the individual contributions to the overall treatment efficiency can often be unraveled through mathematical modeling.

Related Experiments in the Companion Book

12. Electrochemical treatment of gas pollutants
13. Electrochemical treatment of liquid wastes
14. Electrochemical treatment of polluted soils
15. Removal of nitric oxide by complex formation
16. Photocatalytic remediation of pollutants
17. Chemical mineralization of pollutants through the Fenton reaction
18. Production and analysis of chloramines
19. Production and analysis of chlorine dioxide
20. Metal ion recovery by cementation
21. Green chemistry: The recovery and reuse of sulfur dioxide
24. Wastewater disinfection

Additional Related Experiments/Activities

Alvaro, M.; Espla, M.; Llinares, J.; Martinez-Manez, R.; Soto, J. "A Small Scale Easy to Run Waste Water Treatment Plant—The Treatment of an Industrial Water that Contains Suspended Clays and Soluble Salt," *J. Chem. Educ.* **1993**, *70*, A129–A132.

Balko, B. A.; Tratnyek, P. G. "A Discovery-Based Experiment Illustrating How Iron Metal Is Used to Remediate Contaminated Groundwater," *J. Chem. Educ.* **2001**, *78*, 1661–1664.

Birdwhistell, R. K. "Flocculating Agent," *J. Chem. Educ.* **1957**, *34*, A347.

Blume, R.; Bader, H. J. *Environmental Chemistry in Classroom Experiments*; IUPAC Publication, S.M.V. Traders and Printers: Delhi, 1990.

- Model experiment on the catalytic desulphurisation (Experiment 23)
- The Claus process (Experiment 24)
- Chemisorption of sulphur dioxide on activated charcoal (Experiment 27)
- Copper production by cementation (Experiment 76)
- Copper extraction with a liquid ion exchange resin (Experiment 77)
- Adsorption of dichloromethane vapours (Experiment 102)
- Separation of a dye stuff from effluent water by means of adsorbing resins (Experiment 111)
- Treatment of nickel containing effluent (Experiment 112)
- Treatment of copper containing effluent (Experiment 113)
- Removal of chromate ions from electroplating rinsing water (Experiment 115)
- Removal of residual phenol from precleaned effluent by ion exchange (Experiment 117)
- Phosphate elimination by precipitation (Experiment 123)
- Model flocculation experiment (Experiment 129)
- Flocculation of a suspension by aluminum sulphate (Experiment 130)
- Flocculation of floating substances by guar (Experiment 131)
- Deodorising action of hydrogen peroxide (Experiment 132)

Boehnke, D. N.; Delumyea, R. D. *Laboratory Experiments in Environmental Chemistry*; Prentice-Hall: New York, 1999.

- Removal of chromium (VI) from wastewater at the part-per-million level (Experiment 11)

Bruce, D.; Kuhn, A.; Sojic, N. "Electrochemical Removal of Metal Cations from Wastewater Monitored by Differential Pulse Polarography," *J. Chem. Educ.* **2004**, *81*, 255–258.

Bumpus, J. A.; Tricker, J.; Andrzejewski, K.; Rhoads, H.; Tatarko, M. "Remediation of Water Contaminated with an Azo Dye: An Undergraduate Laboratory Experiment Utilizing an Inexpensive Photocatalytic Reactor," *J. Chem. Educ.* **1999**. *76*, 1680–1683.

Chen, X.; Halasz, S. M.; Giles, E. C.; Mankus, J. V.; Johnson, J. C.; Burda, C. "A Simple Parallel Photochemical Reactor for Photodecomposition Studies," *J. Chem. Educ.* **2006**, *83*, 265–267.

Crees, O. L.; Senogles, E.; Jones, Richard F. "An Improved Demonstration of Colloid Flocculation," *J. Chem. Educ.* **1986**, *63*, 715–716.

Dieleren, H. M. L.; Schoutetent, A. P. H. "Removal of Crude Oil From Marine Surfaces—An Ecological Lecture Experiment," *J. Chem. Educ.* **1972**, *49*, 19–20.

Dhawale, S. W. "Introducing the Treatment of Waste and Wastewater in the General Chemistry Course—Applying Physical and Chemical Principles to the Problems of Waste Management," *J. Chem. Educ.* **1993**, *70*, 395–397.

Doolittle, J.; Wei, I. W. "Remediation of Contaminated Soil," *J. New Engl. Water Environ. Assoc.* **1993**, *27*, 98–106.

Escue, R. B. "Condensation of Noxious Gases," *J. Chem. Educ.* **1961**, *38*, A355.

Giokas, D. L.; Paleologos, E. K.; Karayannis, M. I. "Micelle-Mediated Extraction of Heavy Metals from Environmental Samples: An Environmental Green Chemistry Laboratory Experiment," *J. Chem. Educ.* **2003**, *80*, 61–64.

Harle, H. D.; Leber, P. A.; Hess, K. R.; Yoder, C. H. "A Concept-Based Environmental Project for the First-Year Laboratory: Remediation of Barium-Contaminated Soil by In Situ Immobilization," *J. Chem. Educ.* **2003**, *80*, 561–562.

Herrera-Melián, J. A.; Doña-Rodríguez, J. M.; Rendón, E. Tello; Soler Vila, A.; Brunet Quetglas, M.; Azcárate, A. A.; Pascual Pariente, L. "Solar Photocatalytic Destruction of p-Nitrophenol: A Pedagogical Use of Lab Wastes," *J. Chem. Educ.* **2001**, *78*, 775–777.

Ibanez, J. G. *Problem Set* in Chapter 15: "Environmentally Oriented Electrochemistry," in Bockris, J.O'M.; Reddy, A. *Modern Electrochemistry, Vol. 2B: Electrodics in Chemistry, Engineering, Biology, and Environmental Science.* 2nd ed.; Plenum Press: New York, 2000. pp. 2043–2051.

Ibanez, J. G. "Laboratory Experiments on Electrochemical Remediation of the Environment. Part 5: Indirect H_2S Remediation," *J. Chem. Educ.* **2001**, *78*, 778–779.

Ibanez, J. G.; Hernandez-Esparza, M.; Valdovinos-Rodriguez, I.; Lozano-Cusi, M.; de Pablos-Miranda, A. "Microscale Environmental Chemistry. Part 2. Effect of Hydrogen Peroxide in the Presence of Iron (II) (Fenton Reagent) and Other Conditions upon an Organic Pollutant," *J. Chem. Educ.* **2003**, *8(1)* 47–50.

Ibanez, J. G.; Mayen-Mondragon, R.; Moran-Moran, M. T.; Alatorre-Ordaz, A.; Mattson, B.; Eskestrand, S. "Laboratory Experiments on the Electrochemical Remediation of the Environment. Part 7: Microscale Production of Ozone," *J. Chem. Educ.* **2005**, *82*, 1546–1548.

Ibanez, J. G.; Mena-Brito, R.; Fregoso-Infante, A., "Laboratory Experiments on the Electrochemical Remediation of the Environment. Part 8. Microscale Photocatalysis," *J. Chem. Educ.* **2005**, *82*, 1549–1551.

Ibanez, J. G.; Mena-Brito, Rodrigo; Fregoso-Infante, Arturo; Seesing, M.; Tausch, Michael W. "Photoreactions with Titanium Dioxide—A Microscale Experiment," *Prax. Naturwiss. Chem. Sch. (Germany)* **2005**, *54(3)*, 22–24.

Ibanez, J. G.; Miranda, C.; Topete, J.; García, E. "Metal Complexes and the Environment: Microscale Experiments with Iron-EDTA Chelates," *J. Chem. Educ.* **2000**, *5*, 226–230.

Ibanez, J. G.; Tellez-Giron, M.; Alvarez, D.; Garcia-Pintor, E. "Laboratory Experiments on the Electrochemical Remediation of the Environment. Part 6: Microscale Production of Ferrate," *J. Chem. Educ.* **2004**, *81*, 251–254.

Ibanez, J. G.; Singh, M. M.; Pike, R. M.; Szafran, Z. "Laboratory Experiments on Electrochemical Remediation of the Environment. Part 2: Microscale Indirect Electrolytic Destruction of Organic Wastes," *J. Chem. Educ.* **1997**, *74*, 1449–1450.

Ibanez, J. G.; Singh, M. M.; Pike, R. M.; Szafran, Z. "Laboratory Experiments on Electrochemical Remediation of the Environment Part 3: Microscale Electrokinetic Processing of Soils," *J. Chem. Educ.* **1998**, *75*, 634–635.

Ibanez, J. G.; Singh, M. M.; Szafran, Z. "Laboratory Experiments on the Electrochemical Remediation of Environment. Part 4: Color Removal of Simulated Wastewater by Electrocoagulation-Electroflotation," *J. Chem. Educ.* **1998**, *75*, 1040–1041.

Ingles, M.; Bonete, P.; Exposito, E.; Garcia-Garcia, V.; Gonzalez-Garcia, J.; Iniesta, J.; Montiel, V. "Electrochemical Regeneration of a Spent Oxidizing Solution: Example of a Clean

Chemical Process," *J. Chem. Educ.* **1999**, *76*, 1423–1425.

Jacobsen, E. K. "Water Filtration," *J. Chem. Educ.* **2004**, *81*, 224A–224B.

Kovenklioglu, S.; Cao, Z.; Yu, G.; Farrauto, R. J. "Three-Phase Hydrodechlorination Reactors for Unit Operations Laboratory," *ASEE Ann. Conf. Proc.* (ACOPDW) **1995**, *1*, 694–700. Anaheim, CA, USA, Jun 25–28, 1995.

Krow, G. R.; Krow, J. B. "Low-Level Radioactive Waste Disposal: An Exercise in Dealing with Pollution," *J. Chem. Educ.* **1998**, *75*, 1583–1584.

Lodge, K. B.; Davis, R. A.; Dorland, D.; Baria, D. N. "Experiments in Waste Processing for Undergraduates," *ASEE Ann. Conf. Proc.*: Milwaukee, WI, USA, Jun. 15–18, 1997. p. 7.

Mattson, B.; Fujita, J.; Catahan, R.; Cheng, W.; Greimann, J.; Khandhar, P.; Mattson, A.; Rajani, A.; Sullivan, P.; Perkins, R. "Demonstrating Heterogeneous Gas-Phase Catalysis with the Gas Reaction Catalyst Tube," *J. Chem. Educ.* **2003**, *80*, 768–773.

Mihok, M.; Keiser, J. T.; Bortiatynski, J. M.; Mallouk, T. E. "An Environmentally-Focused General Chemistry Laboratory," *J. Chem. Educ.* **2006**, *83*, 250.
http://jchemed.chem.wisc.edu/Journal/Issues/2006/FebACS/ACSSub/ACSSupp/JCE2006p0250W.pdf

- Fe remediation: (Experiment 8)
  - o *Kinetics*
  - o *Liquid/liquid extraction*
- Fe remediation: *degradation of 2, 4-D* (Experiment 9)
- Wastewater treatment (Experiment 10)

Moreira, R. de F. P. M.; José, H. J.; Kuhnen, N. C.; Phillips, A. M. de L.; Pokrywiecki, T. S.; Neto, G. C. "Environmental View of Teaching about Heterogeneous Catalysis: An Undergraduate Laboratory Experiment Directed Towards the Remediation of Water Contaminated with Methylene Blue," Universidade de Santa Catarina, Trindade–Brazil.
http://www.hottopos.com/regeq11/regina.htm

Oliveira, L. C. A.; Rios, R. V. R. A.; Fabris, J. D.; Lago, R. M.; Sapag, K. "Magnetic Particle Technology. A Simple Preparation of Magnetic Composites for the Adsorption of Water Contaminants," *J. Chem. Educ.* **2004**, *81*, 248–250.

Orbell, J. D.; Godhino, L.; Bigger, S. W.; Nguyen, T. M.; Ngeh, L. N. "Oil Spill Remediation Using Magnetic Particles: An Experiment in Environmental Technology," *J. Chem. Educ.* **1997**, *74*, 1446–1448.

Raymundo-Piñero, E.; Cazorla-Amorós, D.; Morallón, E. "Catalytic Oxidation of Sulfur Dioxide by Activated Carbon: A Physical Chemistry Experiment," *J. Chem. Educ.* **1999**, *76*, 958–961.

Romero, A.; Hernández, G.; Suárez, M. F. "Photocatalytic Oxidation of Sulfurous Acid in an Aqueous Medium," *J. Chem. Educ.* **2005**, *82*, 1234–1236.

Roundhill, D. M. "Novel Strategies for the Removal of Toxic Metals from Soils and Waters," *J. Chem. Educ.* **2004**, *81*, 275–282.

Santos, E. S.; Garcia, I. C. G.; Gomez, E. F. L. "Caring for the Environment while Teaching Organic Chemistry," *J. Chem. Educ.* **2004**, *81*, 232–238.

Soltzberg, L. J.; Brown, V. "Note on Photocatalytic Destruction of Organic Wastes: Methyl Red as a Substrate," *J. Chem. Educ.* **2005**, *82*, 526.

Soriano, D. S.; Draeger, J. A. "An Environmental Distillation Experiment for Non Science Majors," *J. Chem. Educ.* **1995**, *72*, 84.

Soriano, D. S.; Draeger, J. A. "A Water Treatment Experiment (Chemical Hardness) For Non Science Majors," *J. Chem. Educ.* **1993**, *70*, 414.

Walczak, M. M.; Lantz, J. M. "A Case on Septic Systems and Well Water Requiring In-Depth Analysis and Including Optional Laboratory Experiments," *J. Chem. Educ.* **2004**, *81*, 218–220.

Wilmer, B. K.; Poziomek, E.; Orzechowska, G. E. "Environmental Chemistry Using Ultrasound," *J. Chem. Educ.* **1999**, *76*, 1657.

Wong, G.; Mark, B.; Chen, X.; Furch, T.; Singmaster, K. A.; Wagenknecht, P. S. "Preparation and Use of a Room-Temperature Catalytic Converter," *J. Chem. Educ.* **2001**, *78*, 1667–1668.

Yu, J. C.; Chan, L. Y. L. "Photocatalytic Degradation of a Gaseous Organic Pollutant," *J. Chem. Educ.* **1998**, *75*, 750–751.

References and Further Reading

Note: Owing to the extensive bibliography in this field, the information on literature references is presented for each subsection, rather than for the whole chapter.

Redox Processes

Baird, N. C. "Free Radical Reactions in Aqueous Solutions: Examples from Advanced Oxidation Processes for Wastewater from the Chemistry in Airborne Water Droplets," *J. Chem. Educ.* **1997**, *74*, 817–819.

Benjamin, K. M.; Savage, P. E. "Supercritical Water Oxidation of Methylamine," *Ind. Eng. Chem. Res.* **2005**, *44*, 5318–5324.

Bryant, E. A.; Fulton, G. P.; Budd, G. C.; Hazen and Sawyer. *Disinfection Alternatives for Safe Drinking Water*; Van Nostrand-Reinhold: New York, 1992.

Denvir, A.; Pletcher, D. "Electrochemical Generation of Ferrate. Part 1. Dissolution of an Iron Wool Bed Cathode," *J. Appl. Electrochem.* **1996**, *26*, 815–822.

Eddy, H. P. "Industrial Waste Disposal," *J. Ind. Eng. Chem.* **1917**, *9*, 696–700.

Eilbeck, W. J.; Mattock, G. *Chemical Processes in Waste Water Treatment*; Ellis Horwood: Chichister, 1987. Chapters 3, 4.

ERCO Worldwide. Production and properties of ClO_2; http://clo2.com/index.html

Faust, S. D.; Aly, O. M. *Chemistry of Water Treatment*; Butterworth: Boston, 1983. Chapter 10.

Foller, P. C.; Goodwin, M. L. "Electrochemical Generation of High-Concentration Ozone for Waste Treatment," *Chem. Eng. Progr.* **1985**, *81(3)* 49–51.

Fujishima, A.; Rao, T. N.; Tryk, D. A. "Titanium Dioxide Photocatalysis," *J. Photochem. Photobiol. C: Photochem. Rev.* **2000**, *1*, 1–21.

Gan, J. "Detoxification of Halogenated Fumigants by Thiosulfate Salts," *Am. Chem. Soc. Meet.*, Boston, MA. August 18–22, 2002. Prepr. Extd. Abstr. **2002**, *42(2)* 387-391.

Gordon, G.; Bubnis, B. "Environmentally Friendly Methods of Water Disinfection: The Chemistry of Alternative Disinfectants," *Progr. Nucl. Energy* **2000**, *37 (1–4)* 37–40.

Greenberg, R. S.; Andrews, T.; Kakarla, P. K. C.; Watts, R. J. "In-Situ Fenton-Like Oxidation of Volatile Organics: Laboratory, Pilot, and Full-Scale Demonstrations," *Remediation* **1998**, *8*, 29–42.

Gu, B.; Dong, W.; Brown, G. M.; Cole, D. R. "Complete Degradation of Perchlorate in Ferric Chloride and Hydrochloric Acid under Controlled Temperature and Pressure," *Environ. Sci. Technol.* **2003**, 37, 2291–2295.

Haggin, J. "New Processes Target Methanol Production, Off-gas Cleaning," *Chem. Eng. News*, Mar. 28, 1994. pp. 29–31.

Heller, A. "Chemistry and Applications of Photocatalytic Oxidation of Thin Organic Films," *Acc. Chem. Res.* **1995**, *28*, 503-508.

Innovative Environmental Technologies, Inc. http://www.iet-inc.net/InSitu_Chemical.htm

Jackson, J. R.; Pitzer, C. L. "Method for the Removal of Chromium Compounds from Aqueous Solutions," US Patent 5,211,853. May 18, 1993.

Johnson, J. "New Rules Target Waste Burners," *Chem. Eng. News* May 15, 2000. pp. 31–33.

Legrini, O.; Oliveros, E.; Braun, A. M. "Photochemical Processes for Water Treatment," *Chem. Rev.* **1993**, *93*, 671–698.

Kwan, W. P.; Voelker, B. M. "Rates of Hydroxyl Radical Generation and Organic Compound Oxidation in Mineral-Catalyzed Fenton-like Systems," *Environ. Sci. Technol.* **2003**, *37*, 1150–1158.

Lin, S. H.; Yeh, K. L. "Looking To Treat Wastewater? Try Ozone," *Chem. Eng.* **1993**, *100(5)*, 112.

Madden, T. H.; Datye, A. K.; Fulton, M.; Prairie, M. R.; Majumdar, S. A.; Stange, B. M. "Oxidation of Metal-EDTA Complexes by TiO_2 Photocatalysis," *Environ. Sci. Technol.* **1997**, *31*, 3475–3481.

Matthews, R. W. "Photooxidative Degradation of Coloured Organics in Water Using Supported Catalysts. TiO_2 on Sand," *Wat. Res.* **1991**, *25*, 1169–1176.

Maui Department of Water Supply. http://www.mauiwater.org/chloramines.html

McKetta, J., ed. "Chlorine Dioxide," in: *Inorganic Chemicals Handbook*, Vol. 2; Marcel Dekker: New York, 1993. pp. 779–810.

McKinzi, A. M.; DiChristina, T. J. "Microbially Driven Fenton Reaction for Transformation of Pentachlorophenol," *Environ. Sci. Technol.* **1999**, *33*, 1886–1891.

Metcalf & Eddy, Inc. *Wastewater Engineering. Treatment, Disposal and Reuse*; McGraw-Hill: New York, 1991. Chapter 7.

My, N. L.; Sahgal, P. N. "Generation of Ozone in Two-Dielectric Ozonizer," *The Chem. Eng. J.* **1989**, *40*, 175.

Norton, C. D.; LeChevallier, M. W. "Chloramination: Its Effect on Distribution System Water Quality," *J. Am. Wat. Work. Assoc.* **1997**, *89 (7)*, 66–77.

Oregon Health and Science University. Department of Environmental and Biomolecular Systems. "Zero-valent iron barriers for teachers and students (a multimedia CD-ROM)." http://cgr.ese.ogi.edu.merl/

Pittman, C. U. Jr.; He, J.; Yang, C.; Tabaiei, M. "Detoxification of PCBs, CFCs, CAHs and Halogenated Biocides in Soils, Sludges and Other Matrices Using Chemical Reductions," *Am. Chem. Soc. Meet.*, Boston, MA. August 18–22, 2002. Prepr. Extd. Abstr. **2002**, *42 (2)*, 422–426.

Prairie, M. R.; Evans, L. R.; Stange, B. M.; Martinez, S. L. "An Investigation of TiO_2 Photocatalysis for the Treatment of Water Contaminated with Metals and Organic Chemicals," *Environ. Sci. Technol.* **1993**, *27*, 1776–1782.

Prasad, J.; Tardio, J.; Akolekar, D. B.; Bhargava, S. K.; Grocott, S. C. "Catalytic Wet Oxidation of Stripped Sour Water from an Oil-Shale Refining Process," *Ind. Eng. Chem. Res.* **2004**, *43*, 6363–6368.

Rajeshwar, K.; Ibanez, J. G. *Environmental Electrochemistry; Fundamentals and Applications in Pollution Abatement*; Academic Press: San Diego, 1997. Chapter 6.

Rajeshwar, K.; Ibanez, J. G. "Electrochemical Aspects of Photocatalysis: Application to Detoxification and Disinfection Scenarios," *J. Chem. Educ.* **1995**, *72*, 1044–1049.

Rajeshwar, K. "Photoelectrochemistry and the Environment." *J. Appl. Electrochem.* **1995**, *25*, 1067–1082.

Sawyer, D. T.; Sobkowiak, A.; Roberts, J. L. Jr. *Electrochemistry for Chemists*, 2nd ed.; Wiley Interscience: New York, 1995.

Sharma, K. V.; Rivera, W.; Smith, J. O.; O'Brien, B. "Ferrate(VI) Oxidation of Aqueous Cyanide," *Environ. Sci. Technol.* **1998**, *32*, 2608–2613.

Southworth, B. A.; Voelker, B. M. "Hydroxyl Radical Production via the Photo-Fenton Reaction in the Presence of Fulvic Acid," *Environ. Sci. Technol.* **2003**, *37*, 1130–1136.

Stumm, W.; Morgan, J. J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters;* Wiley Interscience: New York, 1996. Chapter 11.

Switzer, J. A.; Rajasekharan, V. V.; Boonsalee, S.; Kulp, E. A.; Bohannan, E. W. "Evidence that Monochloramine Disinfectant Could Lead to Elevated Pb Levels in Drinking Water," *Environ. Sci. Technol.* **2006**, *40*, 3384–3387.

Sylvester, P.; Rutherford, L. A. Jr.; Gonzalez-Martin, A.; Kim, J.; Rapko, B. M.; Lumetta, G. J. "Ferrate Treatment for Removing Chromium from High-Level Radioactive Tank Waste," *Environ. Sci. Technol.* **2001**, *35*, 216–221.

Tenney, J.; Crump, B.; Ernst, W.; Gravitt, A.; Isaac, T. "Froth Reactor for Small-Scale Generation of Chlorine Dioxide," *AICHE Journal* **1997**, *43*, 2148–2152.

The Alliance for Environmental Technology (AET). http://www.aet.org/reports/communication_resources/fact_sheets/oneway.html

Theodore, L.; Buonicore, A. J.; McKenna, J. D.; Kugelman, I. J.; Jeris, J. S.; Santoleri, J. J.; McGowan, T. F. *Waste Management*, Section 25 in *Perry's Chemical Engineering Handbook*, 7th ed.; Perry, Robert H.; Green, Don; Maloney, James O., Eds. McGraw Hill: New York, 1997.

U.S. Environmental Protection Agency, "Alternative Oxidants and Disinfectants Guidance Manual," Chapter 5. Apr. 1999. EPA 815-R-99-014. http://www.epa.gov/ogwdw/mdbp/word/alter/chapt_5.doc

U.S. Environmental Protection Agency. Drinking Water Standards. http://www.epa.gov/safewater/standards.html

U.S. Environmental Protection Agency, Locating and Estimating Air Emissions from Sources of Dioxins and Furans (May 1997). http://www.epa.gov/ttnchie1/le/dioxin.pdf

Walte, T.; Fagan, J. "Biofouling Control with Ferrate," *Environ. Sci. Technol.* **1983**, *17*, 123–125.

Wilczak, A.; Hoover, L. L.; Lai, H. H. "Effects of Treatment Changes on Chloramine Demand and Decay," *J. Am. Wat. Work. Assoc.* **2003**, *95(7)*, 94–106.

Wilkins, F. W.; Blake, D. M. "Use Solar Energy to Drive Chemical Processes," *Chem. Eng. Progr.* **1994**, June, 41–49.

Wilson, E. "Titanium Dioxide Catalysts Break Down Pollutants," *Chem. Eng. News, Jan. 15, 1996*, 23–24.

Acid–Base, Precipitation and, Ion-Exchange Processes

Badreddine, R.; Humez, A.-N.; Mingelgrin, U.; Benchara, A.; Meducin, F.; Prost, R. "Retention of Trace Metals by Solidified/Stabilized Wastes: Assessment of Long-Term Metal Release," *Environ. Sci. Technol.* **2004**, *38*, 1383–1398.

Behrens, E. A.; Sylvester, P.; Clearfield, A. "Assessment of a Sodium Nonatitanate and Pharmacosiderite-Type Ion Exchangers for Strontium and Cesium Removal from DOE Waste Simulants," *Environ. Sci. Technol.* **1998**, *32*, 101–107.

Blatter, F.; Schumacher, E. "The Preparation of Pure Zeolite NaY and its Conversion to High-Silica Faujasite," *J. Chem. Educ.* **1990**, *67*, 519–521.

Davis, M. E.; Lobo, R. F. "Zeolite and Molecular Sieve Synthesis," *Chem. Mater.* **1992**, *4*, 756–768.

Eilbeck, W. J.; Mattock, G. *Chemical Processes in Waste Water Treatment;* Ellis Horwood: Chichister, 1987. Chapters 3, 4.

Kim, C. W.; Day, D. E. "Iron Phosphate Glasses for Vitrifying DOE High Priority Nuclear Wastes," *Am. Chem. Soc. Meet.*, Anaheim, CA. March 28–Apr. 1, 2004. Div. Environ. Chem. Sym. Pap., pp. 440–445.

Priestley, A. J. "Innovative Approaches to Water and Wastewater Treatment Developed at CSIRO, Australia," *5th World Congr. Chem. Eng. and Chem.*, Am. Inst. Chem. Eng.: San Diego, CA, Jul. 14–8, 1996. Book of Abstracts, Vol. III, pp. 803–808.

Totura, G. "Innovative Uses of Specialty Ion Exchange Resins Provide New Cost-Effective Options for Metals Removal," *Environ. Progr.* **1996**, *15(3)*, 208–212.

University of Waterloo (Canada). http://www.science.uwaterloo.ca/ cchieh/cact/applychem/watertreatment.html

Yoshida, H.; Kataoka, T.; Fujikawa, S. "Kinetics in a Chelate Ion Exchanger. 1. Theoretical Analysis," *Chem. Eng. Sci.* **1986**, *41*, 2517–2524.

Zagorodni, A. A.; Muhammed, M. "Explanation of the Zn/Cu Dual Temperature Separation on Amberlite IRC-718 Ion-Exchange Resin," *Sep. Sci. Technol.* **1999**, *34*, 2013–2021.

Complexation Processes

Barona, A.; Etxebarria, B. "Distribution and Extraction of Pb and Zn with Chelating Agents in Soils with Varying Pollution Level," Am. Inst. Chem. Eng., *5th. World Congr. Chem. Eng.*, Jul. 14–18, 1996. San Diego, CA., Vol. III, pp. 576–581.

Bolton, H. Jr.; Girvin, D. C.; Plymale, A. E.; Harvey, S. D.; Workman, D. J. "Degradation of Metal-Nitrilotriacetate Complexes by Chelatobacter Heintzii," *Environ. Sci. Technol.* **1996**, *30*, 931–938.

Diallo, M. S.; Balogh, L.; Shafagati, A.; Johnson, J. H. Jr.; Goddard, W. A. III; Tomalia, D. A. "Poly (Amidoamine) Dendrimers: A New Class of High Capacity Chelating Agents for Cu (II) Ions," *Environ. Sci. Technol.* **1999**, *33*, 820–824.

Dunn, K.; Yen, T. F. "Dissolution of Barium Sulfate Deposits by Chelating Agents," *Environ. Sci. Technol.* **1999**, *33*, 2821–2824.

Europ. Pat. Applic. 0864923, cited in *Chem. Ind.*, 5 Oct. 1998, p. 770.

Martin, S. B.; Allen, H. E. "Recycling EDTA after Heavy Metals Extraction," *Chemtech* **1996**, *26(4)*, 23–25.

Mcardell, C. S.; Stone, A. T.; Tian, J. "Reaction of EDTA and Related Aminocarboxylate Chelating Agents with $Co^{III}OOH$ (Heterogenite) and $Mn^{III}OOH$ (Manganite)," *Environ. Sci. Technol.* **1998**, *32*, 2923–2930.

Pichtel, J.; Pichtel, T. M. "Comparison of Solvents for *Ex Situ* Removal of Chromium and Lead from Contaminated Soil," *Environ. Eng. Sci.* **1997**, *14*, 97–104.

Rajeshwar, K.; Ibanez, J. G. *Environmental Electrochemistry; Fundamentals and Applications in Pollution Abatement;* Academic Press: San Diego, 1997.

Rampley, C. G.; Ogden, K. L. "Preliminary Studies for Removal of Lead from Surrogate and Real Soils Using a Water Soluble Chelator: Adsorption and Batch Extraction," *Environ. Sci. Technol.* **1998**, *32*, 987–993.

Theodoratos, P.; Papassiopi, N.; Georgoudis, T.; Kontopoulos, A. "Selective Removal of Lead from Calcareous Polluted Soils using the Ca-EDTA Salt," *Wat. Air Soil Pollut.* **2000**, *122*, 351–368.

Walton, H. F. "Ligand-Exchange Chromatography: A Brief Review," *Ind. Eng. Chem.* **1995**, *34*, 2553–2554.

Wasay, S. A.; Barrington, S. F.; Tokunaga, S. "Remediation of Soils Polluted by Heavy Metals Using Salts of Organic Acids and Chelating Agents," *Environ. Technol.* **1998**, *19*, 369–380.

Zhao, D.; SenGupta, A. K.; Zhu, Y. "Trace Contaminant Sorption through Polymeric Ligand Exchange," *Ind. Eng. Chem.* **1995**, *34*, 2676–2683.

Electrochemical Processes

Bersier, P. M.; Carlsson, L.; Bersier, J. "Electrochemistry for a Better Environment," in *Topics in Current Electrochemistry*, Vol. 170; Springer Verlag: Berlin, 1994.

Fenton, J. M. "Electrochemistry: Energy, Environment, Efficiency, and Economics," *Interface, Electrochem. Soc.* **1994**, *3*, 38–44.

Genders, D.; Weinberg, N., *Electrochemistry for a Cleaner Environment*; The Electrosynthesis Co.: New York, 1992.

Ibanez, J. G. "Environmental Electrochemistry," in: *Electrochemistry Encyclopedia.* Nagy, Z. Ed.; Case Western Reserve University: Cleveland, OH, 2004. (http://electrochem.cwru.edu/ed/encycl/)

Lageman, R. "Electroreclamation," *Environ. Sci. Technol.* **1993**, *27*, 2648.

Pletcher, D.; Walsh, F. *Industrial Electrochemistry*, 2nd ed.; Chapman and Hall: London, 1990.

Rajeshwar, K.; Ibanez, J. G. *Environmental Electrochemistry; Fundamentals and Applications in Pollution Abatement*; Academic Press: San Diego, 1997.

Rajeshwar, K.; Ibanez, J. G.; Swain, G. M. "*Electrochemistry and the Environment," J. Appl. Electrochem.* **1994**, *24*, 1077–1091.

Schmidt, D. S.; Winnick, J. "Electrochemical Membrane Flue-Gas Desulfurization: K_2SO_4/V_2O_5 Electrolyte," *Am. Inst. Chem. Eng. J.* **1998**, *44*, 323–331.

Sequeira, C. A. C. (Ed.), *Environmental Oriented Electrochemistry*; Elsevier: Amsterdam, 1994.

Walsh, F.; Mills, G. "Electrochemical Methods for Pollution Control," *Chem. Technol.–Europe* April/May **1994**, 13.

Other Chemical Processes

Yang, C.; Teo, K.-C.; Xu, Y.-R. "Removal of Organic Contaminants from Water or Wastewater with Liquefied Gases," *J. Environ. Sci.* **2002**, *14(1)*, 1–6.

Wilson, E. K. "Toxic Metals Extracted with Supercritical Carbon Dioxide," *Chem. Eng. News*, Apr. 15, 1996. pp. 27–28.

Physical Processes

Abramovitch, R. A.; ChangQing, L.; Hicks, E.; Sinard, J. "*In situ* Remediation of Soils Contaminated with Toxic Metal Ions using Microwave Energy," *Chemosph.* **2003**, *53*, 1077–1085.

Belhateche, D. H. "Choose Appropriate Wastewater Treatment Strategies," *Chem. Eng. Progr.* **1995**, *91(8)*, 32–51.

Bogatin, J.; Bondarenko, N. Ph.; Gak, E. Z.; Rokhinson, E. E.; Ananyev, I. P. "Magnetic Treatment of Irrigation Water: Experimental Results and Application Conditions," *Environ. Sci. Technol.* **1999**, *33*, 1280–1285.

"Waste Treatment News: An Attractive Way to Clean Up," *Chem. Ind.* March 16, 1998. p. 197.

Hirota, K.; Hakoda, T.; Taguchi, M.; Takigami, M.; Kim, H.; Kojima, T. "Application of Electron Beam for the Reduction of PCDD/F Emission from Municipal Solid Waste Incinerators," *Environ. Sci. Technol.* **2003**, *37*, 3164–3170.

Lepkowski, W. "Arsenic Crisis in Bangladesh," *Chem. Eng. News*, Nov. 16, 1998. pp. 27–29.

Motamedi, S.; Cai, Y.; O'Shea, K. E. "Ultrasonic Treatment of Arsenic in Drinking Water," *Am. Chem. Soc. Meet.*, Orlando, FL. April 7–11, 2002. Prepr. Extd. Abstr. **2002**, *42(1)* 161–165.

Osmonics, Inc. *The Filtration Spectrum:* Minnetonka, MN, USA, 1996.

Patel-Predd, P. "Water Desalination Takes a Step Forward," *Environ. Sci. Technol.* Online Technology News, May 3, 2006.
http://pubs.acs.org/subscribe/journals/esthag-w/2006/may/tech/pp_desalination.html#

Priestly, A. J. "Innovative Approaches to Water and Wastewater Treatment Developed at CSIRO, Australia," *5th World Congr. Chem. Eng. and Chem.*, Am. Inst. Chem. Eng.: San Diego, CA, Jul. 14–18, 1996. Book of Abstracts, Vol. III, pp. 803–808.

Reese, K. M. "Cheap Way to Remove Arsenic," *Chem. Eng. News*, July 8, 2002. pp. 56.

Wang, Jo. S.; Wai, C. M. "Arsenic in Drinking Water—A Global Environmental Problem," *J. Chem. Educ.* **2004**, *81*, 207–213.

Wilson, E. "Coated Mesoporous Silica: Supersoaker for Heavy Metals," *Chem. Eng. News*, May 19, 1997. pp. 46–47.

Zhang, M.; Reardon, E. J. "Removal of B, Cr, Mo, and Se from Wastewater by Incorporation into Hydrocalumite and Ettringite," *Environ. Sci. Technol.* **2003**, *37*, 2947–2952.

Zuo, Y.; Zhang, K.; Deng, Y. "Occurrence and Photochemical Fate of Hormone Steroids in New Bedford Seawater," *Am. Chem. Soc. Meet.*, Anaheim, CA. March 28–Apr. 1, 2004. Div. Environ. Chem. Sym. Pap., pp. 60–64.

Combined Treatments

Horikoshi, S.; Hojo, F.; Hidaka, H.; Serpone, N. "Environmental Remediation by an Integrated Microwave/UV Illumination Technique. 8. Fate of Carboxylic Acids, Aldehydes, Alkoxycarbonyl and Phenolic Substrates in a Microwave Radiation Field in the Presence of TiO_2 Particles under UV Irradiation," *Environ. Sci. Technol.* **2004**, *38*, 2198–2208.

Rivas, F. J.; Beltran, F. J.; Gimeno, O.; Carbajo, M. "Fluorene Oxidation by Coupling of Ozone, Radiation, and Semiconductors: Mathematical Approach to the Kinetics," *Ind. Eng. Chem. Res.* **2006**, *45*, 166–174.

Wada, H.; Naoi, T. "Recycling of Cyanide Wastewater by Ozone Oxidation Combined with UV Radiation and Ion Exchange," *J. Chem. Eng. Jap.* **1994**, *27(2)*, 262.

11

Biological Treatment of Pollutants and Wastes

11.1 Removal of Pollutants from Wastewater

Sewage is composed not only of the waste matter flushed from toilets, but also of the waste collected from all other drains in homes and other buildings. A sewer system brings all the tub, sink, and toilet drains together into larger pipelines and sewers. The final mixture from the collection system is called *raw sewage* or *raw wastewater*. Raw sewage contains about 1 part of waste in 1000 parts of water (i.e., 0.1% waste to 99.9% water). The raw sewage output in developed countries is on the order of 600–800 liters per person per day. This means that a community of 100,000 persons will produce 60–80 million liters of wastewater everyday. With storm water, raw sewage is diluted but the pollutants are nevertheless enough to darken the water and give it a foul smell.

A variety of treatments can remove organic and inorganic materials like those discussed in Chapter 8 before wastewater is discharged into surface water. They can be classified as *aerobic* and *anaerobic* processes. In general, aerobic treatments are used when the concentration of pollutants is not high (as in domestic wastewater), while the anaerobic treatment is preferred for a high concentration of organic matter (usually found in industrial sewage) as shown in Table 11.1.

These processes usually include several steps:

- Preliminary treatment
- Primary treatment
- Secondary treatment
- Tertiary treatment
- Disinfection
- Sludge treatment

11.1.1 Preliminary Treatment

The objective of the preliminary treatment is to eliminate debris and grit. Debris includes rags, plastic bags, and other objects flushed down toilets or washed through storm drains in places where they are connected to sewers. Grit (i.e., coarse sand and gravel) also enters mainly through storm drains. As debris and grit damage or clog up pumps and some treatment processes, removing them is essential. This usually involves two steps: a screening out of debris and a settling of grit. Debris is removed by letting raw sewage flow through a bar or rotating screen and have it taken to an incinerator. A grinder called a *comminute* is used in some systems to reduce the debris to a relatively fine particle size which then continues through the system to be removed at a later stage.

After passing through the screen, water flows through a grit-settling tank where its velocity is slowed down just enough to allow the grit to settle, be mechanically removed, and taken to landfills. Sometimes grit chambers are aerated to prevent anaerobic processes from taking place in the dissolved and suspended organic matter.

11.1.2 Primary Treatment

After preliminary treatment, water moves to a primary treatment where it flows very slowly (about 2 m per hour) through large tanks called *primary*

TABLE 11.1. COD and BOD_5 (as defined in Chapter 8) of selected wastewaters

Sample Parameter	COD (mg/L)	BOD_5 (mg/L)
Domestic wastewater	250–800	110–350
Dairy wastewater	1,800	900
Distillery vinasse	60,000	30,000
Tannery wastewater	13,000	1,270

clarifiers. Because it flows slowly through these tanks, particulate material settles. This material consists of visible particles of organic matter from food wastes in home-garbage disposal units, fecal matter, bits of paper from toilets, and inorganic suspended material. Particulate organic material also comprises living bacteria and other microorganisms (including pathogens) that start to digest the waste.

After the primary treatment, the particulate organic material (about 30–50% of the total organic material) settles to the bottom and can be removed. At the same time, fatty or oily material floats to the surface and can be skimmed. All the material removed—both particulate organic and fatty material—is combined into what is referred to as *raw* or *primary sludge*.

11.1.3 Secondary Treatment

The aim of the secondary treatment is to remove colloidal and dissolved biodegradable organic material. Colloidal organic material originates from the same sources as particulate organic material but has different particle size. Colloidal particles are so fine that they will not settle — at least not within any reasonable time period. Bacteria and other microorganisms (including pathogens) are also present in this category. In addition, there is dissolved organic material from soaps, detergents, shampoos, and other cleaning and washing agents.

The secondary treatment is also called *biological treatment* because it uses organisms—natural decomposers and detritus feeders. Basically, an environment is created to enable these organisms to feed on the colloidal and dissolved organic material, and break it down to carbon dioxide and water via their cell respiration. The sewage water from primary treatment is the food- and water-rich medium.

11.1.3.1 Aerobic Processes

In the case of aerobic processes, the only thing that needs to be added is dioxygen, in order to enhance the respiration and growth of microorganisms already present in the influent. Recall that the dioxygen consumed in the decomposition process is the *biochemical oxygen demand*. Microorganisms may be suspended in wastewater (they are referred to as activated sludge) or attached to surfaces forming a *biofilm*.

A wide variety of microorganisms are found in aerobic suspended and attached-growth treatment processes. Aerobic heterotrophic bacteria can produce extracellular biopolymers that result in the formation of biological flocs, which may be separated from the treated liquid by quality settling with relatively low concentrations of free bacteria and suspended solids. Protozoa also play an important role in aerobic biological treatment processes because they consume free bacteria and colloidal particles (and therefore aid in effluent clarification). Aerobic attached-growth processes generally possess a much more complex microbial ecology than their activated sludge counterparts, with films containing bacteria, fungi, protozoa, rotifers, and even annelid worms, flatworms, and nematodes, if a longer biomass retention time occurs.

The conversion of organic matter during aerobic oxidation is carried out by mixed bacterial cultures according to the following reaction:

$$\underset{\text{Organic matter}}{x\mathrm{CHONSP}} + y\mathrm{O_2} + \text{nutrients} \rightarrow$$

$$\mathrm{aCO_2} + \mathrm{bNH_3} + \underset{\text{new cells}}{\mathrm{cC_5H_7NO_2}} + \text{other end products} \qquad (11.1)$$

These new cells may be further oxidized during *endogenous respiration* as follows:

$$\mathrm{C_5H_7NO_2} + 5\mathrm{O_2} \rightarrow 5\mathrm{CO_2} + 2\mathrm{H_2O} + \mathrm{NH_3} + \text{energy} \qquad (11.2)$$

a. Aerobic Process Based on Suspended Biomass

The *activated sludge system* is the process traditionally used for secondary treatment (see Figure 11.1). Water from primary treatment enters a long tank equipped with an air-bubbling system. A mixture of

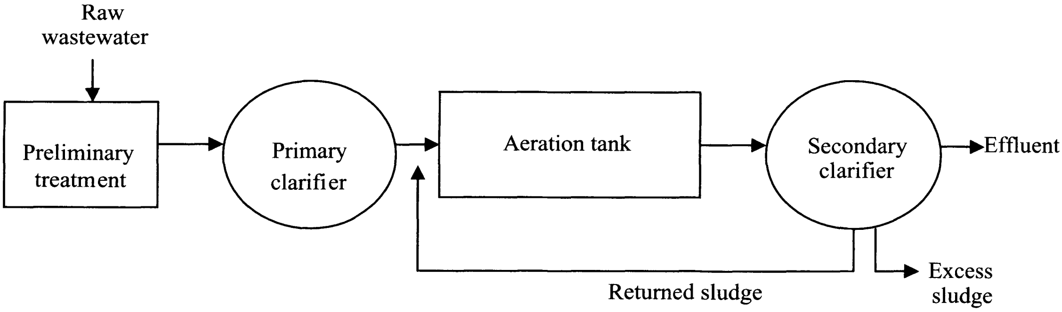


FIGURE 11.1. Conventional activated sludge system.

detritus-feeding organisms is added to the water as it enters the tank, and as it moves through the tank, it is vigorously aerated. Organisms in this well-aerated environment reduce the biomass of organic material (including pathogens) as they feed. As organisms feed on each other they tend to form clumps (*flocs*) that settle readily when the water is stilled. Thus, the water is passed from the aeration tank into a secondary clarifier tank where the organisms settle and the water—with more than 90% of the organic material removed—flows on. The settled organisms are pumped back into the entrance of the aeration tank. They are the activated sludge that is added at the beginning of the process. Surplus amounts of activated sludge occur as populations of growing organisms are removed and added to the raw sludge.

As organisms feed, they convert some organic matter and nutrients into biomass of their own bodies, while another portion is excreted as waste from respiration. Therefore, as food chains proceed toward completion, the amount of biomass may be totally reduced through metabolic processes to carbon dioxide, water, and several mineral nutrients that remain in solution.

With respect to pathogen removal, both the aeration and sedimentation tanks of the activated sludge process affect, to some degree, the removal/inactivation of pathogens and parasites. During the aeration phase, pathogen/parasite survival is influenced by environmental factors (e.g., temperature and sunlight), biological factors (e.g., inactivation by antagonistic microorganisms), and possibly aeration. Floc formation during the aeration phase is also instrumental in removing undesirable microorganisms. During the sedimentation phase, certain organisms (e.g., parasites) undergo sedimentation while floc-entrapped microbial pathogens settle readily in the tank. Compared with other biological treatment processes, activated sludge is relatively efficient in removing pathogenic microorganisms and parasites from incoming primary effluents.

b. Modifications to the Activated Sludge Process

In looking for greater organic material removal and a lower sludge production, specialists have developed several modifications to the conventional activated sludge process. Some of them are indicated in Table 11.2.

c. Aerobic Processes Based on Attached Biofilms

Attached-growth (or fixed-film) systems rely on the ability of microorganisms to attach themselves to inert surfaces. Contaminated water is passed through a bioreactor that houses such media, where the resulting microbial growth attaches and forms a thick film called *biofilm*. The biomass remains in the reactor except for the part that sloughs off the supporting media.

Biofilm reactors comprise trickling filters, rotating biological contractors (RBC) and submerged (downflow and upflow) filters. Support materials include gravels, stones, plastic, sand, and activated carbon particles. Two important factors that influence microbial growth on the support material are wastewater flow rate and the size and geometric configuration of the support. Several rate-limiting phenomena are involved in biofilms. Electron donors and acceptors must diffuse inside the biofilms, whereas reaction products must be transported out of them.

TABLE 11.2. Modifications to the Activated Sludge Process

Process	Characteristics
Extended aeration system (Figure 11.2)	Wastewater entering the aeration tank is not treated by primary settling. The aeration time (about 30 h) is longer than in conventional systems and requires less aeration. The sludge age is greater and can be extended to more than 15 days.
Oxidation ditch (Figure 11.3)	It consists of an aeration oval channel with one or more rotors for wastewater aeration. This channel receives screened wastewater and has a hydraulic retention time of approximately 24 h.
Step aeration	The primary effluent enters the aeration tank through several points, thus improving its distribution into the tank and making more efficient use of dioxygen. This increases the treatment capacity of the system.
Contact stabilization	The mixture flows to a clarifier—following contact of the wastewater with the sludge in a small tank for a short period of time (20–40 min)—and the sludge is returned to a stabilization tank with a retention time of 4–6 h. This system produces less sludge.
Completely-mixed aerated system (Figure 11.4)	A completely mixed system allows a more uniform aeration of wastewater in the aeration tank. This system can sustain shock and toxic loads.
High rate activated sludge	This system is used for the treatment of high strength wastes and is operated at much higher BOD loadings than those in the conventional activated sludge process. There is a shorter hydraulic retention time and shorter aeration periods.
Pure dioxygen aeration	The rate of dioxygen transfer is higher for pure oxygen than for atmospheric oxygen. This results in higher availability of dissolved oxygen, leading to improved treatment and reduced production of sludge.

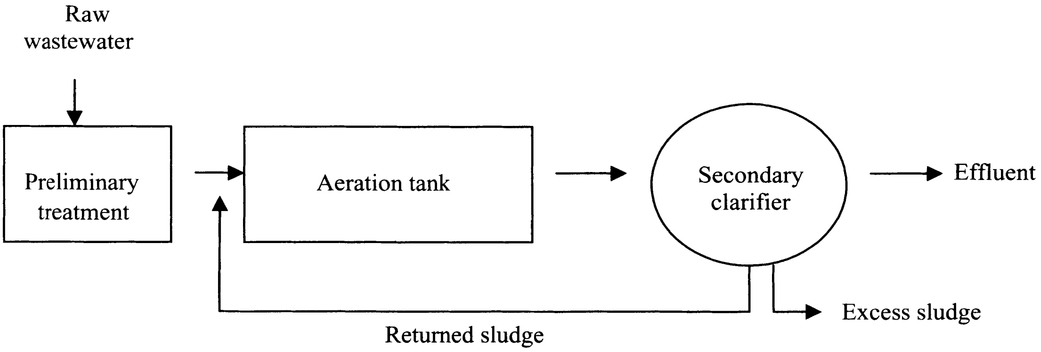


FIGURE 11.2. Extended aeration system.

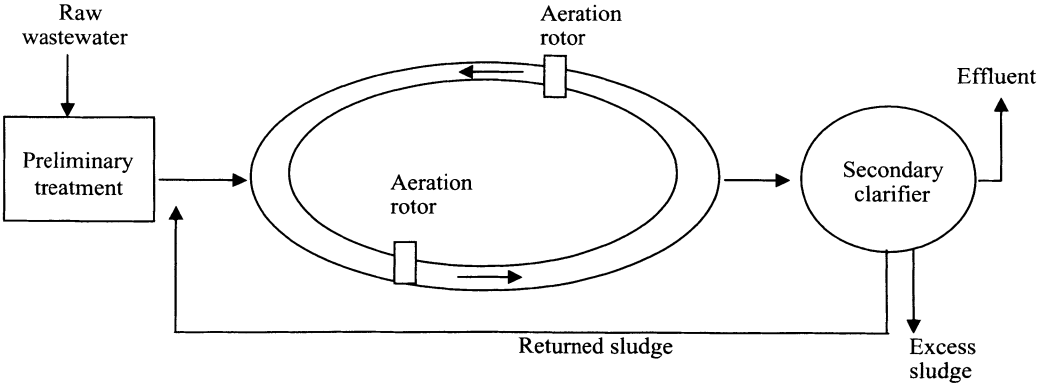


FIGURE 11.3. Oxidation ditch.

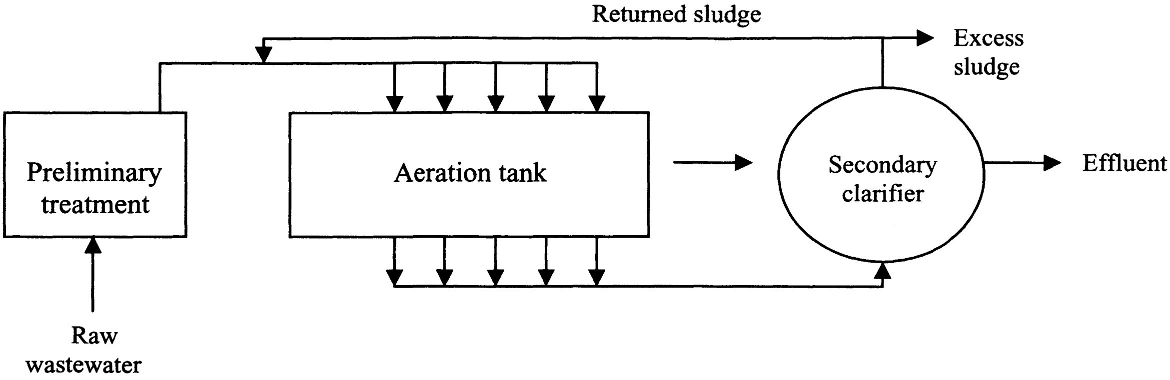


FIGURE 11.4. Completely-mixed aerated system.

Fixed-biofilm processes offer the advantage of high concentrations of biomass in relatively small reactors, as little biomass is lost in the effluent. The result is a long solids retention time (necessary to foster slow-growing microorganisms) and the possibility of degrading hazardous contaminants or wastes with low concentrations of organics.

i. Trickling or percolating filters

In a trickling system, water exiting the primary treatment unit is sprinkled onto—and allowed to percolate through—a bed of stones, ceramic material, treated wood, hard coal, or plastic media with a bed depth of approximately 1.0–2.5 m (see Figure 11.5). The spaces between the filter medium provide a large surface area for microbial biofilm growth and sufficient void space for air diffusion. As in natural streams, the environment supports a complex food web of bacteria, protozoans, rotifers, various small worms, and other detritus feeders attached to the medium. The organic material in the water—including pathogenic organisms—is adsorbed and digested by these organisms as it trickles by. Clumps of organisms that occasionally break free and wash from the trickling filters are removed by passing the water through secondary clarifiers (i.e., tanks that work in the same way as primary clarifiers). Through primary treatment and a trickling-filter system, 85–90% of the total organic material is removed from the wastewater.

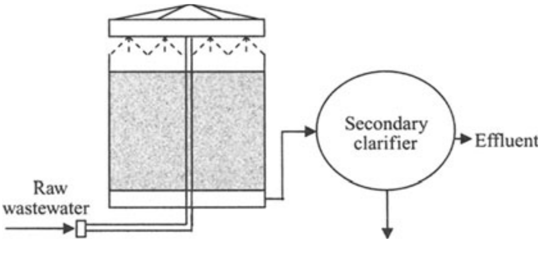


FIGURE 11.5. Trickling filter.

There are several modes in which trickling filters can operate—one is the recirculation mode in which trickling filter effluents are partially re-circulated through the filter media. Changes in the quality and quantity of wastewater can be handled by adjusting the recirculation rate. Recirculation does the following:

- Improves contact between wastewater and the filter material
- Helps dilute toxic wastewater
- Increases dissolved dioxygen for the biodegradation of organics and for tackling odor problems
- Improves distribution of the influent on the filter surface
- Prevents the filter from drying out at night, when the wastewater flow is low
- Avoids ponding

The removal of pathogens and parasites by trickling filters is low and erratic. Removal of bacteria is inconsistent and varies from 20% to 90% depending on the operation of the filter.

ii. Rotating biological contactors

A rotating biological contactor (RBC) is another example of a fixed film bioreactor. An RBC consists of a series of disks mounted on a horizontal shaft that rotate slowly in the wastewater (see Figure 11.6). The disks are submerged approximately 40% into

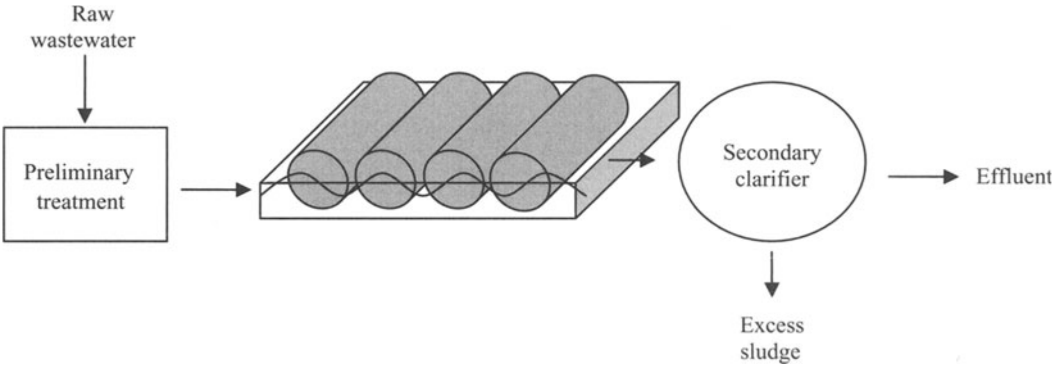


FIGURE 11.6. Rotating biological contactor.

the wastewater. At any time, the submerged portion enhances the contact between the attached biomass and wastewater. The rotations provide aeration as well as the shear force that causes sloughing of the biofilm from the disk surface. The advantages offered by RBCs include:

- Short residence times
- Low operation and maintenance costs
- The production of a readily dewatered sludge that settles rapidly

11.1.3.2 Anaerobic Treatment of Wastewater

Anaerobic digestion is a natural microbiological process in soils, streams, and oceans. The objective of sewage treatment is to confine the natural organisms in a man-made system and to optimize the rates and extents of the natural reactions in such a way that the polluting substances can be destroyed. Three basic steps are involved in anaerobic digestion:

1. Hydrolysis
2. Fermentation or acidogenesis
3. Methanogenesis

The starting point for a particular application depends on the nature of the waste to be processed. See Figure 11.7.

There is growing interest in anaerobic treatment as an energy-efficient approach to waste treatment. Wastewaters treated by anaerobic processes include those from alcohol distillation, brewery, chemical manufacturing, dairy and cheese processing, landfill leachate, pharmaceutical and sugar processing. All of these have a high pollutant concentration. Anaerobic processes have the following advantages:

- Fewer nutrients are required
- Less biological sludge is produced
- Less energy is required
- Methane, a potential energy source, is produced
- Smaller reactor volumes are required

A successful strategy for the treatment of wastewater by anaerobic systems consists in finding means of concentrating the slow-growing microorganisms (see Figure 11.8).

a. Septic Tanks

The septic tank system is the oldest and most widely used anaerobic treatment system. It was introduced at the end of the 19th century and is composed of a tank and an absorption field. The primary function of the tank is the biological digestion of waste organic matter under anaerobic conditions, followed by the separation of solids from the incoming wastewater.

The tank is made of concrete, metal, or fiberglass and is designed to remove wastewater solids so as to avoid clogging of the absorption field. Wastewater undergoes anaerobic digestion, resulting in the production of sludge called *septage* and a floating layer of light solids called *scum*. Septage is disposed of mainly by land application or combined with municipal wastewater sludge. The tank should be inspected regularly and cleaned every 3–5 years to remove accumulated septage. In hot climates, septic tanks provide efficient removal of suspended solids (approximately 80%) and BOD (>90%). Septic tanks typically achieve 65–80% and 70–80%

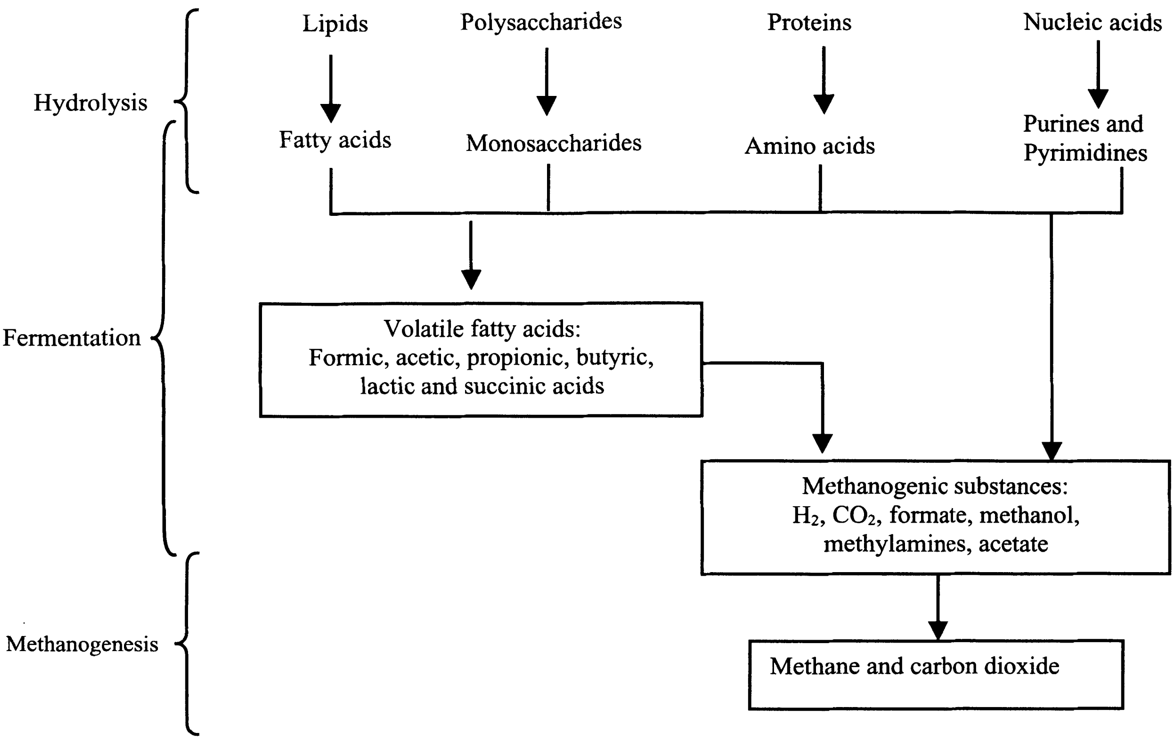


FIGURE 11.7. Metabolic processes in anaerobic oxidation.

removal of BOD and suspended solids, respectively. Anaerobic digestion in the tank provides limited inactivation of pathogens.

Effluents from septic tanks reach the absorption field through a system of perforated pipes surrounded by gravel or crushed stones. The effluent is treated by the soil as it percolates downward to the groundwater. Septic effluents are major contributors to groundwater pollution with pathogenic microorganisms.

b. Upflow Anaerobic Sludge Blanket (UASB)

The UASB digester was introduced at the beginning of the 20th century, and after numerous modifications it was put into commercial use in the Netherlands for the treatment of industrial wastewater generated by the food industry.

The UASB type of digester consists of a bottom layer of packed sludge, a sludge blanket, and an upper liquid layer. Wastewater flows upward through a sludge bed that is covered by a floating blanket of active bacterial flocs. Settler screens separate the sludge flocs from the treated water, and gas is collected at the top of the reactor. The process results in the formation of granular sludge that settles well.

c. Anaerobic Filter

This is the anaerobic equivalent of the trickling filter. It contains support media (rock, gravel, plastic) with a void space of 50% or more. The bulk of anaerobic bacteria grow attached to the filter medium, but some form flocs that become trapped inside this medium. Wastewater upflow through the reactor helps retain suspended solids in the column. This system achieves a modest BOD removal, but a higher removal of solids. Approximately 20% of the BOD is converted to CH_4.

d. Anaerobic Attached Film Expanded-Bed and Fluidized-Bed Reactors

These reactors were introduced in the 1970s. Some features distinguish the expanded beds from the fluidized ones. Bed expansion caused by the upflow of wastewater is much greater in expanded than in

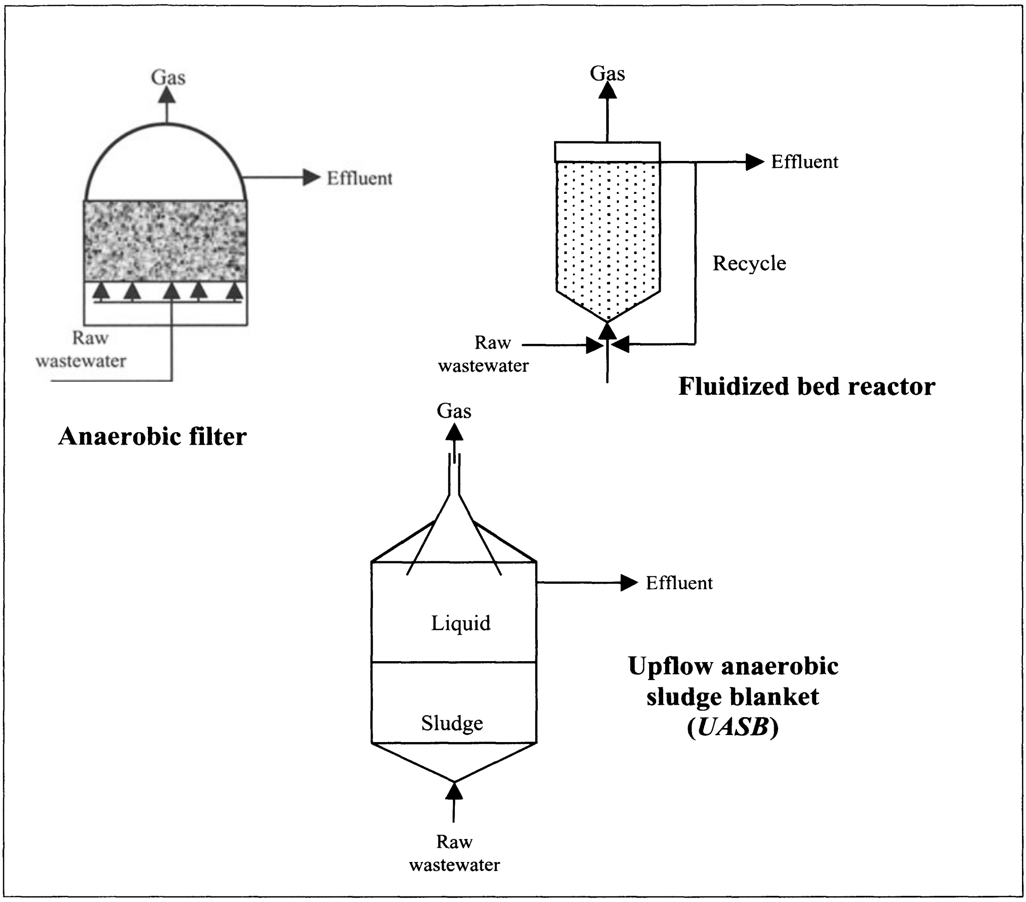


FIGURE 11.8. Anaerobic processes.

fluidized beds. Wastewater flows upwards through a sand bed that provides a surface area for the growth of bacterial biofilms. The flow rate is high enough as to obtain an expanded or fluidized bed. This process is effective for the treatment of low-strength organic substrates and high solid retention times, but its disadvantage is the high energy required for sufficient upflow velocity to achieve bed expansion, and the relatively large volume occupied by the support material.

e. Anaerobic Rotating Biological Contactor

An anaerobic rotating biological contactor is similar to its aerobic counterpart, except that the reactor is sealed to create anoxic conditions. This system allows greater disk submergence because dioxygen transfer is not considered. It has the following advantages:

- Low production of waste solids
- Ability to withstand toxic shock loads
- Methane production

11.1.3.3 Biological Nutrient Removal

Increased knowledge of the problem of cultural eutrophication has led to the modification of secondary activated sludge systems so as to achieve nitrogen and phosphorus removal as well as detritus oxidation, a process known as *biological nutrient removal (BNR).*

Remember that in the natural nitrogen cycle (see Section 7.4.5), bacteria convert nutrient forms of nitrogen (i.e., ammonia and nitrite) back to non-nutritive N_2 in the atmosphere. This process is called *denitrification.* For the biological removal of nitrogen, the activated sludge system is partitioned into zones, and the environment in each zone is

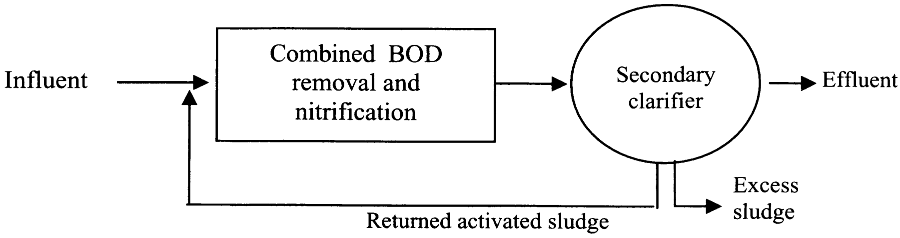


FIGURE 11.9. Single-sludge suspended growth system for nitrification.

controlled in a manner that promotes the nitrifying–denitrifying process.

As an alternative to BNR, various other chemical processes may be used. One simply involves passing the effluent from a standard secondary treatment through a filter of lime, which causes the phosphate to precipitate out as insoluble $Ca_3(PO_4)_2$.

a. Nitrification in Suspended-Growth Reactors

As in BOD removal, nitrification can be accomplished in suspended growth and in attached growth biological processes. For suspended growth processes, a more common approach is to achieve nitrification along with BOD removal in the same *single-sludge process*, which consists of an aeration tank, a clarifier, and a sludge recycle system (see Figure 11.9). This process is characterized by a high organic carbon/nitrogen ratio and a low population of nitrifiers, as most of the oxygen requirement is exerted by heterotrophs.

In cases with a significant potential for toxic and inhibitory substances in wastewater, a *double-sludge suspended growth system* may be considered (see Figure 11.10). This consists of two aeration tanks and two clarifiers in series. The first unit operates at short solids retention times for BOD removal, whereas nitrification occurs in the second unit. Bacteria responsible for nitrification grow much more slowly than heterotrophic bacteria, and therefore systems designed for nitrification generally have a longer hydraulic retention time and a longer sludge age than those systems only designed for BOD removal. *Sludge age* is the time that microorganisms spend in contact with wastewater; nitrification is expected at a sludge age above 4 days.

b. Denitrification Processes

Nitrification must be followed by denitrification to remove nitrogen from wastewater. It implies the reduction of nitrate to nitric oxide, nitrous oxide and nitrogen gas, coupled to the respiratory electron transport chain (because nitrates or nitrites are used as electron acceptors for the oxidation of a variety of organic or inorganic electron donors).

A wide variety of bacteria can effect denitrification. Heterotrophic organisms include *Achromobacter, Acinetobacter, Agrobacterium, Alcaligens, Bacillus*, and *Flavobacterium. Pseudomonas*

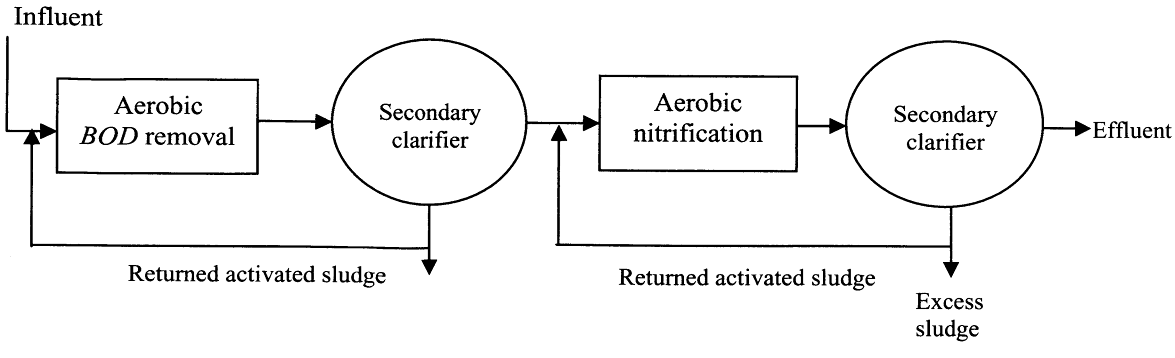


FIGURE 11.10. Double-sludge suspended growth system for nitrification.

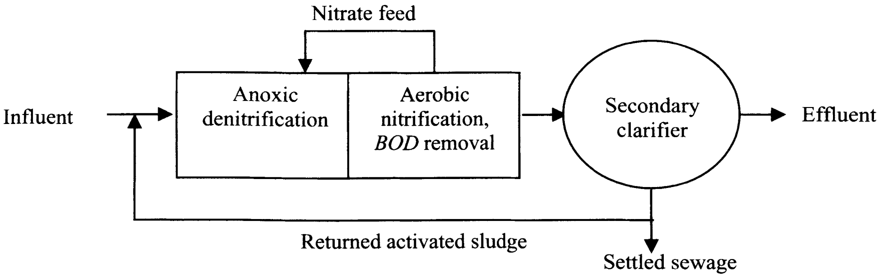


FIGURE 11.11. Single-sludge system for nitrogen removal.

are the most common and widely distributed denitrifiers.

They use an extensive array of organic compounds including hydrogen, methanol, carbohydrates, organic acids, alcohols, and aromatic compounds. Most of these bacteria are facultative aerobic organisms with the ability to use oxygen as well as nitrite or nitrate, although dissolved oxygen can inhibit nitrate reduction.

Autotrophic nitrifying bacteria (e.g., *Nitromonas europea*) can use nitrite to oxidize ammonia with the production of nitrogen gas (when oxygen is absent).

All the biological removal processes include an aerobic zone in which biological nitrification occurs. Anoxic conditions (e.g., deficient in dissolved oxygen, although chemically-bonded oxygen may be present in the form of nitrate or nitrite) must also exist to provide biological denitrification—if a complete total nitrogen removal is required. As nitrate reduction necessitates an electron donor, this can be supplied in the forms of influent wastewater BOD, endogenous respiration, or an external carbon source.

The types of suspended growth biological nitrogen-removal processes can be categorized as single- or double-sludge systems. The term single-sludge implies only one separation device for solids (normally a secondary clarifier). The activated sludge tank may be divided into different zones of anoxic and aerobic conditions, and mixed liquor may be pumped from one zone to another (i.e., internal recycle), but the liquid–solids separation occurs only once. Figure 11.11 shows a diagram of a pre-anoxic process, where nitrate is fed from the aerobic reactor and the return flow contains activated sludge.

In the double-sludge system, which is the most common, an aerobic process (for nitrification) is followed by an anoxic process (for denitrification), each with its own clarifier. This produces two sludges (see Figure 11.12). In the post-anoxic denitrification, an organic substrate—usually methanol—must be added to create a biological demand for the nitrate.

There are several other processes developed for nitrogen removal (e.g., the Bardenpho process) where both pre-anoxic and post-anoxic denitrification are incorporated. As shown in Figure 11.13, this consists of two aerobic and two anoxic tanks followed by a sludge settling tank. Tank 1 is anoxic and is used for denitrification (where wastewater organic matter is used as a carbon source). Tank 2 is an aerobic tank utilized for carbonaceous oxidation as well as nitrification. The mixed liquor from this tank, which contains nitrate, is returned to tank 1. The anoxic tank 3 removes the nitrate remaining in the effluent by denitrification. Finally, tank 4 is an aerobic tank used for stripping the nitrogen gas that results from denitrification, therefore improving the settling of the mixed liquor.

c. Biological Phosphorus Removal

Phosphorus is removed in wastewater treatment plants by chemical means (e.g., phosphorus precipitation with iron or aluminum; see Section 10.1.2) and by microbiological means known as *biological phosphorous removal.* The principal advantages of biological phosphorus removal include reduced chemical costs and a smaller sludge production as compared to chemical precipitation. It is based on the following facts:

1. Several bacteria can store excess amounts of phosphorous as polyphosphates in their cells.
2. Under anaerobic conditions, phosphorous-accumulating organisms assimilate fermentation

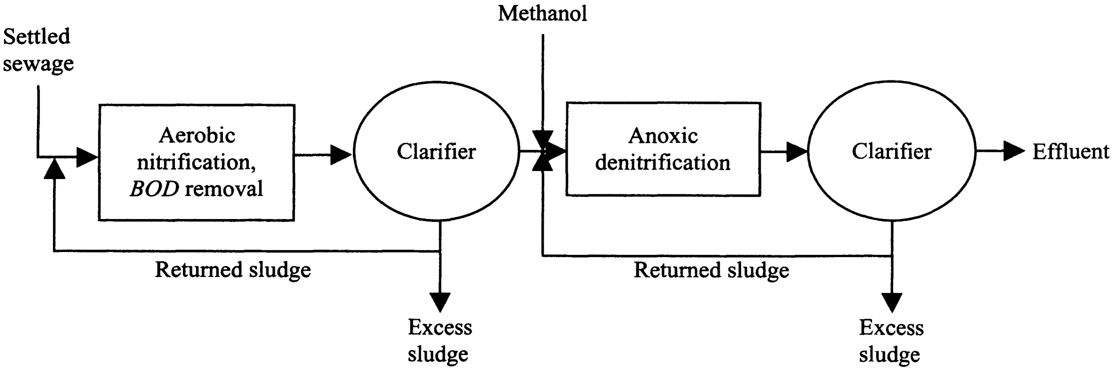


FIGURE 11.12. Double-sludge system for nitrogen removal.

products (e.g., volatile fatty acids) into storage products within the cell (e.g., poly-β-hydroxybutyrate, PHB), with the concomitant release of phosphorous from stored polyphosphate.

3. Energy is produced under aerobic conditions by the oxidation of storage products, and the polyphosphate storage within the cells increases.

Therefore, bacteria take up phosphate from solution and store it in the form of polyphosphate. Phosphate is removed as the excess organisms are separated from the system. These organisms, with the phosphate they contain, are added to and treated with the raw sludge, ultimately producing a treated sludge product richer in nutrients.

All of these processes incorporate aerobic and anaerobic stages, based on phosphorus uptake during the aerobic stage and its subsequent release during the anaerobic stage. Commercial systems can be divided into mainstream and side stream processes. The most popular are described below.

i. Phoredox (A/O)

The *aerobic/oxic process (A/O)* consists of a modified activated sludge system that includes an anaerobic zone upstream of the conventional aeration tank. See Figure 11.14. During the anaerobic phase, inorganic phosphorus is released from the cells as a result of polyphosphate hydrolysis. The energy liberated is used for the uptake of BOD from wastewater. During the aerobic phase, soluble phosphorus is taken up by bacteria, which synthesize polyphosphates, using the energy released from BOD oxidation. The A/O process results in the removal of phosphorus and BOD from effluents and produces a phosphorus-rich sludge.

ii. UCT process

The treatment train in the UCT process includes three tanks (anaerobic, anoxic, aerobic) followed by a final clarifier (see Figure 11.15). This process

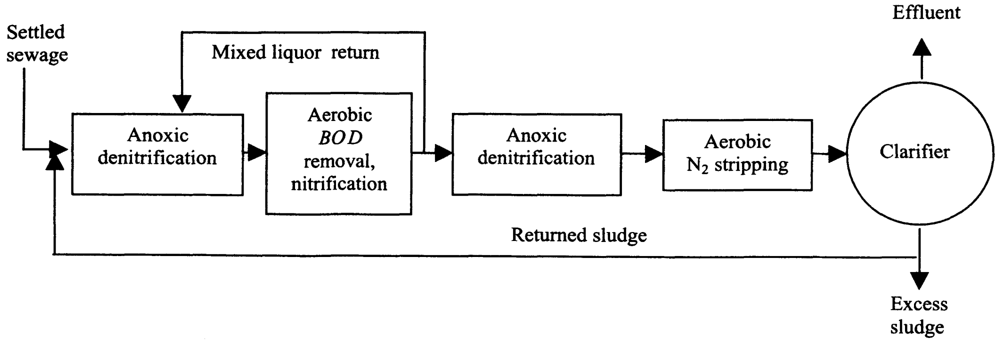


FIGURE 11.13. The Bardenpho process.

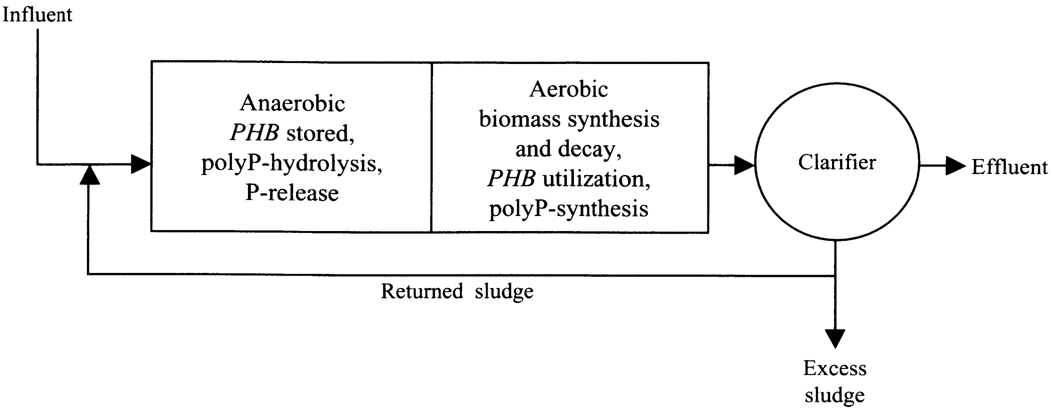


FIGURE 11.14. A/O process for phosphorous removal.

includes denitrification and biological phosphorous removal. The use of the anoxic zone minimizes the amount of nitrate fed into the anaerobic zone. Sludge is not recycled from the final clarifier to the first tank, in order to have strictly anaerobic conditions in the anaerobic tank. The returned activated sludge is directed toward the anoxic zone, and the anoxic mixed liquor is recycled to the anaerobic zone, where the nitrate concentration is minimal.

iii. Modified Baredenpho

The Bardenpho process discussed above can be modified to achieve a combined nitrogen and phosphorous removal. The five-stage system provides anaerobic, anoxic, and aerobic stages for phosphorous, nitrogen, and carbon removal (see Figure 11.16). A second anoxic stage provides additional denitrification using nitrate produced in the aerobic stage as the electron acceptor, and the endogenous organic carbon as the electron acceptor. The final aerobic stage strips residual nitrogen gas from the solution and minimizes the release of phosphorous in the final clarifier. Mixed liquor from the first aerobic zone is recycled into the anoxic zone.

11.1.4 Tertiary Treatment

Tertiary or advanced wastewater treatments are additional treatments needed to remove suspended, colloidal, and dissolved constituents remaining after a conventional secondary treatment. Dissolved constituents may range from relatively simple inorganic ions (e.g., Ca^{2+}, K^+, SO_4^{2-}, NO_3^-, and PO_4^{3-}) to complex synthetic organic compounds, which are removed according to the quality required for the final effluent.

Tertiary treatments may consist of physical processes (e.g., filtration, reverse osmosis,

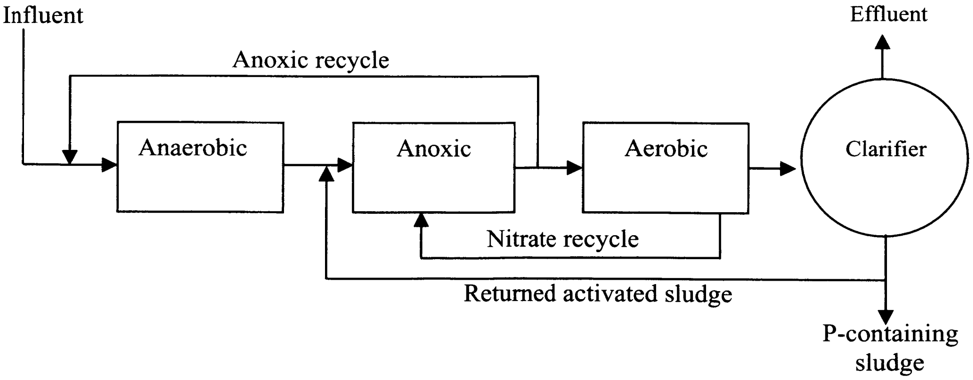


FIGURE 11.15. UCT process for phosphorous and nitrogen removal.

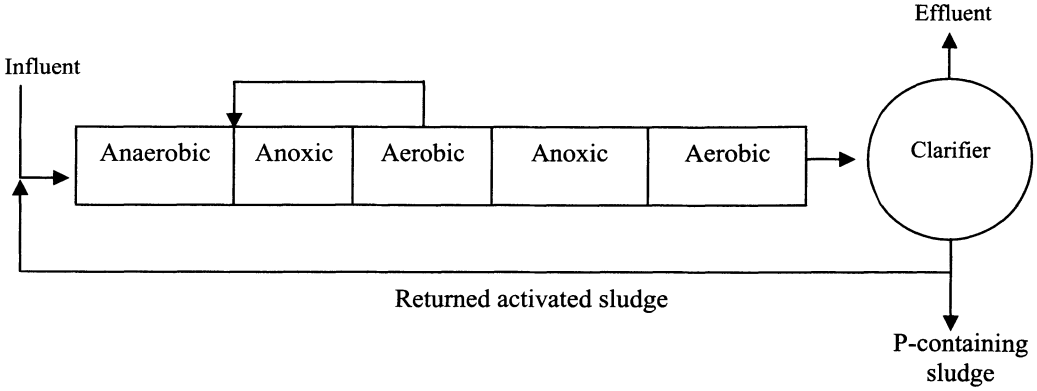


FIGURE 11.16. Modified Bardenpho process for phosphorous and nitrogen removal.

electrodialysis, and carbon adsorption), or chemical processes (e.g., chemical coagulation, disinfection, oxidation, precipitation, and ion exchange).

11.1.5 Chemical and Physical Disinfection

Disinfection is the destruction of pathogenic and other kinds of microorganisms such as viruses, bacteria, and fungi by physical or chemical means.

As discussed in Section 10.1.1, the most widely used disinfecting agent is chlorine gas because it is both effective and relatively inexpensive. It is used to disinfect swimming pools, and is added in small quantities to drinking water to reduce waterborne diseases. However, this treatment also introduces chlorine into natural waterways, and even minute levels of chlorine can harm aquatic organisms. In addition, chlorine reacts with organic compounds to some extent to form simple or complex chlorinated hydrocarbons or trihalomethanes, which tend to be toxic and non-biodegradable. Chlorine dioxide is used as an advanced disinfectant for drinking water. In certain parts of the world, it has largely replaced chlorine because it forms fewer byproducts (see Section 10.1.1.1).

Alternative disinfecting techniques use ozone gas, which is very effective in killing microorganisms. In the process, ozone breaks down into oxygen gas, which improves water quality (see Section 10.1.1.1). Because ozone is unstable, it must be generated at the point of use, a step that demands considerable capital investment and energy.

Another disinfection technique consists in passing the effluent through an array of ultraviolet lights. Ultraviolet radiation kills microorganisms but does not otherwise affect water.

11.2 Sludge Treatment Options

Sludge is mostly composed of solids generated during wastewater treatment processes. The types of sludge that must be treated or disposed of include the following:

- *Grit.* This is a mixture of coarse and dense materials such as sand, bone chips, and glass. They are collected in the grit chamber and are directly disposed of in a landfill.
- *Scum.* It consists of the floatable materials skimmed from the surface of primary and secondary settling tanks. Scum may contain grease, oils, fats, waxes, soaps, hair, paper, cotton, and plastic materials that have specific gravity less than 1.
- *Primary sludge.* This is the sludge generated by the primary treatment that becomes accumulated in the primary clarifier. The potential for the presence of pathogens is significant because it includes material coming directly from toilets; indeed, it is considered as a *biologically hazardous* material. It contains 3–8% solids.
- *Secondary sludge.* It is generated by biological treatment processes. Solids here are mostly organic and their composition ranges from 0.5% to 2% for activated sludge (generated in suspended

aerobic processes) and up to 5% for trickling filter sludge.
- *Tertiary sludge*. This results from the tertiary (i.e., chemical) treatment of wastewater.

Sludge was initially considered only as a material to be disposed of. Therefore, it was put into landfills, incinerated, or even barged to the sea and dumped, all of which create pollution. Only within the last few decades has sewage sludge been converted into organic fertilizer. Even so, the value of sewage sludge as a fertilizer does not balance the costs of its treatment and transportation. The true value must be considered in terms of recreating a sustainable nutrient cycle on the land and protecting waterways from pollution and cultural eutrophication.

The principal methods for sludge processing are used primarily to remove moisture, while digestion, composting, and incineration are used primarily to treat or stabilize the organic material in sludge.

At present, four alternative methods for treating sludge and converting it into organic fertilizer are commonly used: aerobic or anaerobic digestion, composting, pasteurization, and lime stabilization. None of these is capable of removing toxic substances such as heavy metals and non-biodegradable synthetic organic compounds. The presence of such substances can preclude the use of sludge as a fertilizer, and only the incineration of sludge under controlled conditions can destroy the toxic organic substances.

11.2.1 Anaerobic Digestion of Sludge

The raw sludge is put into large air-tight tanks called *sludge digesters*. The biogas thus formed is widely used for heating and as engine fuel. In fact, it is commonly burned to heat the sludge digesters because the bacteria working with the sludge do best when maintained at about 38°C. Also, methane can be cleaned by passing the biogas through a water column. Carbon dioxide is highly soluble in water, whereas methane is not. The resulting nearly pure methane can then be used to supplement natural gas provisions.

After 4–6 weeks, anaerobic digestion is reasonably complete, and what remains is called *treated sludge*. This consists of the remaining organic material, which is now a relatively stable, nutrient-rich, humus-like material in water suspension. Pathogens have been largely, if not entirely, eliminated, and so they no longer pose a significant health hazard.

Such treated sludge makes an excellent organic fertilizer that can be applied directly to lawns and agricultural fields or it can be "dewatered" by means of belt presses. Here, the sludge is passed between rollers that squeeze out most of the water and leave the organic material as a semisolid sludge cake. This cake is easy to stockpile, distribute, and spread on fields with traditional manure spreads.

11.2.2 Composting

Traditional composting consists in putting yard and food wastes in a well-aerated pile and allowing decomposers to reduce waste to a stable, nutrient-rich humus-like material. The same concept is applicable to the treatment of sewage sludge. Raw sludge is mixed with wood chips or other water-absorbing materials to reduce the water content. It is then placed in windows (i.e., long narrow piles that allow air circulation and can be conveniently turned over with machinery). Bacteria and other decomposers break down the organic material into rich, humus-like material. Pathogens lose out in the competition. As long as the piles are kept well aerated the obnoxious odors, typical of anaerobic respiration, are insignificant. After 6–8 weeks of composting, the resulting humus is screened out of the wood chips. The chips may be reused and the humus is ready for application into the soil.

11.2.3 Pasteurization and Drying

Raw sludge may be dewatered and the resulting sludge cake put through drying ovens that operate like oversized laundry dryers, where the sludge is pasteurized (i.e., heated sufficiently so as to kill any pathogens). The products come out as dry, odorless pellets ready to be used as organic fertilizer.

11.2.4 Lime Stabilization

Raw sludge is filter-pressed and the resulting cake is mixed with slaked lime (i.e., calcium oxide). The reaction of lime with moisture increases temperature and pH sufficiently so as to kill pathogens. The entire mixture can be applied as an organic fertilizer, the lime being another fertilizer ingredient and good for neutralizing acidic soils.

11.3 Wastewater Reuse

After wastewater has been treated, it can be reused for:

- Irrigation of agricultural crops
- Landscape irrigation (e.g., schoolyards, golf courses, residential gardens)
- Groundwater recharge
- Recreational use (e.g., lakes and ponds, fisheries, snowmaking, marsh enhancement)
- Non-potable urban use (e.g., fire protection, air conditioning, toilet flushing)
- Potable use
- Industrial use (e.g., cooling, process water)

The main concern in water reuse is to meet the water quality requirements for its intended use. Quality requirements are determined by federal, state, and regional regulatory authorities, and may vary widely from one country to another.

11.4 Biological Treatment of Soil and Groundwater

There is a growing concern over soil and groundwater contamination with hazardous wastes, sometimes caused by effluents from wastewater treatment plants. It has been estimated that groundwater contamination with hazardous chemicals occurs or is suspected in 70–80% of land disposal facilities in the United States. Environmental biotechnologists are working to find ways to reduce environmental contamination by using modern tools in microbiology, molecular ecology, chemistry, and environmental and engineering science. The transformation of xenobiotics by microbial action has already been discussed in Chapter 9. In this section, we concentrate on the biological treatment strategies for soils and aquifers.

The various technologies that rely upon the degradative activities of microorganisms and focus on enhancing natural (although slow) biodegradation processes in soil are encompassed by the term *bioremediation.*

The goal of bioremediation is to degrade organic pollutants to concentrations that are either undetectable or, if detectable, below the limits established as safe or acceptable by regulatory agencies. The list of compounds that may be subject to biological destruction by one or another bioremediation system is long. However, because they are widespread, such compounds represent health or ecological hazards and are susceptible to microbial detoxication. Most interest has been directed to oil and oil products, gasoline and its constituents, polycyclic aromatic hydrocarbons, chlorinated aliphatics such as tetrachloroethylene (TTCE, also called perchloroethylene, PCE), and chlorinated aromatic hydrocarbons. Metals are of interest in bioremediation because they can be altered and rendered less harmful by microorganisms, although they are not biodegraded.

Certain criteria must be met for bioremediation to be seriously considered as a practical means for treatment:

- Microorganisms must exist that have the needed catabolic activity (i.e., capacity to degrade organic matter)
- Those organisms must have the capacity to transform the compound at reasonable rates and bring its concentration to levels that meet regulatory standards
- They must not generate products that are toxic at the concentrations likely to be achieved during the remediation
- The site must not contain concentrations or combinations of chemicals that are markedly inhibitory to the biodegrading species, or means must exist to dilute or otherwise render the inhibitors innocuous
- The target compound(s) must be available to the microorganisms
- Conditions at the site or bioreactor must promote microbial growth or activity (e.g., an adequate supply of inorganic nutrients, sufficient O_2 or some other electron acceptor, favorable moisture content, suitable temperature, and a source of carbon and energy for growth) if the pollutant is to be cometabolized
- The cost of the technology must be lower or, at worst, not higher than that of other technologies which can also destroy the target substance

Failure to meet any one of these criteria has resulted in a rejection of a biodegradative approach or the inability to meet the established cleanup goals.

A variety of different technologies and procedures are currently being used, and a number of new and promising approaches have been suggested or have reached advanced stages of development. Some of these technologies involve *in situ* treatments, in which soil is not removed from the field, or groundwater is not pumped for aboveground treatment. *In situ* bioremediation offers the advantage of having a relatively low cost but the disadvantage of being less subject to rigorous control. Other bioremediation technologies require removal of the contaminated material in some manner from its original location. Such removals increase the costs either moderately or appreciably, but the processes are more subject to control.

11.4.1 *In situ* Bioremediation

Microorganisms in soils have a broad range of catabolic activities, and a simple way of destroying pollutants is to rely on the indigenous microflora. If the pollutant is to be cometabolized, one has to provide an adequate supply of inorganic nutrients, sufficient O_2 or some other electron acceptor, favorable moisture content, a suitable temperature, and a source of carbon and energy for growth. This procedure is often called *biostimulation*. Furthermore, the O_2 demand of the microflora increases with the added organic carbon, and the rate of diffusion of O_2 from the overhead air into the soil is too slow to sustain the aerobic bacteria that are chiefly responsible. The need for supplemental O_2 is satisfied by mixing the soil in some way (e.g., by simple plowing or by more thorough mixing). Another common limiting factor for rapid microbial transformation is moisture. Because surface soil often dries out, arrangements are needed to provide water so as to maintain optimum moisture levels for aerobic organisms.

Remediation by these means is limited to those weather seasons when the soil temperature is in a range that allows reasonably rapid microbial growth and activity. Little or no biodegradation occurs during the cold periods of the year in the temperate zones. Microorganisms are sometimes added to the soil by some form of inoculation in a process called *bioaugmentation*, although such inoculations are not always effective.

The efficacy of land treatment for spills of oil and oil products is confirmed in carefully controlled experiments in the laboratory and in the field. Thus, the hydrocarbons in gasoline, jet fuel, and heating oil are extensively degraded in soils treated with fertilizer, lime, and simulated tilling. This approach reduces the total hydrocarbons by up to 95%, eliminates polycyclic aromatic hydrocarbons, and results in complete detoxification in a few months. Crude oil, crankcase oil, jet fuel, heating oil, and diesel oil disappear faster than in a soil without these treatments.

On the other hand, other hydrocarbon-rich materials (e.g., sediment contaminated with PCP, creosote, and bunker oil) are not readily destroyed by land farming.

In similar *on site* or *off site* technologies, additional engineered controls have been incorporated. These include systems that provide irrigation water and nutrients, a liner at the bottom of the soil, and a means to collect leachate. This is termed a *prepared bed reactor*. These reactors have been used in sites contaminated with polycyclic aromatic hydrocarbons and BTEX (benzene, toluene, ethylbenzene, and xylene). The liner and a system to collect leachate are included because there is concern that a conventional land treatment may result in contamination of the underlying groundwater by the parent compounds or products of microbial transformation that are carried downwards with percolating water. The level of sophistication may vary greatly. In some instances, the leachate is removed and treated in an adjacent bioreactor. Water and nutrients may be dispensed through an overhead spay-irrigation system, and the entire operation may be enclosed in a plastic greenhouse as a precaution in the case that volatile hazardous products were emitted.

Another solid-phase treatment involves the same approach to enhancing microbial activity but relies on a different way of providing O_2. Here, additional air is provided by vacuum extraction of soil above the water table (i.e., the vadose zone or the unsaturated soil layer), thereby supplying the terminal electron acceptor needed by the aerobic bacteria. This process, designed for hydrocarbon-contaminated sites, is termed *bioventing* or simply *venting*.

11.4.2 Treatment of Excavated Soils

11.4.2.1 Composting

In this treatment procedure, the polluted material is mixed in a pile with a solid organic substance that is itself reasonably readily degraded (e.g., fresh straw, wood chips, wood bark, or straw that had been used for livestock bedding). The pile is often supplemented with N, P, and possibly other inorganic nutrients. The material is placed in a simple heap, formed in long rows known as *windrows*, or introduced into a large vessel equipped with some means of mixing and aeration. Moisture must be maintained and aeration provided either by mechanical mixing or by some aeration device. A contained vessel is desirable when the compost contains hazardous chemicals. Heat released onto the solid organic material during microbial growth is not adequately dissipated, and therefore the temperature rises. Higher temperatures (i.e., 50–60°C) are often more favorable for biodegradation than the lower temperatures maintained in some composts. Composting has been used as a means of treating soil contaminated with chlorophenols, TNT, and other explosives. For example, more than 90% of selected explosives present in a contaminated soil can be removed within a few months.

11.4.2.2 Slurry Reactors

Bioremediation can be achieved by a variety of procedures in which contaminated solids are constantly mixed with a liquid in a slurry-phase treatment. The system entails the introduction of the contaminated soil, sludge, or sediment into a lagoon constructed with a liner, or into a sophisticated reactor in which the contaminated materials are mixed. In many ways, the operation resembles the activated sludge procedure that is common for the treatment of municipal wastes, as it allows for the aeration, adequate mixing and control of many of the factors affecting biodegradation. Some designs permit the capture of volatile organic products that may be generated. The level of dissolved O_2, the pH, and the concentration of inorganic nutrients may be monitored and controlled.

Some bioreactors are inoculated with a single species or a mixture of microorganisms capable of functioning effectively under controlled conditions. Control laboratory experiments show that many PAHs, heterocycles, and phenols in creosotes are quickly destroyed. On the other hand, some of the higher-molecular weight PAHs are only slowly destroyed. Anaerobic conditions enhance the degradation of specific compounds, such as dinoseb (a phenolic herbicide).

Addition of microorganisms and enzymes stimulates the biodegradation of xenobiotics in soils. Most efforts have been directed toward the use of bacterial inocula grown in large fermenters for the bioremediation of soils contaminated with PCP. Also, microbial immobilization on bark chips or their encapsulation in polyurethane or alginate, enhances their PCP-degrading ability as well as their resistance to PCP toxicity.

11.4.3 Treatment Strategies for Aquifers

There are three basic approaches to the treatment of contaminated aquifers: physical containment, *in situ* biorestoration, and above-ground treatment.

11.4.3.1 Physical Containment

This involves the use of temporary physical barriers to slow down or halt the movement of contaminants. It has been adopted with some success in many hazardous waste sites.

11.4.3.2 In Situ *Biorestoration*

Contaminated subsurface aquifers can also be treated by relying on the indigenous microflora and introducing nutrients. If necessary, oxygen is added to destroy unwanted molecules. This process is sometimes called *biorestoration*.

A common procedure is to add the nutrients in solution through injection wells into the saturated zone or through infiltration galleries into the unsaturated or surface-soil zone. Water is recovered from production wells, then amended with nutrients, and recirculated. The concentrations of contaminants and nutrients are often measured on a regular basis by taking samples from wells installed between the points of injection and removal. In some instances, water is not recirculated but, instead, is treated at the surface.

Rapid hydrocarbon biodegradation is typically carried out by aerobic bacteria, where their activity must be sustained. This poses major problems because—even under the best conditions—little O_2 is present in groundwater, and at the same time natural sources provide O_2 at exceedingly slow rates. As a result, highly water-soluble H_2O_2 sometimes needs to be added to the nutrient solutions (as it slowly breaks down in the aquifer to give free O_2).

This approach is mostly used for gasoline spills from underground storage tanks when indigenous subsurface bacteria grow on aromatic compounds as their sole carbon and energy sources (e.g., naphthalene, toluene, benzene, ethylbenzene, *p*-cresol, xylene, phenol, and cresol). Groundwater contaminated with diesel and jet fuel is also treated in a similar manner. *In situ* bioremediation of aquifers contaminated with PCP and creosote can be enhanced by injection of H_2O_2 as well as inorganic nutrients (e.g., nitrogen and phosphorus).

Much effort has been concentrated on the fate of chlorinated aliphatic hydrocarbons in aquifers (e.g., trichloroethylene, dichloroethylene). These chemicals undergo reductive dehalogenation under anaerobic conditions. By contrast, these compounds are degraded under aerobic conditions by methane-utilizing bacteria. For example, methanotrophic bacteria can transform more than 50% of trichloroethane into CO_2 and bacterial biomass.

The success of biorestoration depends on the hydrogeology of the site. If the hydrogeology is complex, success is problematic. Adequate procedures to characterize many sites are currently available. Moreover, the subsurface environment must be sufficiently permeable to allow the transport of the added N, P, and O_2 to the microorganisms situated at the various subsurface sites containing the contaminants. This water movement — referred to as *hydraulic conductivity*—is critical for a positive outcome.

As discussed in Chapter 7, some bacteria are able to use nitrate as an electron acceptor, and therefore they grow and degrade a number of substrates in anoxic waters containing nitrates. Nitrate is also attractive because of its high solubility in water and low cost, although caution must be exercised because it may become a pollutant itself if present in drinking water at levels in excess of those established by the corresponding regulatory agencies.

11.4.3.3 Above-Ground Bioreactors (Pump-and-Treat Technology)

The contaminated water is pumped from the aquifer through extraction wells and treated above ground by one of several treatment processes. These may be continuous or in batches (with contaminated material added, and treated material removed intermittently). However, it is difficult to extract chemical contaminants adsorbed onto the aquifer matrix. Because the removal of organic contaminants by this technology is relatively slow, this approach can be regarded as a means for preventing further migration of the contaminant in the aquifer. The major available treatment technologies include:

- Air stripping to remove volatile organic compounds
- Adsorption onto granular activated carbon
- Ultrafiltration
- Oxidation with ozone/UV or ozone/H_2O_2
- Activated sludge
- Fixed-film biological reactors

For example, fixed-film bioreactors (using sand as the biofilm matrix, and methane or natural gas as the primary substrate) can remove up to 60% of trichloroethylene (TCE) from polluted water. They can also remove more than 90% of TCE and trichloroacetic acid (TCA) from vapor streams generated by the air stripping of polluted groundwater.

Mixed microbial cultures can be added to contaminated aquifers to enhance biodegradation. They are obtained by traditional enrichment techniques or by recombinant DNA technology. The added microorganisms must be able to reach the contaminated zone and grow in it. This process consists in the following:

- Contaminated groundwater is treated in above-ground bioreactors in the presence of commercial bacterial cultures
- The treated groundwater is further modified with additional bacteria and re-infiltrated into the contaminated soil for *in situ* treatment of the contaminated soil and aquifer.

11.4.4 Marine Oil Spills

Interest has existed for many years in the cleanup of oil spilled in marine, estuarine, and fresh waters and in the use of microorganisms for freeing the adjacent shorelines of oil.

Early studies showed that hydrocarbon-oxidizing bacteria were widespread, that they were limited by N and P when oil was introduced into the water, and that formulations containing oleophilic fertilizers were particularly beneficial. However, it was not until the tanker Exxon Valdez was grounded on a reef in Prince William Sound, Alaska, that a major bioremediation of oil in surface waters was undertaken. The March 24, 1989 grounding of this tanker released 42 million liters of oil, contaminating both the water and adjacent beaches. As a result, a program was immediately launched to determine, both in the laboratory and in the field, how to promote the biodegradation. The subsequent cleanup represents the largest field bioremediation ever undertaken.

Laboratory investigations conducted shortly after the spill confirmed earlier studies that showed that N and P were limiting, and that almost all of the alkanes in the Alaskan oil and an appreciable amount of the PAHs had been metabolized in 6 weeks with the addition of inorganic salts or an oleophilic fertilizer containing N and P. Field tests confirmed the abundance of hydrocarbon-degrading bacteria. Specific N and P fertilizers were supplemented to the beaches because they would remain associated with the oil. The oleophilic fertilizer was a liquid containing urea in oleic acid as the N source and tri(aureth-4)-phosphate as the P source. Within 2 weeks, differences in the quantities of oil were visually evident between fertilizer-treated and untreated beaches, and subsequent quantitative measurements revealed that 60–70% of the oil had been degraded within 16 months.

The response of microorganisms to N, P, and O_2 and the effectiveness of biodegradation are simple to determine in the laboratory. These are also easy to assess in a bioreactor in which inflow and outflow measurements can be made. The same is not true in an *in situ* bioremediation. The pollutants may disappear from the site as a result of volatilization from the soil or water, or merely by dilution in flowing water. A number of methods can show that biodegradation has occurred or that a deliberate bioremediation has been successful in the field. The issue of confirming the effectiveness of bioremediation was particularly acute at Prince William Sound because of the enormous cost for the cleanup of the large affected area.

Nearly all the successful bioremediations using the techniques described above rely on the action of indigenous microorganisms. Although proprietary concerns in commercial practice usually preclude the release of information on the procedures (and sometimes on the results as well) little information in the peer-reviewed literature suggests that inoculation (or bioaugmentation) is needed for these discussed technologies.

11.5 Biological Treatment of Volatile Compounds

Microorganisms are also used for the destruction of a variety of volatile compounds. In such technologies, the microorganisms are allowed to grow on some solid support, and a stream of a gas containing the unwanted molecules is passed through it. The resulting destruction of contaminants by microbial action is termed *biofiltration*. The trickle-bed reactor, in which bacteria are fixed on a column, may be designed for volatile compounds. Here, the chemical to be degraded (or "scrubbed") is passed through a solution and is dissolved in it. Somewhat similar to biofilters are the *bioscrubbers*. In these devices the gases and O_2 are usually passed first into a unit in which the volatiles dissolve in water; then, the solution is introduced into the system (usually an activated sludge system) in which the organic compounds are degraded by microorganisms dispersed in the aqueous phase. The solid phase of the biofilter may be peat, soil, composted organic matter, sawdust, bark chips, activated carbon, clay particles, or porous glass. These treatment systems are attractive because of their low cost—as compared to physical and chemical methods—and their ability to destroy compounds at low concentrations.

A large number of volatile compounds can be degraded in biofilters, including naphthalene, acetone, volatile S compounds, toluene, benzene, dichloromethane, and vinyl chloride. Particular attention has been given to volatiles with offensive odors, and a number of systems have been designed to remove H_2S, methane thiol, dimethyl disulfide, and dimethyl sulfide. Among the organic pollutants, waste air containing any of the BTEX components can be treated to destroy the aromatic compounds in the vapor phase by passing the air through soil that serves as the biofilter.

Related Experiments in the Companion Book

22. Microorganisms in soil, water, and air
23. Toxicity assay using bacterial growth
24. Wastewater disinfection

Additional Related Experiments/Activities

Dingrando, L.; Tallman, K.; Hainen, N.; Wistrom, C. *Chemistry: Matter and Change (Lab Manual)*; Glencoe Science/McGraw-Hill Ryerson: New York, 2005.

- Organisms that break down oil (Experiment 26.1)

Kelley, C.; Gaither, K. K.; Baca-Spry, A.; Cruickshank, B. J. "Incorporation of Phytoremediation Strategies into the Introductory Chemistry Laboratory," *Chem. Educ.* **2000**, *5(3)*, 140–143.

Van Wyk, J. P. H. "Conversion of Used Paper Materials into Sugars: A Biochemical Process to Limit Environmental Pollution," *Chem. Educ.* **2000**, *5 (6)*, 315–316.

References and Further Reading

Alexander, M. *Biodegradation and Bioremediation*; Academic Press: San Diego, 1994.

Atlas, R. M. "Bioremediation," *Chem. Eng. News* April 3, 1995, pp. 32–42.

Bitton, G. *Wastewater Microbiology*; Wiley-Liss: New York, 1994.

Davis, M. L.; Cornwell, D. A. *Introduction to Environmental Engineering*; McGraw Hill: New York, 1998.

Metcalf & Eddy. *Wastewater Engineering. Treatment and Reuse*; McGraw Hill: New York, 2003.

Nebel, J. B.; Wright, R. T. *Environmental Science. Toward a Sustainable Future*; Prentice Hall: Englewood Cliffs, NJ, 2002.

12

The Minimization and Prevention of Pollution; Green Chemistry

The exact nature of the environmental hazards generated by the release of various synthetic chemicals into the environment is under constant debate. There is little doubt that this debate will continue until science unequivocally resolves the uncertainties in toxicological data (exposure, fate, and transport) and risk analyses.

Industry and society have traditionally dealt with the reduction of these risks focusing on the decrease in exposure. With a fixed hazard and reduced exposure, risk should decrease accordingly. Through the use of well-characterized hazards (i.e., toxicity data) and an awareness of the efficacy of the exposure control method being used, risk can be controlled until it is below some identifiable "acceptable" level, as arbitrarily defined by each society in its laws and regulations.

Risk can be cut down through *pollution prevention* defined as the use of processes, practices, materials, or products that avoid or reduce pollution at the source; when this is not possible, pollution control can be achieved through an environmentally safe treatment. Pollution prevention may include recycling, process changes, environmentally safe control mechanisms, efficient use of resources, and materials substitution.

The U.S. Pollution Prevention Act of 1990 established a national policy to prevent or reduce pollution at its source whenever feasible. It also provided an opportunity to devise creative strategies for the protection of human health and the environment, and to formulate innovative approaches to the challenge of constructing a sustainable planet. In the sections below we will review the new concepts and tools that are relevant for Pollution Prevention.

12.1 Industrial Ecology

Industrial ecology consists in changing an industrial process from an open-loop system in which resource and capital investments move through the system to become waste, to a closed-loop system where wastes become inputs for new processes. Industrial ecology maintains that industrial systems (e.g., a plant, a national, or a global economy) are not to be considered as entities separated from the biosphere, but more accurately as particular cases of an ecosystem. However, such an ecosystem should be based on infrastructural capital (i.e., physical means of production or protection such as tools, clothing, shelter, irrigation systems, dams, roads, boats, ports, and factories) rather than on natural capital (i.e., the mineral, vegetal, and animal formations of the Earth's biosphere when viewed as a means of production). Natural systems do not have wastes—if we want our systems to be sustainable, we should model them after natural systems.

Sustainability is often defined as the use of resources in such a way that the foreseeable needs of future generations are not seriously affected. Industrial ecology provides a systems-based view of how, where, and why environmental improvements can move toward an environmentally sustainable economy.

12.2 Life-Cycle Assessment

This is a powerful tool with which industrial ecology facilitates the understanding and characterization of the range and scope of the environmental impacts at all stages of a product or process. It is a procedure that involves assessing the impacts of a product or material throughout its life cycle—i.e., from raw material extraction or production, through manufacture and use, to disposal or recovery. Life-cycle analysis provides the knowledge as to where the most important problems lie.

12.3 Green Chemistry

Green chemistry, environmentally benign chemical synthesis, alternative synthetic pathways for pollution prevention, or benign-by-design: these phrases all describe essentially the same concept. Green chemistry is the use of chemistry for pollution prevention. Introduced in the early 1990s, green chemistry is an approach for addressing the environmental consequences of products or processes at the *design stage.* It is a new and straightforward method defined as *the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.* These dangers involve the full range of threats to human health and the environment, including toxicity, physical hazards, global climate change, and resource depletion.

The term *chemistry* is used here in its formal definition as relevant to the structure and transformation of all matter, making the applicability extremely broad. Because the consequences of energy generation and use are directly and inextricably linked to the materials used for its generation, capture, storage, and transport, energy concerns are inherently addressed in the above definition.

Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations. The 12 principles of green chemistry, originally developed by Paul Anastas and John Warner, provide a road map for chemists to implement green chemistry (see Table 12.1).

Examples of industry and academia using green chemistry to move toward sustainable manufacturing are well documented and have been lauded through the U.S. Presidential Green Chemistry Challenge Awards. These awards were established in 1995 and are presented annually at the National Academy of Sciences.

TABLE 12.1. The 12 principles of green chemistry

1. Prevent waste.
2. Design safer chemicals and products.
3. Design less hazardous chemical syntheses.
4. Use renewable feedstock.
5. Use catalysts, not stoichiometric reagents.
6. Avoid chemical derivatives.
7. Maximize atom economy.
8. Use safer solvents and reaction conditions.
9. Increase energy efficiency.
10. Design chemicals and products to degrade after use.
11. Analyze processes in real time to prevent pollution.
12. Minimize the potential for accidents.

Source: Anastas and Warner, 2000.

With alternative synthetic design, we look not only at the ultimate molecule but also at the synthetic pathway used to create it. By modifying the synthesis, we can arrive at the same final product yet reduce or eliminate toxic starting materials, byproducts and wastes.

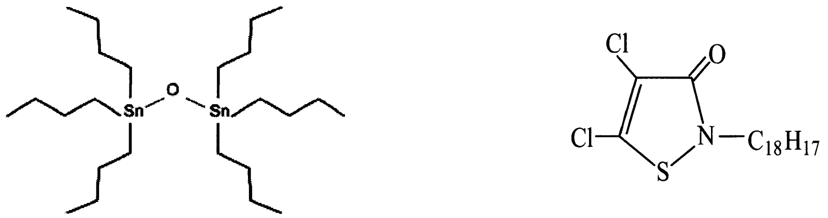
$$\text{Starting materials} \xrightarrow[\substack{\text{reagents,}\\ \text{solvents}}]{\text{energy}} \text{products} + \text{by-products} \tag{12.1}$$

Almost any part of this reaction or process can be changed to produce alternative and improved chemical syntheses by using the principles of green chemistry described below.

12.3.1 Prevent Waste Production

Design chemical syntheses so that there will be no waste to treat or clean up. In other words, it is better to prevent than to treat or clean up waste after it is formed. A cost which has grown considerably over the past few decades is that of the treatment and disposal of chemical substances—the more hazardous the substance, the higher the cost to deal with it. This is generally true whether one is discussing a large chemical manufacturer or a small academic laboratory. Universities and small colleges are meeting the challenge of the cost of waste disposal from chemistry labs, both educational and research ones, by reducing either the number of laboratories or the scale of the experiments.

The only way to minimize or avoid the costs of engineering controls, personal protective gear, regulatory compliance, and the like is to keep from using or generating hazardous substances through the use of green chemistry design techniques.



a) tributyltin oxide (TBTO)

b) 4,5-dichloro-2-N-octyl-4-isothiazolin-3-one (Sea-Nine™)

FIGURE 12.1. Antifouling agents.

One type of common waste (often the most unavoidable) is unconverted starting material. The mere fact that a process generates waste necessitates separation, treatment, and disposal steps.

12.3.2 Design Effective, Non-toxic Products

Design chemical products to be fully effective, yet to have little or no toxicity. This area of green chemistry is often referred to simply as "designing safer chemicals." Knowledge of the molecular structure allows chemists to characterize the toxicity of molecules and design safer chemicals. The goal is to attain a balance between maximizing the desired performance and function of the chemical product, while ensuring that toxicity and hazards are minimized. This can be achieved either by changing a chemical functional group or minimizing the bioavailability. If a substance is toxic yet cannot reach its target organ, then it becomes innocuous. For example, a simple change of polarity can modify the water solubility and the absorbability of a molecule through biological membranes and tissues. Eliminating absorption and bioavailability decreases the risk of intoxication concomitantly.

The case of antifouling agents was an instance where the function was preserved but a new compound was developed (see Cann, 2000). Fouling is the unwanted growth of barnacles, slime, algae, and grasses on a ship's surface, and its occurrence costs the shipping industry approximately US\$3 × 10^9 per year. A significant portion of this expenditure derives from the increased fuel consumption needed to overcome the ensuing hydrodynamic drag. Besides, increased fuel consumption also contributes to pollution, global warming, and acid rain.

The main compounds used worldwide to control fouling are organotins as tributyltin oxide (TBTO; see Figure 12.1a). They are effective at preventing fouling, but they cause widespread environmental problems due to their persistence in the environment and their toxic effects such as acute toxicity, bioaccumulation, decreased reproductive viability, and increased shell thickness in shellfish.

The Rohm and Haas Company developed an environmentally safe alternative to organotins, called Sea-Nine™ (see Figure 12.1b). Extensive environmental testing was done comparing it to TBTO, the current industry standard. Sea-Nine™ degraded very rapidly with a half-life of 1 day in seawater and 1 hour in sediment. TBTO, on the other hand, degraded much more slowly, with a half-life of 9 days in seawater and 6–9 months in sediment. TBTO had a bioaccumulation factor as high as $\times 10^4$, while that of Sea-Nine™ was essentially zero. Both TBTO and Sea-Nine™ were acutely toxic to marine organisms—however, TBTO had widespread chronic toxicity, while Sea-Nine™ showed none. Thus, the *maximum allowable environmental concentration* (*MAEC*) for Sea-Nine™ was set at 0.63 parts per billion (ppb) while that for TBTO was 0.002 ppb. Rohm and Haas thereby obtained the EPA registration for the use of Sea-Nine™, the first new antifoulant registration in over a decade, and won the 1996 Design of Safer Chemicals Award.

12.3.3 Design Good Syntheses

Design syntheses to use and generate substances with little or no toxicity to humans and the environment. Whenever practicable, synthetic

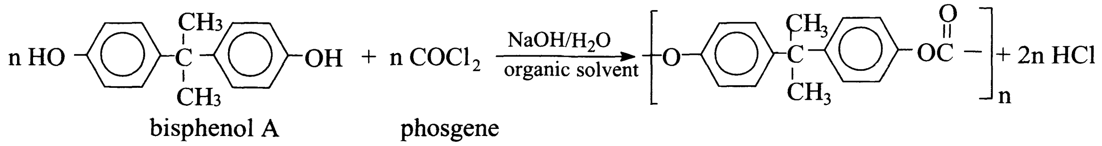


FIGURE 12.2. Synthesis of polycarbonate.

methodologies should be designed to use and generate substances that have little or no toxicity for human health and the environment.

There are only two ways to minimize any risk of harm: minimize the exposure or minimize the hazard. Minimizing the exposure of persons who handle the substances can be done through various means, such as protective clothing, engineering controls, respirators, and the like. However, by designing chemistry that reduces or eliminates the hazard, exposure is no longer a risk.

Green chemistry offers the scientific option to deal with the problems associated with hazardous substances. An example is the alternative synthesis of polycarbonate, a polymer that has been commercially produced by the polycondensation between bisphenol-A and phosgene. The traditional synthesis is shown in Figure 12.2. Because phosgene is highly poisonous, a safer option is to use diphenyl carbonate as a non-toxic carbonylation reagent. See Figure 12.3 (Anastas and Williamson, 1996).

Similarly, dimethyl carbonate (DMC) has been used as a green methylating reagent. See Figure 12.4 (Tundo, 2001). The traditional synthesis of DMC is based on the reaction of phosgene with methanol (see Figure 12.5a). Fortunately, green alternatives such as the catalyzed oxidative carbonylation and carbonyl trans-esterification have been proposed (see Figures 12.5b and c).

12.3.4 Use Alternative Feedstock/ Starting Materials

Use renewable rather than depleting raw materials and feedstock. Renewable feedstocks are often made from agricultural products, or they are wastes from other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.

The selection of a feedstock for the manufacture of a product determines the hazards that will be faced when workers handle the substance, suppliers

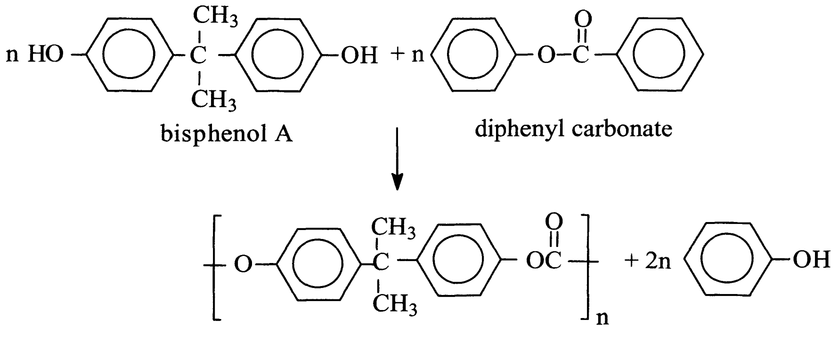


FIGURE 12.3. Green synthesis of polycarbonate.

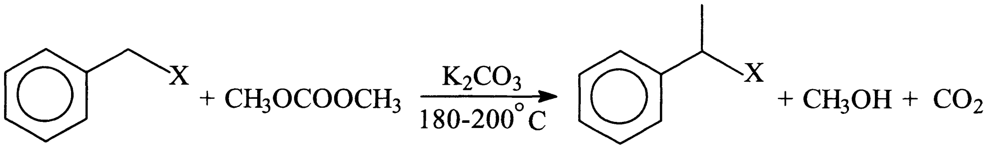


FIGURE 12.4. Dimethyl carbonate as an alkylating agent.

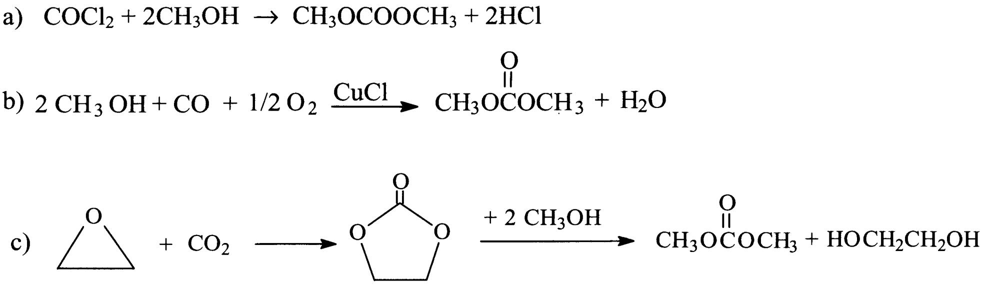


FIGURE 12.5. Synthesis of dimethyl carbonate, DMC. (See Ono, 1996).

manufacture it, and shippers transport it. The use of alternative feedstocks should focus on their innocuous character and their lower potential for generating waste.

Currently, 98% of all organic chemicals synthesized in the United States are made from petroleum feedstock. During conversion to useful organic chemicals, petroleum undergoes oxidation, which has been one of the most environmentally polluting steps in all chemical syntheses. Thus, it is important to reduce the use of petroleum-based products by using alternative feedstocks. In general, agricultural and biological feedstocks can be excellent alternatives. Many of these are already highly oxygenated, which eliminates the polluting oxygenation step. Research has shown that a host of agricultural products (e.g., corn, potatoes, soy, and molasses) can be transformed into consumer products.

The use of renewable feedstocks for creating alternative synthetic routes to chemicals of major industrial importance is exemplified by the biosynthetic method for producing hydroquinone, benzoquinone, catechol, and *cis-cis*-muconic acid from glucose by means of a genetically altered *Escherichia coli* (see Draths and Frost, 1994). Hydroquinone is a very practical intermediate in the manufacture of polymeric materials—almost 2 billion kg of adipic acid are produced from it and used annually in the manufacture of nylon 66. Most commercial syntheses of adipic acid utilize benzene as the starting material, derived from the benzene/toluene/xylene (BTX) fraction of petroleum refining. Benzene is hydrogenated over a metal catalyst to form cyclohexane, which is then oxidized over another catalyst that produces both cyclohexanone and cyclohexanol. See Figure 12.6. These molecules are catalytically oxidized in the presence of nitric acid to form adipic acid.

This adipic acid synthesis poses environmental and health concerns because it has benzene as a starting material. Benzene is a volatile organic compound and its inhalation can lead to leukemia and cancer. This compound, therefore, is often an occupational hazard to those who work with it or come in contact with it. Moreover, benzene is a byproduct of petroleum manufacture; thus, it is produced from a non-renewable source.

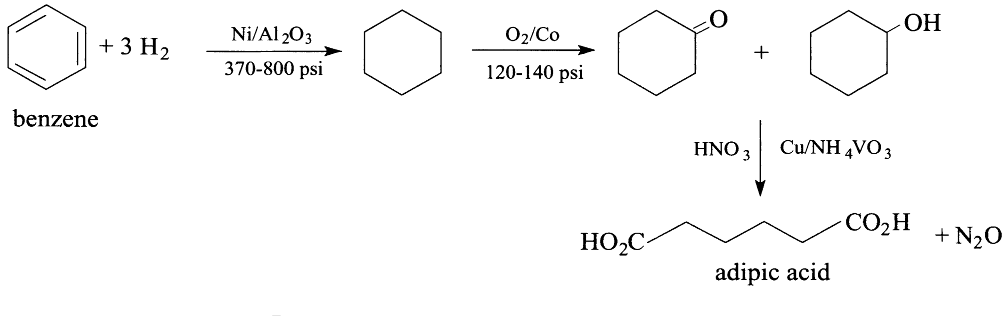


FIGURE 12.6. Industrial synthesis of adipic acid.

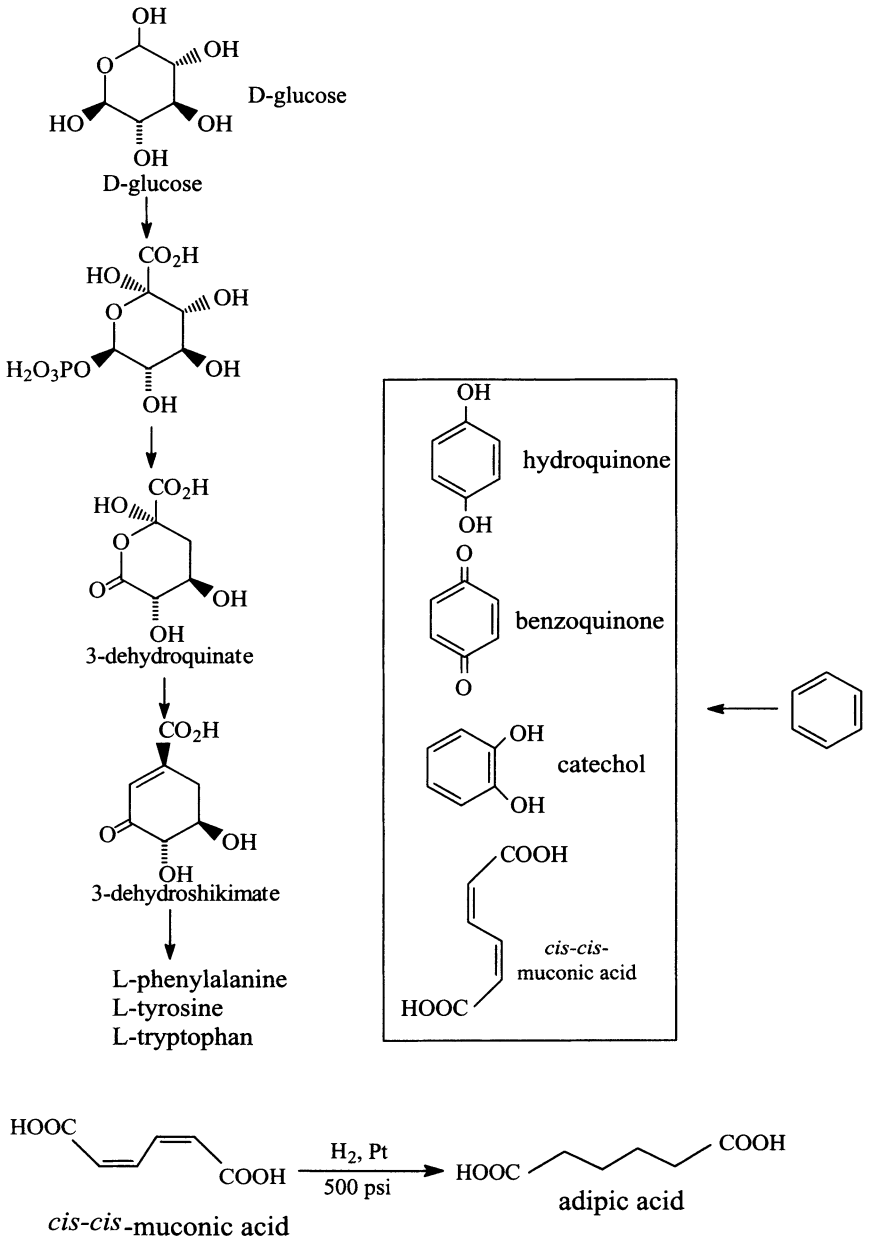


FIGURE 12.7. Draths–Frost synthesis of adipic acid (compare to the benzene-based synthesis).

The last step in the current manufacture of adipic acid involves oxidation by nitric acid, which results in the formation of nitrous oxide (N_2O) that is released into the atmosphere. Given that N_2O has no tropospheric sinks, it can rise to the stratosphere and be a factor in the destruction of the ozone layer. It also acts as a greenhouse gas (see Section 8.4.1). Because of the massive scale on which adipic acid is industrially synthesized, the manufacture of this chemical compound has been estimated to account for 10% of the annual increase in atmospheric nitrous oxide levels.

On the contrary, in the Draths–Frost synthesis of adipic acid (see Figure 12.7) the starting material is glucose, and glucose itself derives from renewable carbohydrate feedstocks such as starch, hemicellulose, and cellulose. In addition, water is used as the primary reaction solvent, thereby avoiding the generation of toxic intermediates and environment-damaging byproducts.

Glucose is transformed into hydroquinone, benzoquinone, catechol and *cis,cis*-muconic acid by means of a genetically engineered microbe expressing a biosynthetic pathway that does not exist in nature. This novel biosynthetic pathway was assembled using recombinant DNA technology. In this process, the segment of DNA responsible for a desired quality is spliced out of one organism and subsequently added into the DNA of another organism, giving the latter the desired quality that was present in the former. In this case, genes from different microbes including *Klebsiella pneumoniae* and *Acinetobacter calcoaceticus* were transferred to *Escherichia coli* to overexpress certain enzymes. The strategy consisted in making the organism direct the largest possible percentage of consumed D-glucose into the common pathway of aromatic amino acid biosynthesis, and then siphoning the flow of carbon away from aromatic amino acids into the synthesis of the desired industrial chemicals. The *cis,cis*-muconic acid accumulates extracellularly and can be hydrogenated so as to supply adipic acid. This process won an academic Presidential Green Chemistry Challenges Award in 1998.

12.3.5 Minimize Waste Using Catalytic Reactions

Catalysts may carry out up to thousands, if not millions, of transformations before they are exhausted, and therefore they are needed in small amounts (see also Section 3.2.5). Using them is preferable to using stoichiometric reagents, as the latter generate one mole of product for every mole of reagent used.

There are a few reactions where reactant A and reactant B form product C, after which all of the atoms contained within A and B then reside in C and no other reagents are needed nor additional products generated. In such rare cases, stoichiometric reactions are as environmentally benign as any other type of reaction, viewed with the criterion of material usage. However, with stoichiometric reactions it is more often the case that:

- One of the starting materials (A or B) is a limiting reagent and consequently, unreacted starting material will be left over even in a reaction with 100% yield.
- One or both of the starting materials are only partially needed for the end-product, and therefore the rest of the molecules go to the waste stream.
- Additional reagents are needed to carry out or facilitate the reaction, and when the reaction is completed those reagents must be discarded in the waste stream.

The role of a catalyst is to facilitate a desired transformation, yet not be consumed as part of the reaction nor be incorporated in the final product. Catalysts afford characteristics associated with green chemistry as indicated below:

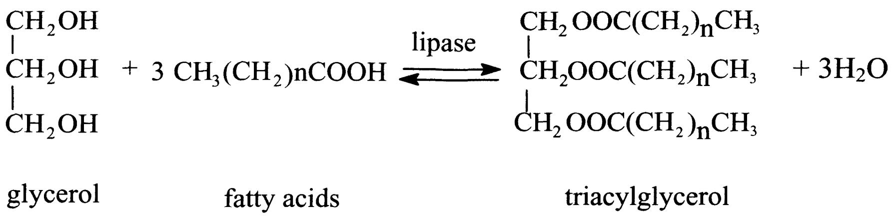
(a) *Enhance selectivity.* The reaction yield, the site of reaction (e.g., C-methylation vs O-methylation) and the stereochemistry (e.g., R vs S enantiomers) may be controlled. Advances in catalytic selectivity allow concurrent benefits for green chemistry because the utilization of the starting materials is enhanced and waste production is minimized.

(b) *Reduce quantities of reagents.* Through the use of new catalysts, chemists have found ways to eliminate the need for large quantities of reagents that would have otherwise been necessary to carry out the transformations, and that would have ultimately contributed to the waste stream (especially the heavy metal-based catalysts).

(c) *Minimize the use of energy.* In addition to benefits in material usage and generation, catalysts lower the activation energy of a reaction pathway, and thus the temperatures that are required to effect the reaction. In large-scale commodity chemical processes, this energy balance issue can be the single most important factor from the viewpoint of environmental and economic impact assessment.

Enzymes as green catalysts

Enzymes are catalysts that occur in all living organisms. They control a wide variety of chemical processes necessary for the maintenance, growth, and reproduction of cells. It has long been known that the role of enzymes in life processes is to modify naturally occurring compounds. More recently



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \\ | \\ CH_2OH \end{array} + 3\,CH_3(CH_2)nCOOH \underset{}{\overset{\text{lipase}}{\rightleftarrows}} \begin{array}{l} CH_2OOC(CH_2)_nCH_3 \\ | \\ CH_2OOC(CH_2)_nCH_3 \\ | \\ CH_2OOC(CH_2)_nCH_3 \end{array} + 3H_2O$$

FIGURE 12.8. The synthesis and hydrolysis of triacylglycerols are catalyzed by lipases.

it has become apparent that enzymes can also carry out highly controlled reactions on non-natural compounds. Moreover, the natural catalysts are often capable of promoting conversions that are impossible to emulate with other techniques of chemistry. Enzyme-catalyzed conversions (i.e., biotransformations) have been used to make highly pure intermediates into new pharmaceuticals—for example, antibiotics, anticancer compounds, and vitamins. Enzymes may be purified before use in biotransformations or they may be used in their native environment (e.g., in whole bacterial cells). Sometimes the enzyme complement of the whole cell is genetically engineered to provide better access to a desired chemical feedstock.

Enzymes are ideal natural catalysts compared to chemical catalysts because they are more environmentally benign than heavy metal catalysts, and they can utilize benign substrates, work under mild reaction conditions, and provide high structural selectivity in products while cutting down byproducts. Other advantages of enzymes are particularly apparent in the synthesis and modification of complex polymers, including those that are chiral, electrochemically active, biodegradable, or biocompatible—features that may be difficult to attain with traditional chemical catalysts.

Lipases are enzymes that hydrolyze ester linkages present in lipids, such as triacylglycerols, in order to obtain glycerol and the corresponding fatty acids. Different types of lipases have been isolated and used for this purpose (see Figure 12.8). The equilibrium in this reaction can be displaced towards products with non-aqueous solvents (e.g., hexane, toluene, and ionic liquids).

These enzymes can be used to make polyesters, polyacrylates, polysaccharides, polyphenols, and other polymers. An example of such an application was acknowledged with the 2003 Academic Green Chemistry Award to Richard A. Gross for a broad range of lipase-catalyzed polyester syntheses (see Ritter, 2003). The reaction shown in Figure 12.9 occurs under mild conditions and high selectivity using the immobilized lipase B, harvested from the bacterium *Candida antarctica.*

The mild reaction conditions required allow the polymerization of chemically and thermally sensitive molecules. The highly versatile polymerizations can simultaneously polymerize lactones, hydroxyacids, cyclic carbonates, cyclic anhydrides,

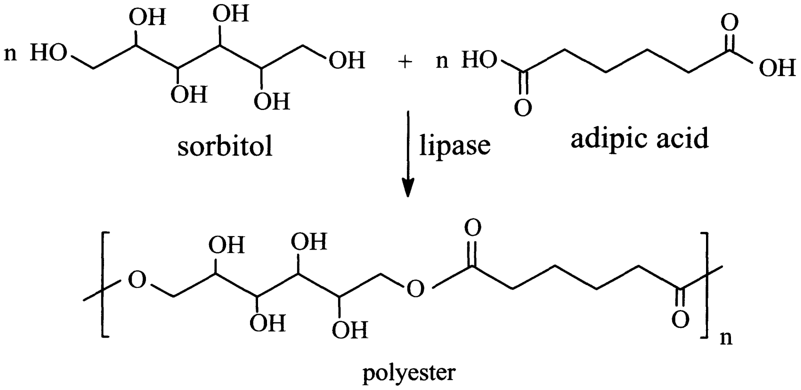


FIGURE 12.9. An enzymatic polymerization reaction (water is also a product).

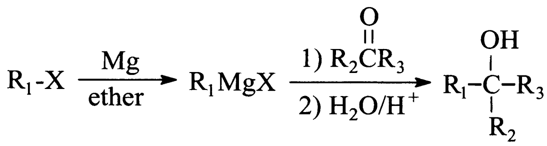
amino alcohols, and hydroxylthiols. The method just described offers simplicity, mild reaction conditions, and the ability to incorporate carbohydrates (e.g., sugars) into polyesters without protection–deprotection steps. Current alternative chemical routes require coupling agents (e.g., carbodiimides) that would be consumed in stoichiometric quantities relative to the reactants.

12.3.6 Avoid Temporary Modifications

Avoid the use of blocking or protecting groups, or any temporary modifications. Unnecessary derivatization (e.g., blocking groups, protection/deprotection, and temporary modification of physical/chemical processes) should be avoided whenever possible.

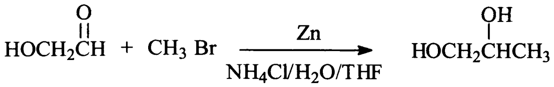
(a) Protecting groups

When it is necessary to achieve a reaction in the presence of a labile functional group, the approach that has been developed often requires generating a molecular modification or a derivative of the substance needed in order to carry out a particular transformation. For example, the Grignard reaction is a method to synthesize alcohols starting with a carbonyl compound. See Figure 12.10.



$$R_1\text{-}X \xrightarrow[\text{ether}]{Mg} R_1MgX \xrightarrow[2)\ H_2O/H^+]{1)\ R_2\overset{O}{\overset{\|}{C}}R_3} R_1\text{-}\underset{R_2}{\overset{OH}{C}}\text{-}R_3$$

FIGURE 12.10. Synthesis of a tertiary alcohol by the Grignard reaction.



$$HOCH_2\overset{O}{\overset{\|}{C}}H + CH_3\,Br \xrightarrow[NH_4Cl/H_2O/THF]{Zn} HOCH_2\overset{OH}{C}HCH_3$$

FIGURE 12.12. The green Barbier–Grignard reaction.

If the molecule contains hydroxyl, amine or other reactive groups, they must be protected, as the intermediate (an alkyl magnesium halide) can be destroyed by such groups. See Figure 12.11.

In the Barbier–Grignard reaction (Figure 12.12), the protection–deprotection sequence can be avoided and the products isolated by simple phase separation (rather than by distillation of an organic solvent). This modification involves the use of zinc instead of magnesium to form the organometallic intermediate (see Li and Chan, 1997).

(b) Salt formation

Properties such as viscosity, dispersability, vapor pressure, polarizability, and water solubility often have to be temporarily modified in order to allow for various processing conditions that a reaction may require. These modifications can be as simple as making a salt derivative so as to facilitate processing. When the functional requirement is completed, the parent compound can be easily regenerated. Obviously, this process uses materials to make the derivative and produces a waste in regenerating the original substance.

(c) Halogen derivatives for selective reactions

In designing a synthetic methodology, a chemist strives for high selectivity in each reaction. When

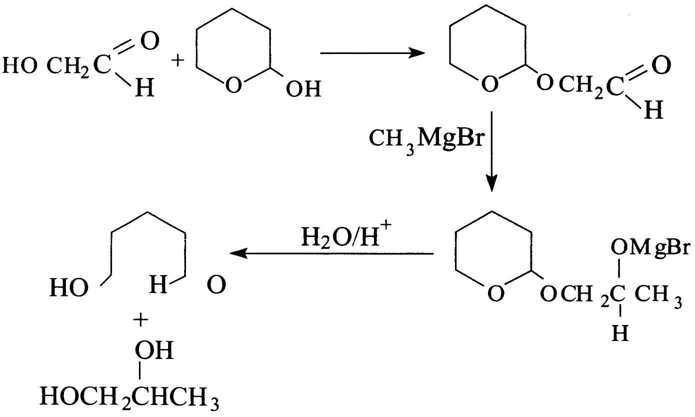


FIGURE 12.11. Protection of a reactive hydroxyl group before a Grignard reaction.

there are several reactive sites in a molecule, it is often wise to direct the reaction to the desired site. This can be accomplished by derivatizing this site in a way that will make it more attractive to the reactive species and that will provide a good leaving group. For example, it is common to use halogen derivatives to carry out nucleophilic substitution reactions. The halogen makes the site more attractive by decreasing its electron density, and the halogen itself serves as a good leaving group. Needless to say, the derivative consumes reagents and ends up as a halogen waste.

12.3.7 Maximize the Use of Starting Materials

Design syntheses so that the final product contains the highest proportion of starting materials. There should be few, if any, wasted atoms. The classic evaluation parameter for the effectiveness and efficiency of a synthesis is the *yield*, which totally ignores the use or generation of any undesirable products that are an intrinsic part of the process. A synthetic pathway, or even a single synthetic step, can (and very often does) achieve a 100% yield, but it concurrently generates waste that is far greater in mass and volume than the desired product. In terms of the *yield criterion*, if a mole of starting material produces a mole of desired product, the yield is 100% and the synthesis is considered completely efficient. This reaction, however, may produce one or more moles of waste for every mole of product.

This discrepancy therefore necessitates the introduction of the concept of *atom economy*. Atom economy is an assessment in which one looks at all the reactants to measure the degree of their incorporation in the product. Thus, if all the reactants are completely incorporated into the product, the synthetic pathway is said to be 100% atom economical because it will not generate waste. The atom economy is calculated with the following equation (see Trost, 1991):

$$\text{Atom economy} = \frac{\text{molecular weight of the product}}{\text{sum of the molecular weights of the reactants}} \times 100 \tag{12.2}$$

The synthesis of ibuprofen will now be used as an example of the determination of atom economy (see Cann, 2000). This synthesis results in rather small amounts of unwanted by-products, thus lessening the need for disposal and remediation of waste products. Ibuprofen is widely used for the relief of headache (including migraine). It is marketed as an analgesic agent for general pain conditions that arise from various injuries. The synthetic route commonly used is shown in Figure 12.13.

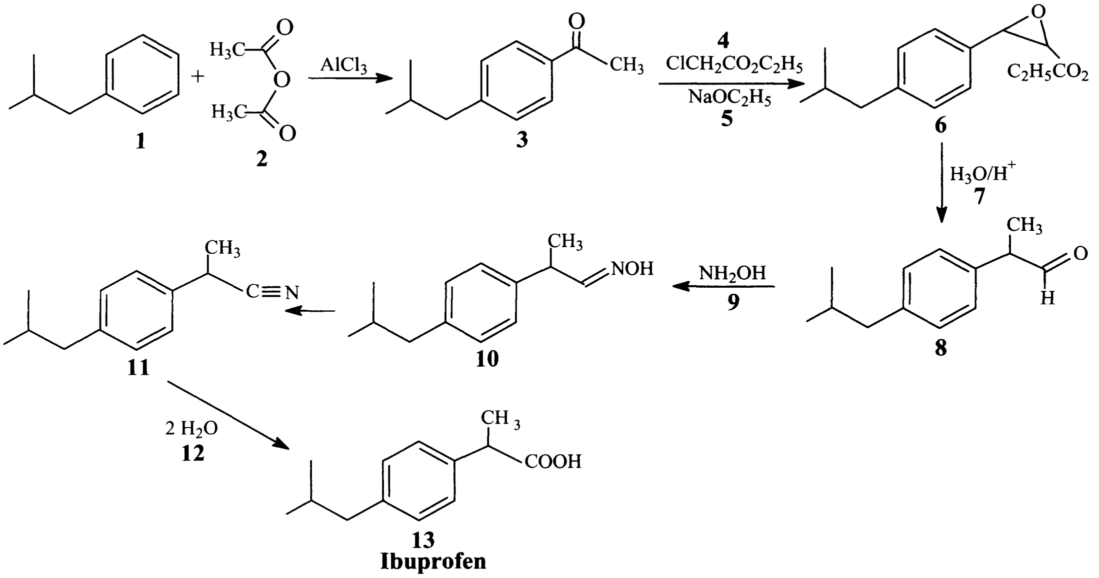


FIGURE 12.13. Conventional synthesis of ibuprofen.

TABLE 12.2. Materials involved in the traditional synthesis of ibuprofen

Formula of reactants	M.W.	Utilized atoms	M.W.	Unutilized atoms	M.W.
1 $C_{10}H_{14}$	134	$C_{10}H_{13}$	133	H	1
2 $C_4H_6O_3$	102	C_2H_3	27	$C_2H_3O_3$	75
4 $C_4H_7ClO_2$	122.5	CH	13	$C_3H_6ClO_2$	109.5
5 C_2H_5ONa	68		0	C_2H_5ONa	68
7 H_3O	19		0	H_3O	19
9 NH_3O	33		0	NH_3O	33
12 H_4O_2	36	HO_2	33	H_3	3
Total		**Ibuprofen**		**Waste products**	
$C_{20}H_{42}NO_{10}ClNa$	*514.5*	$C_{13}H_{18}O_2$	*206*	$C_7H_{24}NO_8ClNa$	*308.5*

In order to determine the atom economy, one may use Table 12.2.

$$\text{Atom economy} = \frac{\text{M.W. ibuprofen}}{\text{M.W. of reactants}} \times 100 = \frac{206}{514.5} \times 100 = 40.0\% \quad (12.3)$$

A green synthesis of ibuprofen was developed by the BHC Company, an accomplishment that was given the 1997 U.S. Alternative Synthetic Pathways Award. The synthesis is shown in Figure 12.14. This figure shows that the number of steps goes from six to only three. The first step in both processes yields the same product **3** via acylation of isobutylbenzene. However, the stoichiometric use of $AlCl_3$ generates its hydrate as a waste product. In contrast, green synthesis uses hydrogen fluoride as a catalyst that is recovered and reused. The Raney nickel and the palladium catalysts in steps **2** and **3** are also recovered and reused. The atom economy of this green synthesis can be calculated by using Table 12.3 and eq. 12.4.

$$\text{Atom economy} = \frac{\text{M.W. ibuprofen}}{\text{M.W. of reactants}} \times 100 = 77.4\% \quad (12.4)$$

The atom economy of a reaction or process does not take into consideration the actual amount of product obtained in a reaction; thus, it does not consider the starting materials left in the reaction mixture that must be separated from the product, or the by-products generated by secondary reactions (see Example 12.1). Several metrics have been proposed to assess the economic and environmental impact of a chemical synthetic pathway (often called

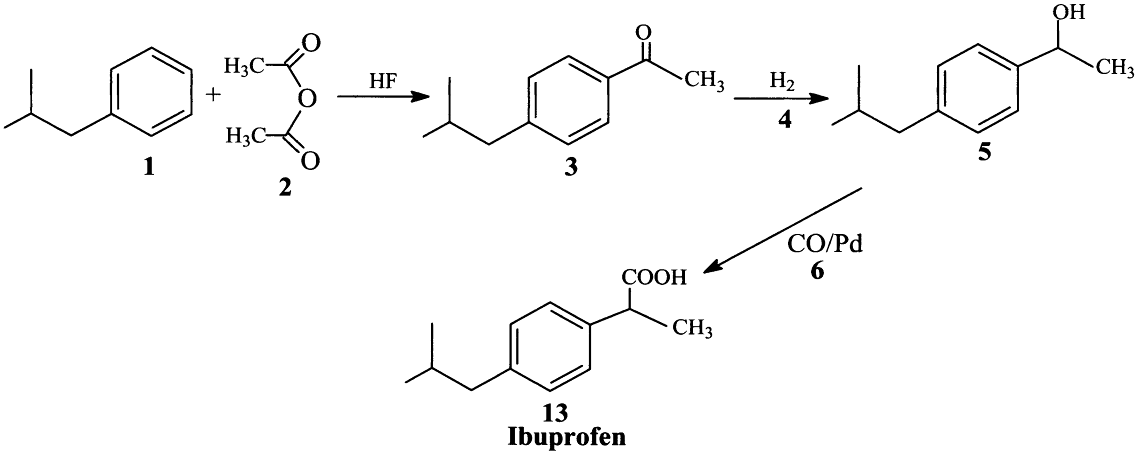


FIGURE 12.14. Green synthesis of ibuprofen.

TABLE 12.3. Materials involved in the green synthesis of ibuprofen

Reactants	M.W.	Utilized atoms	M.W.	Unutilized atoms	M.W.
1 $C_{10}H_{14}$	134	$C_{10}H_{13}$	133	H	1
2 $C_4H_6O_3$	102	C_2H_3O	43	$C_2H_3O_2$	59
4 H_2	2	H_2	2	—	0
6 CO	28	CO	28	—	0
Total		**Ibuprofen**		**Waste products**	
$C_{15}H_{22}O_4$	*266*	$C_{13}H_{18}O_2$	*206*	$C_2H_4O_2$	*60*

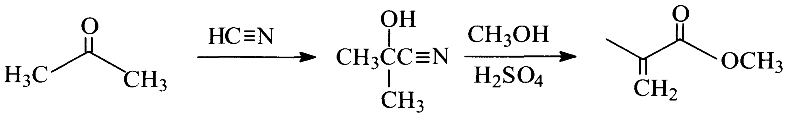
eco-efficiency), some of which are the following (see Curzons et al., 2001):

$$\text{Mass efficiency} = \frac{\text{total mass of the product (kg)}}{\text{total mass of the reagents (kg)}} \tag{12.5}$$

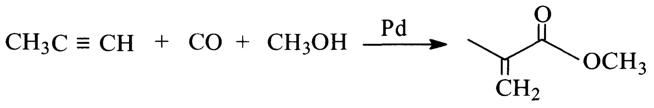
$$\text{Mass intensity} = \frac{\text{total mass of reagents and solvents (kg)}}{\text{total mass of products (kg)}} \tag{12.6}$$

$$\text{Carbon efficiency} = \frac{\text{carbon mass in the product (kg)}}{\text{carbon mass in the reagents (kg)}} \times 100 \tag{12.7}$$

Example 12.1 Poly(methyl methacrylate) is used in the manufacture of resins and plastics. The traditional synthesis of the monomer, methyl methacrylate, uses acetone and hydrogen cyanide as reagents, followed by the acidic hydrolysis and esterification of the nitrile group, as shown below:



A green synthesis is the following (see Sheldon, 1977):



Determine the atom economy of both processes.

Answer

Traditional synthesis:

Reagents and product		M.W.
acetone	C_3H_6O	58
hydrogen cyanide	HCN	27
methanol	CH_4O	32
sulfuric acid	H_2SO_4	98
methyl methacrylate	$C_5H_8O_2$	100

$$\text{Atom economy} = \frac{100}{58 + 27 + 32 + 98} \times 100 = 46.5\%$$

Green synthesis:

Reagents and product		M.W.
propyne	C_3H_4	40
carbon monoxide	CO	28
methanol	CH_4O	32
methyl methacrylate	$C_5H_8O_2$	100

$$\text{Atom economy} = \frac{100}{40 + 28 + 32} \times 100 = 100\%$$

$$\text{Reaction selectivity} = \frac{\text{yield of product}}{\text{amount of substrate converted}} \times 100 \tag{12.8}$$

$$\text{Environmental factor} = \frac{\text{kg of secondary products}}{\text{kg of product}} \tag{12.9}$$

See Examples 12.2 and 12.3.

12.3.8 Minimize the Use of Auxiliary Chemicals

Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, then use innocuous chemicals. In the manufacture, processing, and use of chemicals, auxiliary substances are utilized at every step. An auxiliary substance aids in the manipulation of a chemical or chemicals, but it is not an integral part of the target molecule itself. This is the case of solvents and separation agents. Solvents play many crucial roles in the synthesis of chemical products. Those most evident are as reaction media and as factors in product separation and purification (i.e., solvents for recrystallization, mobile and stationary phases for chromatographic separations, and the like).

Separation processes by and large imply one of the most cost-intensive aspects of a chemical process, and generally have a strong environmental impact due to the type and volume of the separating agents, which are usually discarded as wastes or only partially recycled. There are several solvents that involve few environmental concerns as they are biodegradable and they have little or no toxicity (e.g., water, hexane, acetone, ethyl acetate, ethanol, and methanol).

In contrast, the most common industrial halogenated solvents such as methylene chloride, chloroform, perchloroethylene, and carbon tetrachloride have long been identified as suspected human carcinogens. Benzene and other aromatic hydrocarbons have also been associated with the causation or promotion of cancer in humans and animals. All of these substances are widely used because of their excellent solvent properties in a wide range of applications. Nevertheless, regulations have been issued in the United States, for example (under the Clean Air Act) to control many of these chemicals that are classified as hazardous by the U.S. EPA. Many companies are looking at alternative substances to use as solvents or—in a more fundamental approach—alternatives to make the use of solvents unnecessary.

The strategy best developed to date consists in the use of new types of solvents: *ionic liquids, fluorous phase chemistry, supercritical carbon dioxide*, and *"biosolvents."* Other technologies include the use of water as solvent, and the solventless approach which avoids the use of such substances.

Many of these novel solvent technologies have particular advantages that are as important as their environmental profile. Of particular relevance are the ease of product isolation and catalyst recycling, the cost, and the potential to carry out reactions which are not possible under more conventional conditions. These technologies may all lead to potential commercial benefits that are so important in the industrial sector.

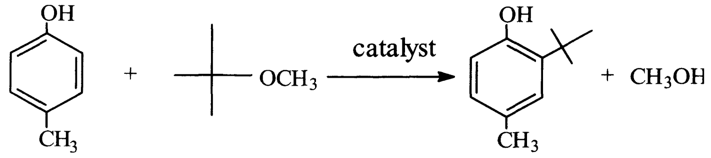
12.3.8.1 Ionic Liquids (ILs)

The term *ionic liquid* usually refers to a salt that exists in the liquid state at or around ambient temperatures. An ionic liquid usually consists of a salt where one or both ions are large and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt, and hence lower its melting point. Ionic liquids have an organic cation (often a nitrogen heterocycle) and an inorganic anion.

Ionic liquids (ILs) tend to have good thermal stability, they exhibit liquid ranges of up to 300°C, and because they have negligible vapor pressure, they do not evaporate—all of which explains their use as replacements for volatile organic compounds. This also makes them very easy to contain and transfer, and allows their use under high vacuum conditions. Another quite important aspect is that ILs can be recycled (often with associated catalysts dissolved in them): this considerably minimizes waste production in accordance with green chemistry, and it lessens expenditure in view of the high cost of many ILs compared with that of conventional solvents.

The imidazolium salts are the ILs most studied to date, particularly dialkyl imidazolium salts with several anionic species such as hexafluorophosphate,

Example 12.2 Determination of the "greenness" of a reaction: The alkylation of *p*-cresol using a heterogeneous acid catalyst.



In a particular experiment, *p*-cresol (23.54 g, 0.22 mol), methyl-*t*-butyl ether (19.36 g, 0.22 mol) and a silica/zirconia catalyst (3.5 wt%) were heated at 100°C for 3 hours. After cooling, 13.0 g of the product, 2-*t*-butyl-*p*-cresol was obtained, and 10.78 g of *p*-cresol was left unreacted. The FW of the product = 164 g/mol. Calculate the atom economy, yield, selectivity, carbon efficiency, and environmental factor.

Answer

$$\text{Atom economy} = \frac{164}{107+88} \times 100 = 84.1\%$$

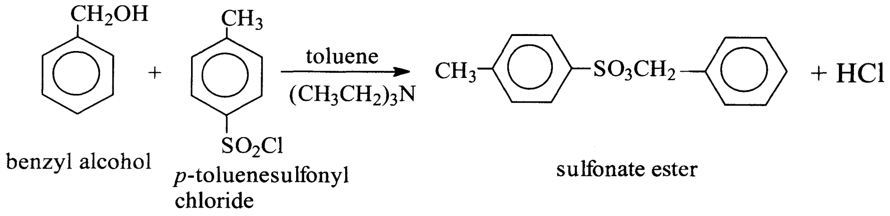
$$\text{Yield} = \frac{13\,\text{g}/(164\,\text{g/mol})}{0.22\,\text{mol}} \times 100 = 36.03\%$$

$$\text{Selectivity} = \frac{36.03\%}{23.54\text{g} - 10.78\text{g}} = 2.82\%/\text{g}$$

$$\text{Carbon efficiency} = \frac{12(11) \times 100}{12(7) + 12(5)} = \frac{0.132\,\text{kg}}{0.144\,\text{kg}} \times 100 = 91.7\%$$

$$\text{Environmental factor} = \frac{10.78\,\text{g}}{13\,\text{g}} = 0.83$$

Example 12.3 The reaction of benzyl alcohol (10.81 g, 0.10 mol, FW 108.1 g/mol) with *p*-toluenesulfonyl chloride (21.9 g, 0.114 mol, FW = 190.65) in toluene (500 g) and triethylamine (15 g, FW = 101) produces the ester benzyl *p*-methylbenzenesulfonate (FW = 262.29), isolated in 90% yield (0.09 mol, 23.6 g) and hydrochloric acid (3.28 g, FW 36.45).



Calculate the mass intensity, the mass efficiency, and the atom economy.

Answer

$$\text{Mass intensity} = \frac{10.81 + 21.9 + 500 + 15}{23.6 + 3.28} = 20.37\text{g/g}$$

$$\text{Mass efficiency} = \frac{0.0236}{0.0108 + 0.0219} = 0.721\,\text{kg/kg}$$

$$\text{Atom economy} = \frac{262.29}{108.1 + 190.65 + 101} \times 100 = 65.8\%$$

1-butyl-3-methyl imidazolium
hexafluorophosphate
$[bmim][PF_6]$
m.p. 10°C

1-ethyl-3-methyl imidazolium
tetrafluoroborate
$[emim][BF_4]$
m.p. -81°C

1-butyl-3-methyl pyridinium chloride
[bmpy][Cl]
m.p. 41°C

1,3-dimethyl imidazolium
methylsulfate
m.p. -50°C

FIGURE 12.15. Structure of some ionic liquids.

tetrafluoroborate, bromine, nitrate, perchlorate, methylsulfate, and the like. See Figure 12.15.

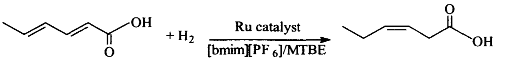
A number of ILs are hydrophobic, yet they readily dissolve many organic molecules—with the exception of alkanes and alkylated aromatic compounds (e.g., toluene). Among such ILs we find $[bmim][PF_6]$, which forms triphasic mixtures with alkanes and water. This multiphasic behavior has decisive implications for clean synthesis. For example, transition-metal catalysts can be exclusively dissolved in the ionic liquid, thus allowing products and by-products to be separated from the ionic liquid by solvent extraction with either water or an organic solvent. This is advantageous when using expensive metal catalysts, as it enables both the ionic liquid and the catalyst to be recycled and reused. Alternatively, some volatile products can be separated from the IL by distillation, as it has negligible vapor pressure.

Extraction may also be performed with supercritical solvents. Ionic liquids have been described as designer solvents: that is, their properties can be adjusted to suit the requirements of a particular process. Properties such as melting point, viscosity, density, and hydrophobicity can be modified by simple changes in the structure of the ions (Table 12.4). For example, the melting points of 1-alkyl-3-methylimidazolium tetrafluoroborates and hexafluorophosphates are a function of the length of the alkyl groups, and form liquid crystalline phases for alkyl lengths greater than 12 carbon atoms.

Some of the organic reactions performed in ILs are: hydroformylation, hydrogenation, isomerization, oligomerization, polymerization, C–C bonding, and acid-catalyzed Friedel-Crafts reactions.

Examples of reactions developed in ILs

- The ruthenium-catalyzed hydrogenation of sorbic acid to *cis*-hexenoic acid is achieved in a biphasic $[bmim][PF_6]$-methyl-*tert*-butyl ether (MTBE) system (see Steines, 2000):



(12.10)

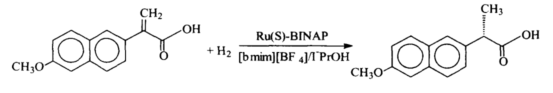
- Enantioselective hydrogenation in ILs is of particular interest as it could provide a means for uncomplicated recycling of metal complexes formed with expensive chiral ligands. An example is the extension of this ruthenium-catalyzed

TABLE 12.4. Physical properties of some ionic liquids

	Water content, ppm	Melting point, °C	Thermal decomposition, °C	Viscosity, cP	Density, g/mL
$[C_2mim][PF_6]$	miscible	60	375		
$[C_3mim][PF_6]$		38	335		
$[C_4mim][PF_6]$	11700	10	349	450	1.36
$[C_6mim][PF_6]$	8837	−61	417	585	1.29
$[C_8mim][PF_6]$	6666	−75	376	682	1.22
$[C_2mim][BF_4]$	miscible	13	412	43	1.34
$[C_3mim][BF_4]$		−17	435	103	1.24
$[C_4mim][BF_4]$	miscible	−81	403	154	1.12
$[C_6mim][BF_4]$				314	1.14

Source: Huddleston, 2001.

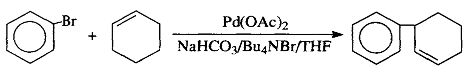
hydrogenation using the chiral ligand (S)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (abbreviated as BINAP), which forms a complex with $RuCl_2$. The anti-inflammatory drug (S)-naproxen is obtained with 80% enantioselective purity using $[bmim][BF_4]$ and isopropyl alcohol as solvents:



(12.11)

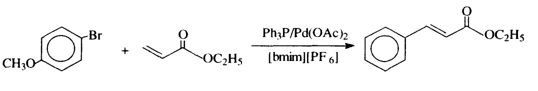
The product can be quantitatively separated, and the ionic liquid catalyst solution that is recovered can be recycled several times without any significant change in activity or selectivity (see Monteiro, 1977).

- Oxidative addition to Pd (0) is the oxidation of choice used in several methods to form C–C bonds. Aryl and alkenyl halides react with alkenes in the presence of catalytic amounts of Pd and substitute the halide with the alkenyl group. This is called the *Heck reaction* (see Welton, 1999):



(12.12)

Heck's reaction can result in regioisomers, depending on whether the reaction proceeds at the α or β carbons in the alkene. A selectivity > 99% to the α-arylation product was achieved in the Heck coupling of 1-bromonaphthalene to butyl vinyl ether in $[bmim][BF_4]$. In contrast, the same reaction in toluene, acetonitrile, DMF, or DMSO afforded mixtures of the α and β regioisomers. Other 4-substituted bromobenzenes give α/β regioselectivities >99% (see Carmichael, 1999).



(12.13)

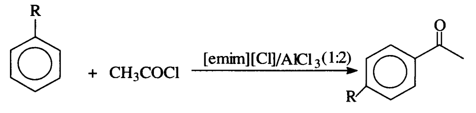
- Ionic liquids containing chloroaluminate anions are strong Lewis acids. This characteristic, coupled with the fact that they are relatively easy to handle, makes them attractive alternatives to standard Lewis and Bronsted acids such as HF. The IL can function both as a catalyst and a solvent for acid-catalyzed processes. Some of the first reactions studied in ILs were Friedel–Crafts alkylations and arylations. The $[emim][Al_2Cl_7]$ affords complete conversion of benzene and acetyl chloride to acetophenone in less than 5 minutes at room temperature.
- The Friedel–Crafts alkylation of benzene with long chain olefins is used industrially worldwide for the annual manufacture of more than two million tons of linear alkylbenzenes. The products are precursors of the corresponding alkylbenzene sulfonates that are widely used as surfactants. Traditionally, the reaction has been performed using liquid HF or $AlCl_3$ as the catalyst. The production of linear alkylbenzenes using chloroaluminate ILs promises enormous benefits with regard to reduced catalyst consumption, ease of product separation, and elimination of the caustic quenching associated with catalyst leaching.
- The Friedel-Crafts acylation of toluene, chlorotoluene, and anisole with acetyl chloride in [emim] $[Cl]/AlCl_3$ gives excellent regioselectivities to the

TABLE 12.5. Various enzymes used with ILs as solvents

Biocatalyst	Ionic liquid	Reaction
alkaline phosphatase	$[H_3NEt][NO_3]$	hydrolysis of phosphate
α-chymotrypsin	$[emim][[PF_6]$	*trans*-esterification
thermolysine	$[bmim][PF_6]$	synthesis of Z-aspartame
formate dehydrogenase	$[mmim][CH_3SO_4]$	redox
lipases	$[bmim][BF_4]$, $[bmim][PF_6]$, other ILs	esterifications, *trans*-esterifications, kinetic resolution of secondary and allylic alcohols

Source: Krag, 2002.

para isomer (see Sheldon, 2001):



(12.14)

where R = MeO, Me, or Cl; yields = 97–99%.

- The application of ILs is most surprising and intriguing in the area of biotransformations. Many enzymes are catalytically active in ILs or in aqueous biphasic ionic liquid systems. Lipases maintain their activity in anhydrous IL media, and their enantioselectivity and operational stability are often better than in traditional media. See Table 12.5.

In spite of their promising future, ILs have characteristics that may not be very kind to the environment, especially when they have to be discarded. This aspect should be carefully considered. One should seek to combine the cationic and anionic elements that are adequate for the process yet will represent the minimum environmental impact.

12.3.8.2 Fluorous Compounds and Solvents

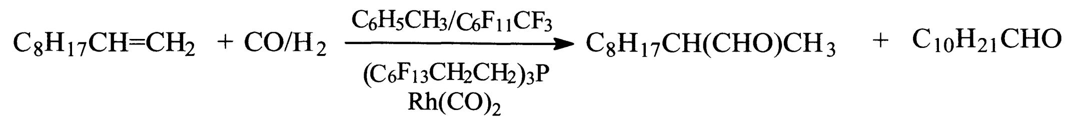
Fluorous compounds and solvents have emerged as powerful tools in modern synthetic organic chemistry. The concept of *fluorous biphasic system* and *fluorous biphasic catalysis* is based on catalysis through the use of reagents that have perfluorinated carbon chains.

Fluorous molecules typically have two domains: the organic domain that resembles a standard organic parent molecule and dictates its reactivity, and the fluorous domain, which is a highly fluorinated group that controls the separation features of the molecule. Fluorous domains are often perfluoroalkyl groups. For example, the so-called FC-72 is a solvent mixture consisting mostly of perfluorohexanes, and it boils at 56°C. The FC-72 mixture and related solvents (perfluorohexane, perfluoroheptane, perfluorodecalin) show some unique properties which render them attractive alternatives to conventional organic solvents: they are outstandingly inert against chemical treatment, predominantly those of the non-polar type, and they have high thermal stability which allows for reactions under relatively drastic conditions. Because they are immiscible in water and in most common organic solvents, they represent a third liquid phase—the *fluorous phase.* Individual components of reaction mixtures, which bear perfluoroalkyl substituents of sufficient size and number, can be selectively extracted into the fluorous phase. This is the base of the so-called *fluorous synthesis.*

Fluorous biphasic catalysis exploits not only this principle, but also the ability of certain perfluorocarbon/hydrocarbon biphasic mixtures to form a homogenous solution at high temperatures. An extremely fluorinated catalyst can thus be applied under homogeneous conditions and recovered from the fluorous phase subsequent to a phase separation step at lower temperatures.

Fluorous biphasic catalysis was first reported with the hydroformylation reaction depicted in Figure 12.16 (Curran and Lee, 2001).

To effect the reaction, one heats a biphasic mixture of an alkene, toluene (the organic solvent), a fluorous phosphine, a standard Rh salt, perfluoromethylcyclohexane (the fluorous solvent), CO, and H_2. When the hydroformylation is complete, the mixture is cooled so as to induce the phases to separate. After cooling, the toluene phase containing the organic products is separated from the fluorous



$$C_8H_{17}CH{=}CH_2 + CO/H_2 \xrightarrow[\substack{(C_6F_{13}CH_2CH_2)_3P \\ Rh(CO)_2}]{C_6H_5CH_3/C_6F_{11}CF_3} C_8H_{17}CH(CHO)CH_3 + C_{10}H_{21}CHO$$

FIGURE 12.16. Fluorous hydroformylation reaction.

phase containing the catalyst. This fluorous phase can then be reused to catalyze another reaction. Therefore, the technique can in effect be considered as a liquid-phase catalyst immobilization method. A number of these useful reactions utilize organic/fluorous solvent pairings that are miscible at higher temperatures but which separate upon cooling.

Another example is the *trans*-esterification reaction shown in Figure 12.17, performed at 150°C with equimolar amounts of the alcohol and the ester, which gives a 99% yield.

This reaction uses a fluorinated tetraalkyldistannoxane catalyst in perfluorohexanes. Here, the catalyst and solvent form one layer, while the ester and alcohol reactants form a separate organic layer. On heating, the two layers are sufficiently miscible for the reaction to occur; on cooling, the organic and fluorinated layers separate. The pure ester is recovered by evaporation of the ethanol co-product. The catalyst can be recovered from the perfluorocarbon solvent.

The variety of separation processes offered by fluorous chemistry will undoubtedly continue to have an impact on new synthetic methods requiring efficient separation procedures. Besides being compatible with a wide variety of chemical reactions, fluorous chemistry works well with several new synthetic technologies, including automated synthesis, the use of supercritical CO_2, and microwave synthesis.

12.3.8.3 Supercritical Fluids

A supercritical fluid is a substance above its critical point (i.e., above its critical temperature and pressure). This point represents the highest temperature and pressure at which the substance can coexist as a vapor and a liquid in equilibrium, as shown in Figure 12.18 for CO_2.

The gas–liquid coexistence curve is known as the boiling curve. If one moves upwards along the boiling curve, increasing both temperature and pressure, the *liquid* then becomes less dense due to thermal expansion, and as the pressure rises the *gas* becomes denser. Eventually, the densities of the two phases converge and become identical, eliminating the distinction between gas and liquid. For example, the critical point of CO_2 occurs at a pressure of 73.8 bar and a temperature of 31.1°C.

Supercritical fluids have physical properties intermediate to those of gases and liquids. Therefore, they are considered useful as reaction media because of the surprisingly high solubility of liquid and solid solutes in them, particularly when compressed to liquid-like densities.

As solubility is related to density, such media have the added benefit of being solubility-tunable, thereby allowing control of the solubility of an organic solute. This offers the potential for reaction control or for purification by the selective precipitation of a product. Furthermore, they have a particularly powerful ability to dissolve gaseous, liquid, and solid materials—and thus homogenize reaction mixtures in the supercritical fluid. This phenomenon is important in hydrogenation, oxidation and other types of reactions, where the solubility of gaseous reagents in the liquid solvent is rate limiting.

Carbon dioxide is a non-polar molecule and therefore the solubility of non-polar solutes is significantly higher than that of polar molecules.

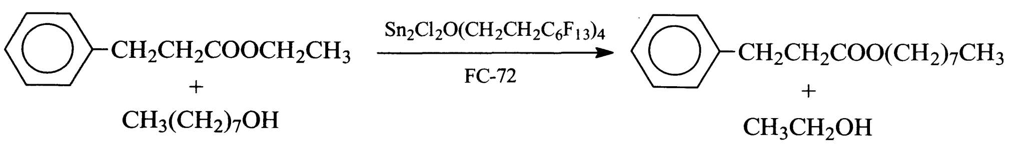


FIGURE 12.17. A fluorous *trans*-esterification. (Source: Xiang, 2001).

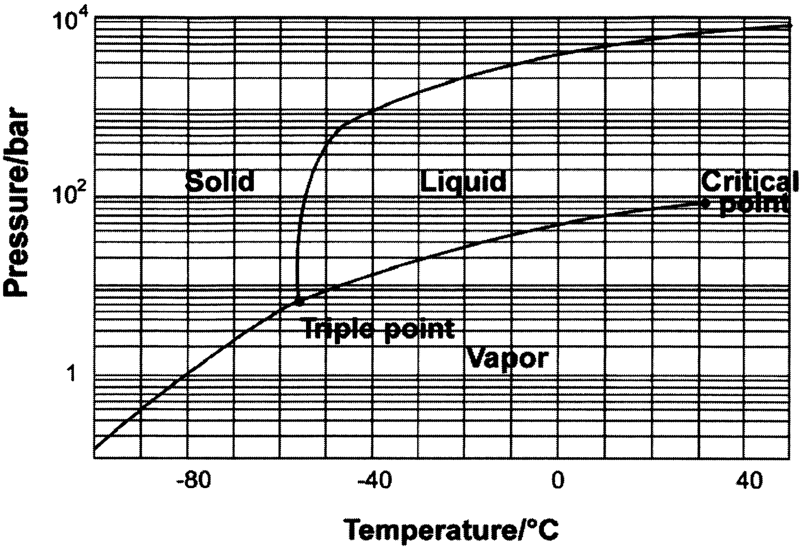


FIGURE 12.18. The phase diagram for pure carbon dioxide. (Adapted from Chemical Logic Corporation, 2006).

Potentially, supercritical carbon dioxide ($scCO_2$) is the ideal green solvent. It is non-toxic for both humans and the environment. It is chemically inert under most conditions, whether they be non-flammable or non-protic, and it is inert to radical and oxidizing conditions. This gas can be obtained in large quantities as a by-product of fermentation, combustion, and ammonia synthesis and it is relatively cheap, particularly compared with conventional solvents. Supercritical carbon dioxide presents other practical advantages as well, such as the possibility of achieving product isolation to total dryness by simple evaporation.

The ability of supercritical fluids to bring together gases, reagents, and catalysts in a single homogeneous phase offers a significant potential rate advantage for hydrogenation reactions over more conventional processes. An example is the hydrogenation of maleic anhydride (Figure 12.19), which is an important industrial reaction as are its products: succinic anhydride, succinic acid, γ-butyrolactone (GBL), and tetrahydrofuran (i.e., commodity chemicals of considerable importance). GBL is currently one of the most valuable alternatives to the environmentally harmful chlorinated solvents, widely used in the polymer and paint industries. Hydrogenation of maleic anhydride is the most direct method for producing GBL and it does not involve the use of hazardous materials. This can be achieved by using a simple alumina-supported Pd catalyst in $scCO_2$. The results are far superior to those obtained with other solution or gas phase reactions.

The prospect of using enzymes as heterogeneous catalysts in $scCO_2$ media has created significant interest. Their low viscosity and high diffusion rates offer the possibility of increasing the rate of mass-transfer controlled reactions. Also, because enzymes are not soluble in supercritical fluids, dispersion of the free enzymes potentially allows simple separations without the need for immobilization.

There are many reports of enzymatic catalysis in $scCO_2$ performing hydrolysis, oxidations, esterifications, and *trans*-esterification reactions. For example, the enzymatic kinetic resolution of 1-phenylethanol with vinyl acetate in $scCO_2$ using lipase from *Candida antarctica* B produces (R)-1-phenyethylacetate in >99% *ee* (i.e., enantiomeric excess, a measure of how much of one enantiomer is present as compared to the other), as shown in Figure 12.20.

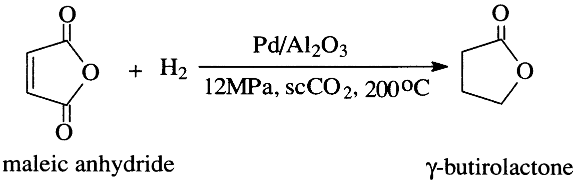


FIGURE 12.19. Hydrogenation using $scCO_2$. (Source: Pillai and Sahle-Demessi, 2002).

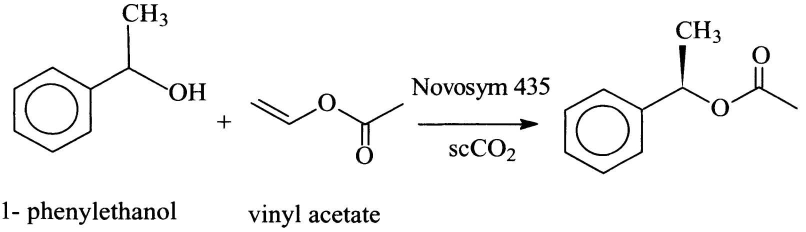


FIGURE 12.20. Esterification reaction using an enzyme and $scCO_2$. (Source: Overmeyer, 1999).

12.3.8.4 Solventless Reactions

Solventless systems have a most obvious advantage for human health: reagents either serve as the solvent or react in the molten state for proper mixing and optimal reaction conditions.

Innovative work is being done whereby heterogeneous organic reactions take place in specialized clays as zeolites, montmorillonite, and hydrocalcites. These clays have several advantages: they are easily separated from the reaction mixture, they are reusable catalysts, and their surface and pore structure can be easily modified. A case in point is the catalytic acylation of amino groups, which is a fundamental reaction in organic synthesis. This reaction is generally performed with acetic anhydride or acetyl chloride in the presence of bases such as triethylamine or pyridine along with certain co-catalysts. Protic acids such as *p*-toluenesulfonic acid, Lewis acids such as $ZnCl_2$, $CoCl_2$, and $MgBr_2$ are also known to catalyze the reaction. One can achieve this reaction in a solventless manner using zeolites, which are effective heterogeneous catalysts due to their unique physical and chemical properties such as shape. selectivity, acid/base nature and thermal stability. See Figure 12.21.

In addition, the use of acetic acid rather than acetic anhydride or acetyl chloride is advantageous both economically and environmentally.

12.3.8.5 Aqueous Systems

Organic chemists do not consider water to be a good solvent for organic reactions, as apolar organic compounds often have limited solubility in this liquid. Besides, the sensitivity of many reagents and functional groups towards water, among other factors, makes apolar and inert organic solvents a better choice. However, while on the one hand, the selective molecular recognition processes and chemical transformations in biological systems are confined to aqueous reaction media, on the other hand a series of organic reactions are favored in water. For example, the Diels–Alder reactions of a series of diene/dienophile combinations are greatly enhanced in aqueous solution (see Figure 12.22). Several other organic transformations are substantially accelerated in water, including the aldol condensation, the benzoin condensation, and the Claisen rearrangement. For the most part, attention has focused on carbon–carbon bond formation processes.

An additional example is the reduction of aromatic nitro compounds to anilines. This reduction is a very important synthetic transformation because the nitro group is often used to activate the aromatic nuclei for nucleophilic substitutions. The amino group, however, is frequently utilized for further derivatization towards valuable products such as pharmaceuticals.

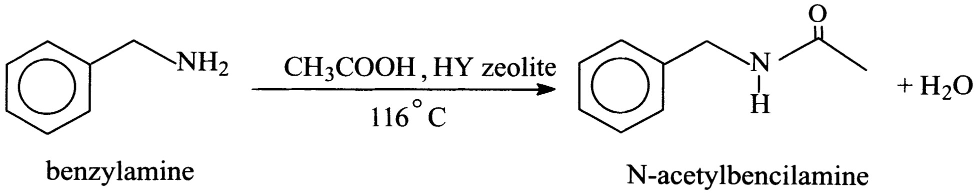


FIGURE 12.21. Solventless amide formation. (Source: Narender, 2000).

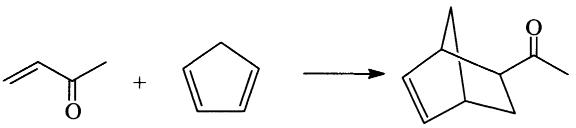


FIGURE 12.22. Diels–Alder reaction in aqueous media. (Source: Sijbren and Engberts, 2000).

The traditional reduction of the nitro group is achieved by hydrogenation using several catalysts. The reduction can be done in aqueous media and a good yield obtained using Zn and an ammonium salt, a greener reaction because the conditions are milder and the hazardous use of hydrogen gas is avoided (see Figure 12.23).

12.3.8.6 Biosolvents

Biosolvents or "green solvents"—as they are sometimes called—are derived from agrochemicals (see Figure 12.24). Some of the better known biosolvents are limonene (derived from citrus fruits), methyl soyate (produced from soy), and ethyl lactate (produced mainly from corn).

Biosolvents are biodegradable, easy to recycle, non-carcinogenic, and non-ozone depleting. Besides, they have very low volatility, high solvency power, high boiling point, low vapor pressure, and low surface tension (which translates into good wetting properties). These solvents are used in coatings, inks, and cleaners in substitution of many hazardous solvents.

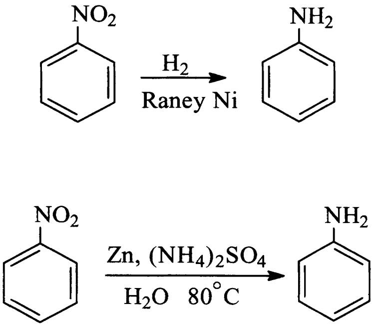
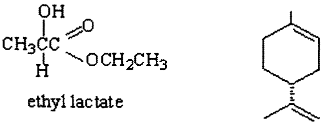


FIGURE 12.23. Traditional and green reductions of a nitro compound. (Source: Tsukinoki and Hirohisa, 2001).



ethyl lactate

(R)-4-isopropyl-1-methyl- cyclohexene (limonene)

FIGURE 12.24. Chemical structures of two biosolvents.

Nevertheless, the denomination "green solvents" does not imply that there is no risk associated with them. For example, ethyl lactate is a strong irritant that is also flammable—its use therefore is still risky. Likewise, many solvent substitutes currently under development present the same or similar characteristics, which is why care must be taken in the knowledge that nothing can be absolutely risk-free.

12.3.9 Energy Requirements

These should be analyzed on the basis of their environmental and economic impact. They should be reduced when their impact is threatening. Chemical reactions should be run at ambient temperature and pressure whenever possible.

Under the present circumstances, industry uses a tremendous share of all the energy consumed in industrialized nations. Chemistry and chemical transformations play a major role in trapping substances and converting them into energy as well as in changing existing sources of energy into a practical form for society.

Studies show that industry is not the most energy-efficient consumer and that its major sources of energy (and sometimes also of feedstock) are derived from fossil fuels. This has two disadvantages: (a) large consumption of non-renewable resources and (b) high environmental impact from the exploitation and consumption of such resources, which generates problems that range from a local to a global magnitude such as source depletion and air pollution.

In many reactions, reagents are dissolved and heated to reflux for a pre-specified time or until the reaction is concluded, but there is often a deficient analysis of the heating requirements for that particular reaction. For example, energy may be utilized to offset the activation energy required for bringing the reaction to completion. One of the great advantages of catalysts is their capacity to lower this energy of activation, thereby minimizing the amount of thermal energy needed to accomplish a transformation.

In other cases, reactions are so exothermic that they must be controlled through cooling. Also, slowing the reaction rate through cooling is sometimes necessary in chemical manufacturing to prevent an

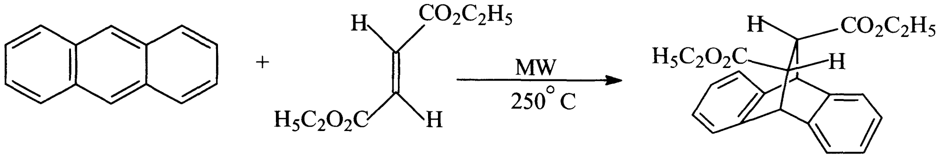


FIGURE 12.25. Diels–Alder reaction with microwave radiation. (Source: Nücher, 2004).

uncontrolled reaction, which could result in a severe chemical accident or an undesirable reaction path. In any event, there are both environmental and monetary costs that are incurred with cooling, as much as there are with heating.

Among the most energy-intensive processes in the chemical industry, the purification and separation processes stand out, whether they are carried out through distillation, re-crystallization, or ultrafiltration. By designing a process that minimizes the need for separations of this kind, one also ensures that the energy requirements (thermal, electric, or others) will decrease considerably.

Other energy-efficient alternatives for chemical syntheses are discussed below.

12.3.9.1 Microwave Radiation

Microwave radiation is becoming an increasingly popular method of heating samples in the laboratory. The reason is that it offers a clean, inexpensive and convenient method of heating that often results in higher yields and shorter reaction times.

Microwaves (MW) lie in the wavelength region of the electromagnetic spectrum between 0.01 and 1 meter, corresponding to frequencies between 0 to 0.3 GHz. Microwave RADAR equipment operates in the lower wavelengths (0.01–0.25 m) of the band, and telecommunications use much of the region. In order to prevent interference, governments and international agencies regulate the wavelength at which industrial and domestic microwave apparatus may operate at both national and international levels. In most countries, 2.450 GHz is the major operating frequency for this purpose. Dipolar solvents are essential in microwave heating, and it is often necessary to use a high boiling point solvent (e.g., diglyme, b.p. 162°C).

The Diels–Alder reaction between fumaric diethyl ester and anthracene can be done in 30 minutes at 250°C with microwave radiation, whereas its conventional counterpart in *p*-xylene requires several hours. See Figure 12.25.

Reactions can be performed in the solid state as well, by soaking the reagents on silica, alumina, or clays. Avoiding the use of organic solvents in the reactions leads to clean, efficient, and economical technologies. The Friedel–Crafts acylation shown in Figure 12.26 is an example.

As discussed earlier, whenever possible chemists should include in their evaluation process the energy requirements for all stages of a synthetic route, and should strive to minimize them.

12.3.9.2 Green Photochemistry

Recent calls for sustainable development and reduction of CO_2 emissions, as well as the growing requirement for environmentally friendly technologies, have led to increasing interest in the Sun as an energy and light source. Owing to their absorption at wavelengths above 350 nm, quinones are especially versatile substrates for the use of sunlight and can be utilized in the field of green photochemistry. An example is the photo Friedel–Crafts acylation as a mild and efficient alternative to thermal Friedel–Crafts acylation (see Figure 12.27). The classical

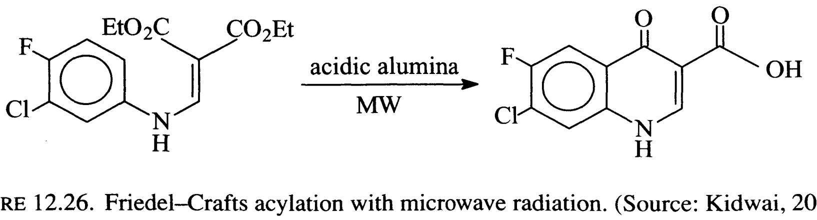


FIGURE 12.26. Friedel–Crafts acylation with microwave radiation. (Source: Kidwai, 2001).

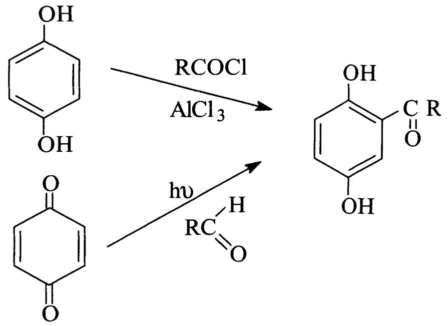


FIGURE 12.27. Traditional (top) and green (bottom) acylation. (Source: Schiel, 2001).

method often suffers from the use of carboxylic acid chlorides and equimolar amounts of harmful Lewis acids (usually $AlCl_3$), together with the formation of undesired by-products (especially volatile HCl).

The classical Friedel–Crafts reaction has functional restrictions for the starting materials, as highly electronegative atoms cannot be present. The photochemical reaction has no such restrictions, and a variety of substituted aldehydes and quinones have been successfully utilized.

12.3.10 Design Benign Products

Design chemical products that break down to innocuous substances after use so that they do not accumulate in the environment. Chemical products should be designed so that, at the end of their function, they do not persist in the environment but break down into innocuous degradation products. The development of synthetic biodegradable polymers, discussed below, is a case in point.

12.3.10.1 Synthetic Biodegradable Polymers

Synthetic polymers are large molecules composed of many smaller repeating units (monomers), bonded together. Today we speak of polymers meaning in fact synthetic organic polymers rather than natural organic biopolymers such as DNA, cellulose, and protein, or inorganic polymers such as glass and concrete.

The first organic polymers, polyvinyl chloride and polystyrene, were first introduced in the 1930s. We have been literally surrounded by synthetic polymers for a long time. The world annual production of polymers is approximately 200 × 10^9 kg. In the United States alone, 5 × 10^9 kg of plastic resins (typically used in packaging and transportation) are produced every year. Disposable goods and packing material represent about one-third of the total plastic production and have the largest environmental impact. More than 90% of the plastic material in municipal waste consists of polyethylene, polyvinyl chloride, and polystyrene, which are all resistant to biodegradation (see Table 9.1).

Biodegradation of polymers occurs when their constituent polymers are depolymerized, usually by the action of enzymes secreted by microorganisms. These enzymes act by hydrolyzing or oxidizing the polymer. The most biodegradable fibers thus tend to be hydrophilic and consist of short, flexible chains with low levels of crystallization. Such fibers often have chain backbones with oxygen or nitrogen links and/or pendant groups containing O or N atoms. This description clearly fits most natural fibers as well as fibers made of natural polymers.

Biodegradation-resistant polymers have the opposite characteristics and—unsurprisingly—are used to make the stronger, more durable polymers. Oxygen-free polymers such as polypropylene and polyethylene resist biodegradation entirely.

Despite its oxygen content, polyester (i.e., the aromatic polyethylene terephthalate) is degradation-resistant probably because of its rigid, rod-like chains. The same is true for polyamides in spite of their nitrogen content.

Unlike aromatics, aliphatic polyesters are generally biodegradable (see Table 9.2). More than a hundred species of bacteria are known to synthesize and store aliphatic polyesters for future use as an energy source. Examples are poly-β-hydroxybutyrate and poly-α-hydroxyvalerate (see Figure 12.28). These

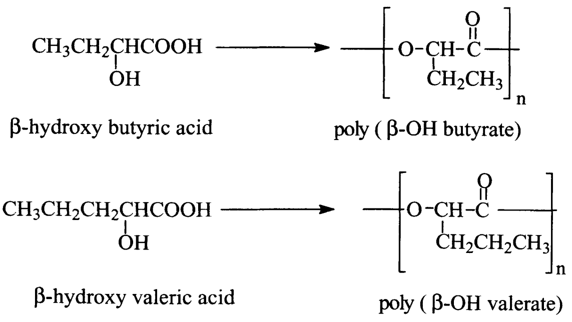


FIGURE 12.28. Examples of natural polyesters of bacterial origin.

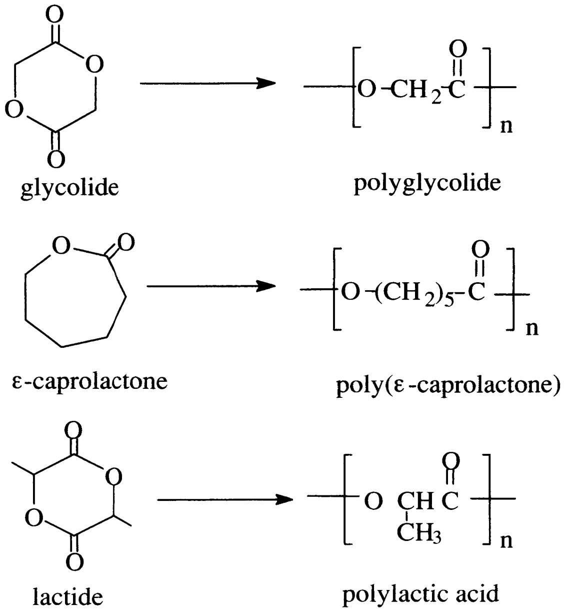


FIGURE 12.29. Synthetic biodegradable polyesters.

polyesters are not only naturally biodegradable but also thermoplastic, and they can be extracted and formed into films and fibers like any other polyester.

Nonetheless, artificial biodegradable aliphatic polyesters are still mainly based on the industrial polymerization of monomers such as glycolic acid (PGA), lactic acid (PLA), and caprolactone (PCL). (See Figure 12.29). These polyesters are applied in implants, absorbable sutures, controlled-release packaging, and degradable films and moldings.

12.3.10.2 Starch-Based Biodegradable Plastics

Starch is a linear polymer (polysaccharide) made up of repeating glucose groups joined by glucosidic linkages in the 1–4 carbon positions. The average length of the starch chains varies with the plant source (i.e., 500–2000 glucose units). There are two major molecules in starch: α-amylose and amylopectin. The alpha linkage of amylose starch makes it flexible and digestible.

Starch-based polymers can be based on crops such as corn (maize), wheat, or potatoes. Starch content may range from 10% to >90%, but significant material breakdown occurs above 60%. As the starch content increases, the polymer composites become more biodegradable and leave less recalcitrant residues. Starch-based polymers are often blended with high-performance polymers (e.g., aliphatic polyesters and polyvinyl alcohols) for different applications.

Biodegradation of starch-based polymers is a result of enzymatic attack at the glucosidic linkages between sugar groups, leading to a reduction in chain length and the splitting off of sugar units (i.e., monosaccharides, disaccharides, and oligosaccharides) that are readily utilized in biochemical pathways.

At lower starch contents (i.e., less than 60%) the starch particles act as weak links in the plastic matrix and become sites for biological attack. The polymer matrix can therefore disintegrate into small fragments, but this does not mean that the entire polymer structure will actually biodegrade.

Thermoplastic starch polymers are generally used as films in shopping bags, bread bags, bait bags, over wrap, "flushable" sanitary product backing material, and mulch films.

12.3.11 Optimize Monitoring and Control

Include in-process, real-time monitoring and control during product synthesis to minimize or eliminate the formation of by-products. The term *process analytical chemistry* implies real-time measurement of reaction conditions during chemical synthesis, coupled with the ability to alter the reaction depending on the outcome of such analyses. A considerable amount of research is currently being done in the field of process analytical chemistry. The technique is particularly applicable to biotechnological syntheses, where the reactions are usually quite complex and the value of the resulting product is high, thus making process analytical chemistry cost-effective.

An area for analytical chemists to focus on is the development of methods and technology that will allow preventing and reducing the generation of hazardous substances in chemical processes. In order to be able to effect changes, we require reliable sensors, monitors, and analytical techniques to assess the hazards in process streams. When toxic substances (e.g., by-products and side reactions) are detected, their formation may normally be controlled or prevented.

The use of process analytical chemistry can be further exemplified in the monitoring of reactions to observe their progress and determine their completion. In many cases, chemical processes require the continuous addition of reagents until the reaction is completed. If there is real-time, in-process monitoring to allow completion follow-up, then the need for adding more reagents can be eliminated and there will be none in the waste stream.

12.3.12 Minimize the Potential for Accidents

In process design, chemicals and their phase (solid, liquid, or gas) should be selected in such a way that the potential for chemical accidents (including explosions, fires, and releases to the environment) is minimized. The hazards posed by toxicity and by the risk of explosion and flaming also need to be addressed in the design of chemical products and processes. The goals of green chemistry must involve the full range of dangers and should not be focused merely on pollution or ecotoxicity.

Minimizing waste of a solvent in a given process may inadvertently increase the accident potential. Even though such an action may be beneficial from the perspective of pollution and release to the environment, it may also heighten the potential for a chemical accident or a fire, for example due to product dryness. A process must balance pollution prevention against accident prevention.

Approaches to the design of inherently safer chemistry can include the use of solids or low-vapor pressure substances as opposed to the volatile liquids or gases associated with most chemical accidents. Another approach consists in avoiding the use of large quantities of molecular halogens by substituting them with halogenated reagents that can be transferred in a more innocuous manner.

Hazards may be reduced if a process involves near-ambient temperatures and pressures. Thermal separations, such as distillation and evaporation, as well as solvent extractions can be risky operations. It is better to use, for example, more environmentally friendly separation techniques such as gas membranes or adsorption, which are separations that do not require heating of volatile solvents, and to reduce the number of separation stages.

Related Experiments in the Companion Book

20. Metal ion recovery by cementation
21. Green chemistry: The recovery and reuse of sulfur dioxide

Additional Related Experiments/Activities

Andrews, L.; Smith, W. L. "The Liquid Phase of Carbon Dioxide: A Simple Lecture Demonstration," *J. Chem. Educ.* **1989**, *66*, 597–598.

Arnáiz, F. J.; Pedrosa, M. R. "Microscale Transformations of Some Lead Compounds. A Cycle for Lead Minimizing the Production of Wastes," *J. Chem. Educ.* **1999**, *76*, 1687–1688.

Bauer, R.; Birk, J.; Sawyer, D. *Laboratory Inquiry in Chemistry*, 2nd ed.; Brooks-Cole: Stamford, CT, 2005.

- How can the waste be made useful? (Experiment 6)
- Is it economical to recycle aluminum? (Experiment 12)

Brodemus, J. S. "Obtaining the Corning Catalytic Combustor: A Low-Cost Method to Demonstrate Catalysis," *J. Chem. Educ.* **1989**, *66*, 768.

Buell, P.; Girard, J. *Laboratory Manual for Chemistry Fundamentals*, 2nd ed.; Jones and Bartlett: Boston, MA, 2002

- Classification of plastics for recycling (Experiment 18)

Cann, M. C. "Bringing State-of-the-Art, Applied, Novel, Green Chemistry to the Classroom by Employing the Presidential Green Chemistry Challenge Awards," *J. Chem. Educ.* **1999**, *76*, 1639–1641.

Cave, G. W. V.; Raston, C. L. "Green Chemistry Laboratory: Benign Synthesis of 4,6-Diphenyl[2,2′]bipyridine via Sequential Solventless Aldol and Michael Addition Reactions," *J. Chem. Educ.* **2005**, *82*, 468–469.

Clarke, N. R.; Casey, J. P.; Brown, E. D.; Oneyma, E.; Donaghy, K. J. "Preparation and Viscosity of Biodiesel from New and Used Vegetable Oil. An Inquiry-Based Environmental Chemistry Laboratory," *J. Chem. Educ.* **2006**, *83*, 257–259.

Crumbie, R. L. "Environmentally Responsible Redox Chemistry: An Example of Convenient Oxidation Methodology without Chromium Waste," *J. Chem. Educ.* **2006**, *83*, 268–269.

Donahue, C. J.; Exline, J. A.; Warner, C. "Chemical Recycling of Pop Bottles: The Synthesis of Dibenzyl Terephthalate from the Plastic Polyethylene Terephthalate," *J. Chem. Educ.* **2003**, *80*, 79.

Doxsee, K. M.; Hutchison, J. E. *Green Organic Chemistry: Strategies, Tools, and Laboratory Experiments*; Thomson-Brooks/Cole Publishing: London, 2004.

El-Halwagi, M. M.; Spriggs, D. H. "Educational Tools for Pollution Prevention through Process Integration," *Chem. Eng. Educ.* **1998**, *32*, 246–249.

Harper, B. A.; Rainwater, J. C.; Birdwhistell, K.; Knight, D. A. "Aqueous-Phase Palladium-Catalyzed Coupling. A Green Chemistry Laboratory Experiment," *J. Chem. Educ.* **2002**, *79*, 729–731.

Harris, M. E.; Harris, H. H. "Sorting Recycled Trash," *J. Chem. Educ.* **2007**, *84*, 207–210.

Ingles, M.; Bonete, P.; Exposito, E.; García-García, V.; González-Garcia, J.; Iniesta, J.; Montiel, V. "Electrochemical Regeneration of a Spent Oxidizing Solution: Example of a Clean Chemical Process," *J. Chem. Educ.* **1999**, *76*, 1423–1425.

Jacobsen, E. K. "JCE Resources for Chemistry and Recycling," *J. Chem. Educ.* **2007**, *84*, 212–213.

Johnston, J. E. "Catalysis and Cleanliness," *J. Chem. Educ.* **1969**, *46*, A547.

Kaufman, D.; Wright, G.; Kroemer, R; Engel, J. "New Compounds from Old Plastics: Recycling PET Plastics via Depolymerization. An Activity for the Undergraduate Organic Lab," *J. Chem. Educ.* **1999**, *76*, 1525–1526.

Kirchhoff, M.; Ryan, M. A., Eds: *Greener Approaches to Undergraduate Chemistry Experiments*; American Chemical Society: Washington, 2002. (The following experiments are all authored by John C. Warner):

- Biosynthesis of ethanol: renewable feedstock and enzyme catalysis (p. 11)
- Benzoin condensation using thymine as a catalyst instead of cyanide (p. 14)
- Water soluble catalysis: aqueous analogue of the Grignard reaction (p. 23)
- Synthesis of 7-hydroxy-4-methylcoumarin by a solid-catalyzed Pechmann reaction (p. 25)
- Construction of solar energy devices with natural dyes (p. 42)
- Aqueous photoresists (p. 45)
- Microwave-assisted Diels-Alder reaction of anthracene and maleic anhydride (p. 85)

Mattson, B.; Fujita, J.; Catahan, R.; Cheng, W.; Greimann, J.; Khandhar, P.; Mattson, A.; Rajani, A.; Sullivan, P.; Perkins, R. "Demonstrating Heterogeneous Gas-Phase Catalysis with the Gas Reaction Catalyst Tube," *J. Chem. Educ.* **2003**, *80*, 768–773.

Meyer, S. A.; Morgenstern, M. A. "Small Scale Biodiesel Production: A Laboratory Experience for General Chemistry and Environmental Science Students," *Chem. Educ.* **2005**, *10*, 130–132.

Moya, H. D.; Neves, E. A.; Coichev, N. "A Further Demonstration of Sulfite-induced Redox Cycling of Metal Ions Initiated by Shaking," *J. Chem. Educ.* **1999**, *76*, 930–932.

Pohl, N.; Clague, A.; Schwarz, K. "Chiral Compounds and Green Chemistry in Undergraduate Organic Laboratories: Reduction of a Ketone by Sodium Borohydride and Baker's Yeast," *J. Chem. Educ.* **2002**, *79*, 727–728.

Reed, S. M.; Hutchison, J. E. "Green Chemistry in the Organic Teaching Laboratory: An Environmentally Benign Synthesis of Adipic Acid", *J. Chem. Educ.* **2000**, *77*, 1627–1629.

Orecchio, S. "Recovery and Reutilization of Waste Matter from Coffee Preparation. An Experiment for Environmental Science Courses," *J. Chem. Educ.* **2001**, *78*, 1669–1671.

van Wyk, J. P. H. "Conversion of Used Paper Materials into Sugars: A Biochemical Process to Limit Environmental Pollution," *Chem. Educ.* **2000**, *5*, 315–316.

Venditti, R. A. "A Simple Flotation De-Inking Experiment for the Recycling of Paper," *J. Chem. Educ.* **2004**, *81*, 693.

Vidal, M. M.; Filipe, O. M. S.; Cruz Costa, M. C. "Reducing the Use of Agrochemicals: A Simple Experiment," *J. Chem. Educ.* **2006**, *83*, 245–247.

References and Further Reading

American Chemical Society's Education and Internatinal Activities Division, U.S. Environmental Protection Agency's Green Chemistry Program, Office of Pollution Prevention and Toxics. "Innovations for a Cleaner World". Video. http://www.chemistry.org/portal/a/c/s/1/acsdisplay.html?DOC=education%5cgreenchem%5cvideo.html

American Chemical Society. *Green Chemistry: Meeting Global Challenges*; Green Chemistry on DVD, American Chemical Society: Washington, 2002.

American Plastics Concil. http://www.americanplasticscouncil.org/s_apc/sec.asp? CID=296&DID=895

Anastas, P. T.; Warner, J. C. *Green Chemistry. Theory and Practice*; Oxford University Press: Oxford, 2000. p. 30.

Anastas, P. T.; Williamson, T. C., Eds. *Green Chemistry: Designing Chemistry for the Environment*; ACS Symposium Series 626; American Chemical Society: Washington, 1996.

Cann, M. C.; Connally, M. E. *Real-World Cases in Green Chemistry*; American Chemical Society: Washington, 2000.

Cann, M. C.; Dickneider, T. A. "Infusing the Chemistry Curriculum with Green Chemistry Using Real-World Examples, Web Modules, and Atom Economy in Organic Chemistry Courses," *J. Chem. Educ.* **2004**, *81*, 977–980.

Carmichael, A. J.; Earle, M. J.; Holbrey, J. D.; McCormac, P.B.; Seddon, K. R. "The Heck Reaction in Ionic Liquids: A Multiphasic Catalyst System," *Org. Lett.* **1999**, *1*, 997–1000.

Chemical Logic Corporation. http://www.chemicalogic.com/download/co2_phase_diagram.pdf

Curran, D., Lee, Z. "Fluorous Techniques for the Synthesis and Separation of Organic Molecules," *Green Chem.* **2001**, *3(1)*, G3–G7.

Curzons, A. D.; Constable, D. J. C.; Mortimer, D. N.; Cunningham, V. L. "So You Think Your Process is Green, How do You Know?—Using Principles of Sustainability to Determine what is Green—A Corporate Perspective," *Green Chem.* **2001**, *3(1)*, 1–6.

Domenech, X.; Ayllon, J. A.; Peral, J.; Rieradevall, J. "How Green is a Chemical Reaction? Application of LCA to Green Chemistry," *Environ. Sci. Technol.* **2002**, *36*, 5517–5520.

Draths, K. M.; Frost, J. W. "Environmentally Compatible Synthesis of Adipic Acid from D-Glucose," *J. Am. Chem. Soc.* **1994**, *116*, 399–400.

DuBay, K.; Schweitzer, J.; Dunn, T.; Keoleian, G. A.; Osborn, N. A. "Annotated Bibliography of Chemistry-Related Pollution Prevention Sources," National Pollution Prevention Center for Higher Education. http://css.snre.umich.edu/

Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer H. D.; Broker, G. A.; Rogers, R. D. "Characterization and Comparison of Hydrophilic and Hydrophobic Room Temperature Ionic Liquids Incorporating the Imidazolium Cation," *Green Chem.* **2001**, *3*, 156–164 (see also http://lem.ch.unito.it/didattica/infochimica/Liquidi%20Ionici/GreenAspects.html **and** http://pb.merck.de/servlet/PB/menu/1061480/index.html).

Hutchinson, J. University of Oregon, Green Chemistry Program. http://darkwing.uoregon.edu/ hutchlab/greenchem/index.html

Illman, D. L. "GREEN Technology Presents Challenges to Chemists", *Chem. Eng. News*, Sept. 6, 1993, pp. 26–30.

Kidwai, M. "Dry Media Reactions," *Pure Appl. Chem.* **2001**, *73*, 147–151.

Kirchhoff, M. M. "Topics in Green Chemistry," *J. Chem. Educ.* **2001**, *78*, 1577.

Kragl, U.; Eckstein, M.; Kaftzik, N. "Enzyme Catalysis in Ionic Liquids," *Curr. Opin. Biotechnol.* **2002**, *13*, 565–571.

Laschowski, André. Postdam University. http://www.chem.uni-potsdam. de/apc/polymer_toppage.html

Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; Wiley: New York, 1997.

McKenzie, L. C.; Huffman, L. M.; Parent, K. E.; Hutchison, J. E.; Thompson, J. "Patterning Self-Assembled Monolayers on Gold. Green Materials Chemistry in the Teaching Laboratory," *J. Chem. Educ.* **2004**, *81*, 545–548.

Monteiro, A. L.; Zinn, F. K.; de Souza, R. F.; Dupont, J. "Asymmetric Hydrogenation of 2-Arylacrylic Acids Catalyzed by Immobilized Ru-BINAP Complex in 1-*n*-Butyl-3-Methylimidazolium Tetrafluoroborate Molten Salt," *Tetrahed. Asymm.* **1977**, *8*, 177–179.

Narender, N.; Srinivasu, P.; Kulkarni, S. J.; Raghavan, K. V. "Liquid Phase Acylation of Amines with Acetic Acid over HY Zeolite," *Green Chem.* **2000**, *2*, 104–105.

Nüchcher, M.; Ondruschka, B.; Bonrath, W.; Gum, A. "Microwave Assisted Synthesis—A Critical Technology Overview," *Green Chem.* **2004**, *6*, 128–141.

Ono, Y. "Dimethylcarbonate for Environmentally Benign Reactions," *Pure Appl. Chem.* **1996**, *68*, 367–375.

Overmeyer, A.; Schrader-Lippel, S.; Kasche, V.; Brunner, G. "Lipase-catalyzed Kinetic Resolution of Racemates at Temperatures from 40°C to 60°C in Supercritical CO_2," *Biotech. Lett.* **1999**, *21*, 65–69.

Pillai, U.; Sahle-Demessi, E. "Selective Hydrogenation of Maleic Anhydride to γ-Butyrolactone over Pd/Al_2O_3 Catalyst Using Supercritical CO_2 as Solvent," *Chem. Commun.* **2002**, *5*, 422–423.

Ritter, S. K. "Green Rewards," *Chem. Eng. News*, June 30, 2003. pp. 30–35.

Ryan, M. A.; Tinnesand, M. J. Eds. *Introduction to Green Chemistry*; American Chemical Society: Washington, 2002.

Schiel, Ch.; Oelgemöler, M.; Ortner, J.; Mattay, J. "Green Photochemistry: The Solar-Chemical 'Photo-Friedel-Crafts Acylation' of Quinones," *Green Chem.* **2001**, *3*, 224–228.

Sheldon, R. "Catalytic Reactions in Ionic Liquids," *Chem. Commun.* **2001**, *23*, 2399–2407.

Sheldon, R. A. "Catalysis and Pollution Prevention," *Chem. Ind.* **1997**, (Jan. 6), 12–15.

Sijbren, O.; Engberts, J. B. F. N. "Diels-Alder Reactions in Water," *Pure Appl. Chem.* **2000**, *72*, 1365–1372.

Sime, J. T. "Applications of Biocatalysis to Industrial Processes," *J. Chem. Educ.* **1999**, *76*, 1658–1661.

Singh, M. M.; Szafran, Z.; Pike, R. M. "Microscale Chemistry and Green Chemistry: Complementary Pedagogies," *J. Chem. Educ.* **1999**, *76*, 1684–1686.

Song, Y.; Wang, Y.; Geng, Z. "Some Exercises Reflecting Green Chemistry Concepts," *J. Chem. Educ.* **2004**, *81*, 691–692.

Steines, S.; Wasserscheid, P.; Driessen-Hölscher, B. "An Ionic Liquid as Catalyst Medium for Stereoselective Hydrogenations of Sorbic Acid with Ruthenium Complexes," *J. Prakt. Chem.* **2000**, *342*, 348–354.

Trost, B. M. "The Atom Economy—A Search for Synthetic Efficiency," *Science* **1991**, *254*, 1471–1477.

Tsukinoki, T.; Hirohisa, Tsuzuki. "Organic Reaction in Water. Part 5. Novel Synthesis of Anilines by Zinc Metal-Mediated Chemoselective Reduction of Nitroarenes," *Green Chem.* **2001**, *3*, 37–38.

Tundo, P. "New Developments in Dimethylcarbonate Chemistry," *Pure Appl. Chem.* **2001**, *73*, 1117–1124.

Uffelman, E. S. "News from Online: Green Chemistry," *J. Chem. Educ.* **2004**, *81*, 172–176.

Van Arnum, S. D. "An Approach Towards Teaching Green Chemistry Fundamentals," *J. Chem. Educ.* **2005**, *82*, 1689–1692.

Welton, T. "Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis," *Chem. Rev.* **1999**, *99*, 2071–2083.

Xiang, J.; Toyoshima, S.; Orita, A.; Otera, J. "A Practical and Green Chemical Process: Fluoroalkyldistannoxane-catalyzed Biphasic Transesterification," *Angew. Chem., Int. Ed.*, **2001**, *40*, 3670–3672.

Index

Printed in the United States of America.