GREEN CHEMISTRY AND THE TEN COMMANDMENTS OF SUSTAINABILITY

Stanley E. Manahan
University of Missouri

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Since about the 1990s, “green” has come into widespread use as a term to describe practices and disciplines that deal with sustainability and the maintenance of environmental quality. One area that has been particularly active is in chemistry with green chemistry the subject of large numbers of symposia, international meetings, books, and journal papers. In addition, green chemistry institutes and academic programs have been established in various countries.

Green Chemistry and the Ten Commandments of Sustainability, Third Edition, is a basic book on green chemistry and environmental sustainability designed for readers who have a need to learn about these topics at a fundamental level. Most works on green chemistry have concentrated on aspects of chemical synthesis, especially organic chemical synthesis. *Green Chemistry and the Ten Commandments of Sustainability*, discusses chemistry as a whole particularly as it relates to the environment and sustainability. In addition to covering green chemistry, the book deals with sustainable science and technology in general. In so doing, it views Earth and its environment as consisting of five highly interactive spheres: (1) The hydrosphere, (2) the atmosphere, (3) the geosphere, (4) the biosphere, (5) and the anthrosphere. It is particularly important to consider the anthrosphere, that part of Earth’s environment made and operated by humans, because of its overwhelming importance in determining Earth’s environment.

Chapter 1, “Sustainability and the Environment,” consists of an introduction to environmental science and the concept of sustainability. It introduces and defines the five environmental spheres.Green science and green technology are introduced and explained. In recognition of the overwhelming importance of energy in sustainability, this chapter includes a section entitled“Sustainable Energy: Away from the Sun and Back Again” that explains how humankind relied on solar energy, such as photosynthetically produced food and wood, for most of its time on Earth, then entered an approximately two-century era in which fossil fuels became dominant energy sources, but now must return to the sun directly and indirectly for basic energy supply.

Chapter 3, “The Key Role of Chemistry and Making Chemistry Green” outlines the importance and role of chemistry in sustainability. Environmental chemistry is introduced as a key discipline in sustainability. Green chemistry is defined and the twelve principles of green chemistry are listed and explained. The chapter provides a brief introduction to the most basic aspects of chemistry to aid in understanding chemical concepts in later chapters. Chapters 3 through 7 cover the fundamentals of chemistry from a green chemistry perspective. Chapter 6 is a basic coverage of organic chemistry and Chapter 7 deals with biochemistry as it relates to green chemistry.

Chapters 8 through 13 are organized according to the five spheres of the environment. Chapter 8, “The Five Environmental Spheres and Biogeochemical Cycles,” defines and explains each of these spheres and how they relate and interact through biogeochemical cycles of matter. Chapter 9, “Water, the Ultimate Green Substance,” covers the hydrosphere. It also emphasizes the unique properties of water as related to the structure of the water molecule and explains the important role of water in green technology. Chapter 10, “The Atmosphere: Blue Skies for a Green Environment,” deals with air and the atmosphere, the natural capital provided by the atmosphere, the protective role of the atmosphere, and threats to the atmosphere and climate from activities in the anthrosphere, including the combustion of carbonaceous fuels. Chapter 11, “The Geosphere and a Green Earth,” covers a number of topics related to the geosphere including aspects of geology, natural hazards of the geosphere (volcanoes, earthquakes), natural capital of the geosphere (minerals), and the geosphere as a repository of wastes. Important sections of this chapter discuss soil, how its productive capacity may be lost through erosion and desertification, and how green technology may prevent these harmful effects. Chapter 12, “The Biosphere and the Role of Green Chemistry in Feeding a Hungry World,” begins with a basic coverage of biology as it relates to sustainability and among other topics discusses the production of food and fiber by the biosphere (agriculture). It also contains a discussion of agricultural applications of genetically modified organisms as well as a section on how the anthrosphere may be operated in a way that supports and benefits the biosphere. Chapter 13, “The Anthrosphere, Industrial Ecology, and Green Chemistry,” begins with a discussion of the emerging area of industrial ecology, which treats industrial systems in a manner analogous to natural ecosystems including industrial metabolism through which materials are processed to produce manufactured products. Life cycles of materials are discussed with respect to sustainability. The role of green chemistry in sustainable manufacturing is explained in this chapter.

As the title implies, Chapter 14, “Feeding the Anthrosphere: Utilizing Renewable and Biological Materials,” discusses how feedstocks for manufacturing may be produced sustainably. Emphasis is placed upon biological sources of feedstocks produced through photosynthesis. Biorefineries and their role in biomass utilization are explained.

Chapter 15, “Sustainable Energy: The Essential Basis of Green Systems,” explains the key importance of sustainable energy in sustainability and how most environmental and sustainability problems can be solved if abundant sources of energy are available and if they can be used without doing unacceptable harm to the environment. Part of the chapter pertains to green technology for efficient energy conversion and utilization. Renewable sources of energy including solar electric, wind, moving water, and biomass are discussed in this chapter.

Chapter 16, “Terrorism, Toxicity, and Vulnerability: Green Chemistry and Technology in Defense of Human Welfare,” discusses the role of green chemistry, science, and technology in dealing with terrorist threats. A major part of the chapter deals with toxic substances and toxicology as they relate to terrorist threats. The chapter also covers potential biohazards in terrorism and protecting water, food, and air.

Chapter 17, “The Ten Commandments of Sustainability and Sensible Measures,” presents ten important rules for the achievement of sustainability upon which part of the book title is based. It concludes with a section on “sensible measures” that might be taken to enhance sustainability. Designed to provoke thought, these suggestions range from small measures to grandiose schemes. The author welcomes input from readers and may be contacted at the following e-mailaddress:manahans@missouri.edu

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TABLE OF CONTENTS

Preface

Licensing

1: Sustainability and the Environment

- 1.1: Sustainability
- 1.2: The Environment and the Five Environmental Sphere
- 1.3: Seeing Green
- 1.4: Natural Capital of the Earth
- 1.5: Sustainability as a Group Effort- It Takes a (Very Big) Village
- 1.6: Sustainable Energy- Away from the Sun and Back Again
- 1.7: Green Science
- 1.8: Green Technology
- 1.9: Sustainability and the Eco-Economy
- 1.10: Green Products and Services- Design for Sustainability
- Questions and Problems

2: The Key Role of Chemistry and Making Chemistry Green

- 2.1: Chemistry is Good (and Unavoidable)
- 2.2: The Environment and its Chemistry
- 2.3: What is Environmental Chemistry?
- 2.4: Environmental Pollution
- 2.5: Practice of Green Chemistry
- 2.6: Green Chemistry and Synthetic Chemistry
- 2.7: Reduction of Risk- Hazard and Exposure
- 2.8: The Risks of No Risks
- 2.9: Waste Prevention
- 2.10: Basic Principles of Green Chemistry
- 2.11: Some Things to Know About Chemistry before You Even Start
- 2.12: Combining Atoms to Make Molecules and Compounds
- 2.13: The process of making and breaking chemical bonds- chemical reactions
- 2.14: The Nature of Matter and States of Matter
- References and Questions

3: The Elements - Basic Building Blocks of Green Chemicals

- 3.1: Elements, Atoms, and Atomic Theory
- 3.2: Hydrogen - The Simplest Atom
- 3.3: Helium - The First Noble Gas
- 3.4: Lithium, The First Metal
- 3.5: The Second Period of the Periodic Table
- 3.6: The Magic Octet of 8 Outer-Shell Electrons
- 3.7: Completing the 20-Element Periodic Table
- 3.8: The Brief Periodic Table is Complete
- 3.E: The Elements - Basic Building Blocks of Green Chemicals (Exercises)
- 3.R: References

4: Compounds- Safer Materials for a Safer World

- 4.1: Chemical Bonds and Compound Formation
- 4.2: Electrons Involved in Chemical Bonds and Octets of Electrons
- 4.3: Sodium Chloride and Ionic Bonds
- 4.4: Covalent Bonds in H2 and Other Molecules
- 4.5: Covalent Bonds in Compounds
- 4.6: Covalent Bonds and Green Chemistry
- 4.7: Predicting Formulas of Covalently Bound Compounds
- 4.8: Chemical Formulas, the Mole, and Percentage Composition
- 4.9: What Are Chemical Compounds Called?
- 4.10: Acids, Bases and Salts
- Questions and Problems

5: Chemical Reactions- Making Materials Safely and Sustainable

- 5.1: Describing What Happens with Chemical Equations
- 5.2: Balancing Chemical Equations
- 5.3: Just Because You Can Write It Doesn't Mean That It Will Happen
- 5.4: Yield And Atom Economy in Chemical Reactions
- 5.5: Catalysts That Make Reactions Go
- 5.6: Kinds of Chemical Reactions
- 5.7: Oxidation-Reduction Reactions and Green Chemistry
- 5.8: Quantitative Information from Chemical Reactions
- 5.9: Energy in Chemical Reactions
- 5.10: Stoichiometry by the Mole Ratio Method
- 5.11: Limiting Reactant and Percent Yield
- 5.12: Titrations - Measuring Moles by Volume of Solution
- 5.13: Industrial Chemical Reactions - The Solvay Process
- Questions and Problems

6: The Wonderful World of Carbon - Organic Chemistry and Biochemicals

- 6.1: Rings and Chains of Carbon Atoms
- 6.2: Compounds of Carbon and Hydrogen - Hydrocarbons
- 6.3: Using Lines To Show Organic Structural Formulas
- 6.4: Functional Groups
- 6.5: Giant Molecules from Small Organic Molecules
- Questions and Problems
- Supplementary References

7: Chemistry of Life and Green Chemistry

- 7.1: Green Biochemistry
- 7.2: Biochemistry and the Cells
- 7.3: Carbohydrates
- 7.4: Proteins
- 7.5: Lipids - Fats, Oils, and Hormones
- 7.6: Nucleic Acids
- 7.7: Enzymes
- 7.8: Biochemical Processes in Metabolism
- 7.9: Biochemistry of Toxic Substances and Toxicological Chemistry
- Literature Cited
- Questions and Problems

- Supplementary References

8: The Five Environmental Spheres and Biogeochemical Cycle

- 8.1: Five Environmental Spheres
- 8.2: The Hydrosphere
- 8.3: The Atmosphere
- 8.4: The Geosphere
- 8.5: The Biosphere
- 8.6: The Anthrosphere
- 8.7: Cycles of Matter
- Questions and Problems
- Supplementary References

9: Water - the Ultimate Green Substance

- 9.1: H_2O - Simple Formula, Remarkable Molecule
- 9.2: Occurrence, Availability , and Utilization of Water on Earth
- 9.3: Water Chemistry
- 9.4: Water Pollution
- 9.5: Greening of Water - Purification Before Use
- 9.6: Wastewater Treatment
- 9.7: Advanced Wastewater Treatment and Recycling
- 9.8: The Many Uses of Water
- 9.9: Hot Water - Pressurized Subcritical Water
- 9.10: Supercritical Water
- Literature Cited
- Questions and Problems
- Supplementary References

10: Blue Skies for a Green Environment

- 10.1: More Than Just Air to Breathe
- 10.2: The Gas Laws
- 10.3: The Protective Atmosphere
- 10.4: Atmospheric Chemistry and Photochemical Reactions
- 10.6: The Enormous Importance of Climate
- 10.7: Atmospheric Particle Pollutants
- 10.8: Pollutant Gaseous Oxides
- 10.9: Acid Rain
- 10.10: Miscellaneous Gases in the Atmosphere
- 10.11: Photochemical Smog
- 10.12: Natural Capital of the Atmosphere
- 10.5: Energy and Mass Transfer in the Atmosphere
- Questions and Problems
- Supplementary References

11: The Geosphere and a Green Earth

- 11.1: Probing Deep into the Geosphere - A Well Too Far?
- 11.2: The Nature of the Geosphere
- 11.3: The Geosphere as a Source of Natural Capital
- 11.4: Environmental Hazards of the Geosphere
- 11.5: Water on and in the Geosphere

- 11.6: Anthrospheric Influences on the Geosphere
- 11.7: The Geosphere as a Waste Repository
- 11.8: Have You Thanked a Clod Today?
- 11.9: Plant Nutrients and Fertilizers in Soil
- 11.10: Soil and Plants Related To Wastes and Pollutants
- 11.11: Soil Loss - Desertification and Deforestation
- Literature Cited and Supplementary References
- Questions and Problems

12: The Biosphere and the Role of Green Chemistry in Feeding a Hungry World

- 12.1: Pigweed’s Revenge
- 12.2: The Biosphere
- 12.3: Cells - Basic Units of Life
- 12.4: Metabolism and Control in Organisms
- 12.5: Reproduction and Inherited Traits
- 12.6: Stability and Equilibrium of the Biosphere
- 12.7: DNA and the Human Genome
- 12.8: Genetic Engineering
- 12.9: Biological Interaction with Environmental Chemicals
- 12.10: Biodegradation
- 12.11: Production of Food and Fiber by the Biosphere - Agriculture
- 12.12: Agricultural Applications of Genetically Modified Organisms
- 12.13: The Anthrosphere in Support of the Biosphere
- 12.14: Livestock and their Wastes
- Questions and Problems
- Supplementary References

13: The Anthrosphere, Industrial Ecology, and Green Chemistry

- 13.1: Industrial Ecology and Industrial Ecosystems
- 13.2: Metabolic Processes in Industrial Ecosystems
- 13.3: Life Cycles in Industrial Ecosystems
- 13.4: Kinds of Products
- 13.5: Attributes Required by an Industrial Ecosystem
- 13.6: The Kalundborg Industrial Ecosystem
- 13.7: Environmental Impacts of Industrial Ecosystems
- 13.8: Green Chemistry and Industrial Ecology
- 13.9: Predicting and Reducing Hazards
- 13.10: The E-Factor in Green Chemistry
- 13.11: Catalysts and Catalysis
- 13.12: Biocatalysis with Enzymes
- 13.13: Energizing Chemical Reactions and Process Intensification
- 13.14: Solvents and Alternate Reaction Media
- 13.15: Feedstocks and Reagents
- Literature Cited and Supplementary References
- Questions and Problems

14: Feeding the Anthrosphere- Utilizing Renewable and Biological Materials

- 14.1: Feeding the Anthrosphere
- 14.2: Utilization of Feedstocks
- 14.3: Biological Feedstocks
- 14.4: Biological Sources of Chemicals
- 14.5: Biorefineries and Biomass Utilization
- 14.6: Monosaccharide Feedstocks - Glucose, Fructose, and Xylose
- 14.7: Cellulose
- 14.8: Feedstocks from Cellulose Wastes
- 14.9: Lignin
- 14.10: Direct Biosynthesis of Polymers
- 14.11: Bioconversion Processes for Synthetic Chemicals
- 14.12: Bamboo - Ancient Material for the Future
- Literature Cited
- Questions and Problems

15: Sustainable Energy- The Essential Basis of Green Systems

- 15.1: Sustainability and Energy
- 15.2: What is Energy?
- 15.3: Radiant Energy from the Sun
- 15.4: Sources of Energy Used in the Anthrosphere
- 15.5: Conversions Between Forms of Energy
- 15.6: Green Technology for Energy Conversion
- 15.7: Energy Conservation
- 15.8: Depletable Fossil Fuels
- 15.9: Carbon Sequestration for Fossil Fuel Utilization
- 15.10: Nuclear Energy
- 15.11: Renewable Energy Sources - Solar Energy
- 15.12: Energy from Wind and Water
- 15.13: Biomass Energy
- 15.14: Geothermal Energy
- 15.15: Hydrogen for Energy Storage and Utilization
- Literature Cited and Supplementary References
- Questions and Problems

16: Terrorism, Toxicity, and Vulnerability- Green Chemistry and Technology in Defense of Human Welfare

- 16.1: Vulnerability to Terrorist Attack
- 16.2: Protecting the Anthrosphere
- 16.3: Substances That Explode, Burn, or React Violently
- 16.4: Toxic Substances and Toxicology
- 16.5: Toxic Chemical Attack
- 16.6: Protecting Water, Food, and Air
- 16.7: Detecting Hazards
- 16.8: Green Chemistry to Combat Terrorism
- 16.9: Green Chemistry for Sustainable Prosperity and a Safer World
- 16.10: Green Chemistry to Combat Terrorism
- 16.11: Green Chemistry for Sustainable Prosperity and and a Safer World
- Literature Cited

- Questions and Problems

17: The Ten Commandments of Sustainability and Sensible Measure

- 17.1: We Cannot Go on Like This
- 17.2: The First Commandment
- 17.3: The Second Commandment
- 17.4: The Third Commandment
- 17.5: The Fourth Commandment
- 17.6: The Fifth Commandment
- 17.7: The Sixth Commandment
- 17.8: The Seventh Commandment
- 17.10: The Ninth Commandment
- 17.11: The Tenth Commandment
- 17.12: Some Sensible Measures for Sustainability
- 17.9: The Eighth Commandment
- Literature Cited
- Questions and Problems
- Supplementary References

Index

Glossary

Detailed Licensing

Licensing

A detailed breakdown of this resource's licensing can be found in ***Back Matter/Detailed Licensing***.

CHAPTER OVERVIEW

1: Sustainability and the Environment

1.1: Sustainability
1.2: The Environment and the Five Environmental Sphere
1.3: Seeing Green
1.4: Natural Capital of the Earth
1.5: Sustainability as a Group Effort- It Takes a (Very Big) Village
1.6: Sustainable Energy- Away from the Sun and Back Again
1.7: Green Science
1.8: Green Technology
1.9: Sustainability and the Eco-Economy
1.10: Green Products and Services- Design for Sustainability
Questions and Problems

“If we do not change direction, we are likely to end up where we are headed,” (old Chinese proverb).“If we make the effort to learn its language, Earth will speak to us and tell us what we must do to survive.”

1.1: Sustainability

The old Chinese proverb certainly applies to modern civilization and its relationship to world resources that support it. Evidence abounds that humans are degrading the Earth life support system upon which they depend for their existence. The emission to the atmosphere of carbon dioxide and other greenhouse gases is almost certainly causing global warming and climate change. Discharge of pollutants has degraded the atmosphere, the hydrosphere, and the geosphere in industrialized areas and has placed great stress on parts of the biosphere. Natural resources including minerals, fossil fuels, fresh water, and biomass have become stressed and depleted. The productivity of agricultural land has been diminished by water and soil erosion, deforestation, desertification, contamination, and conversion to non-agricultural uses. Wildlife habitats including woodlands, grasslands, estuaries, and wetlands have been destroyed or damaged. About 3 billion people (half of the world's population) live in dire poverty on less than the equivalent of U.S. $2/day. The majority of these people lack access to sanitary sewers and the conditions under which they live give rise to debilitating viral, bacterial, and protozoal diseases. At the other end of the living standard scale, a relatively small fraction of the world's population consumes an inordinate amount of resources with lifestyles that involve living too far from where they work in energy-wasting houses that are far larger than they need, commuting long distances in large "sport utility vehicles" that consume far too much fuel, and overeating to the point of unhealthy obesity with accompanying problems of heart disease, diabetes, and other obesity-related maladies.

As We Enter the Anthropocene

Humans have gained an enormous capacity to alter Earth and its support systems. Their influence is so great that we are now entering a new epoch, the **Anthropocene**, in which human activities have effects that largely determine conditions on the planet. The major effects of humans upon Earth have taken place within a minuscule period of time relative to that during which life has been present on the planet or, indeed, relative to the time that modern humans have existed. These effects are largely unpredictable, but it is essential for humans to be aware of the enormous power in their hands — and of their limitations if they get it wrong and ruin Earth and its climate as life support systems.

Achieving Sustainability

Although the condition of the world and its human stewards outlined above sounds rather grim and pessimistic, this is not a grim and pessimistic book. That is because the will and ingenuity of humans that have given rise to conditions leading to deterioration of Planet Earth can be — indeed, are being — harnessed to preserve the planet, its resources, and its characteristics that are conducive to healthy and productive human life. The key is **sustainability** or **sustainable development** defined by the Bruntland Commission in 1987 as *industrial progress that meets the needs of the present without compromising the ability of future generations to meet their own needs*. 1A key aspect of sustainability is the maintenance of Earth's **carrying capacity**, that is, its ability to maintain an acceptable level of human activity and consumption over a sustained period of time. Although change is a normal characteristic of nature, sudden and dramatic change can cause devastating damage to Earth support systems. Change that occurs faster than such systems can adjust can cause irreversible damage to them. In addition to its main theme of green chemistry, a major purpose of this book is to serve as an overview of the science and technology of sustainability emphasizing sustainable chemistry as well as the general science and technology of sustainability.

Rethinking Environmentalism and Sustainability

The common view of a good, sustainable environment as a rural, low-population-density area may be misleading. A convincing argument for this proposition is made in the 2009 book *Green Metropolis: Why Living Smaller, Living Closer, and Driving Less are the Keys to Sustainability*.2Classified as an "eco-urbanist manifesto," this book makes the somewhat surprising case that New York City's Manhattan is a model of sustainability for the modern overpopulated world. This densely populated compact city emits less than one third as much greenhouse gas per person compared to the average for the United States. One reason why this is so is that the large apartment buildings and other large structures in New York City are very efficient in conserving heat; that which leaks from one tends to end up heating another. Cold air produced by air conditioning in the summer is similarly conserved. Another reason that the city is energy-efficient stems from its outrageously congested traffic and lack of affordable parking meaning that the automobile is impractical for most residents thereby forcing reliance on far more efficient public transportation. Only about one-fifth of New York City's residents regularly commute with individual automobiles. In contrast, those who live "close to nature" in rural settings tend to dwell in free-standing houses that are inherently less energy efficient than apartment buildings and by necessity they must commute with energy-wasting vehicles. If they live on unimproved roads they may require especially inefficient large, rugged four-wheel-drive vehicles. Compensation cannot be made for such a lifestyle by measures advocated by many environmentalists, such as backyard compost piles and fuel-efficient vehicles.

According to *Green Metropolis*, New York City, which has a population density more than 800 times that of the U.S. as a whole and about 30 times that of Los Angeles, offers a model for a growing world population to exist within the confines of Earth's limited resources. The prescription for sustainability is to "live smaller, live closer, and drive less." To that may be added "reproduce less" in that dense urban environments tend to discourage large families. A major culprit in the development of modern environmental problems is the public obsession with the private automobile, which enables destructive urban sprawl and excessive consumption of gasoline. One of the unintended consequences of the laudable goal of increased fuel economy in automobiles is to make them more affordable to use, thus facilitating destructive urban sprawl. The automobile-based societies of the U.S. and many other industrialized nations has been made possible by the exploitation of relatively abundant and inexpensive petroleum. In years to come, as petroleum inevitably becomes more scarce and expensive, these societies will have to undergo wrenching changes, the best end result of which would be much more sustainable, compact urban societies

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1.2: The Environment and the Five Environmental Sphere

Since this book deals with the environment, it is important to know what is meant by the environment. Essentially, the **environment** consists of our surroundings, which may affect us and which, in turn, we may affect. A part of the environment may consist of rock formations several kilometers below Earth's surface, so deep that humans cannot reach them and of which they are scarcely aware except in those instances when the rock formations shift along a fault line and cause an earthquake, which may be very destructive and take many lives. Another part of the environment is the atmosphere touching Earth's surface, a part of the environment with which humans are always in contact and which is essential for the life-giving oxygen that they require. In discussing the environment it is helpful to regard it as consisting of the following five spheres as shown in Figure 1.1: (1) The **hydrosphere**, (2) the **atmosphere**, (3) the **geosphere**, (4)the **biosphere**, and (5) the **anthrosphere** (that part of the environment constructed and operated by humans). These spheres overlap and interact strongly. For example, fish are part of the biosphere, dwell in the hydrosphere, and acquire dissolved oxygen that they need from the atmosphere. Mineral nutrients required by the fish and by the algae upon which the fish feed come from the geosphere. The part of the hydrosphere in which the fish reside may be a reservoir constructed by impounding a stream with a dam that is part of the anthrosphere. Many other such examples may be cited.

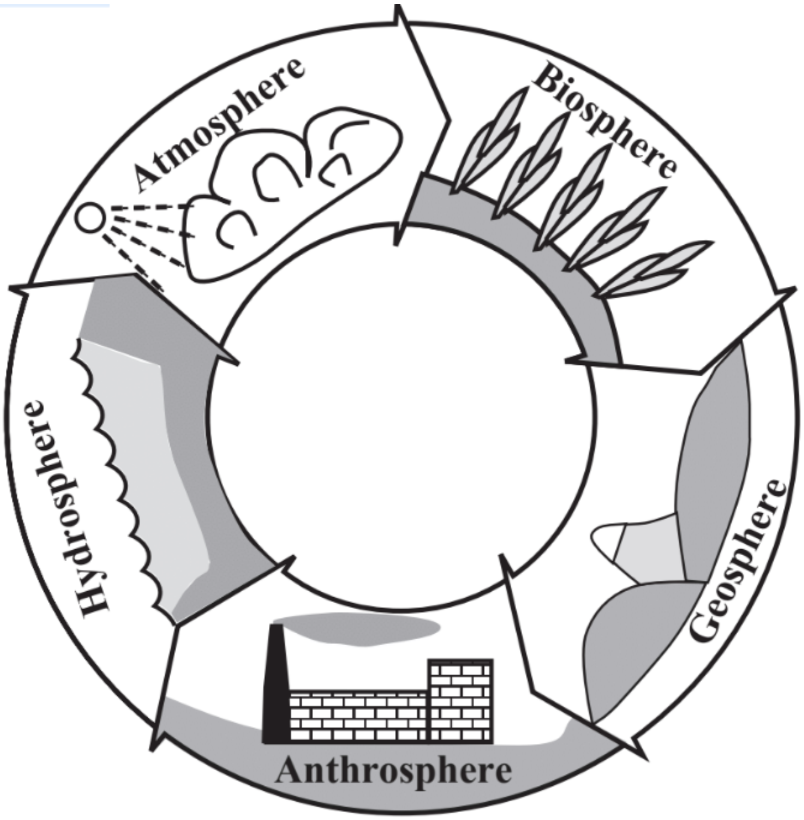

Figure 1.1. The environment may be considered as consisting of five spheres that exchange materials and energy, largely through biogeochemical cycles.

Biogeochemical cycles describe the exchange of materials among the five environmental spheres. Aspects of these environmentally crucial cycles are covered in various parts of this book. As the name implies, these cycles involve biological and geochemical phenomena but may also include processes that occur in the atmosphere and the hydrosphere as well as human influences on them. An important part of these cycles consists of the interfaces between the environmental spheres. The interfaces are often very thin with respect to Earth's whole environment. An important example of such an interface is the one between the geosphere and the atmosphere where most plants grow that support life on Earth. Typically this region extends into the geosphere for only the meter or less penetrated by plant roots and into the atmosphere only to the height of the plants. Within this region there are other interfaces including the biosphere/geosphere boundary between plant roots and soil and the biosphere/atmosphere boundary across which oxygen and carbon dioxide gas are exchanged between leaf surfaces and the atmosphere.

The study of the environment is **environmental science**, in its broadest sense the science of the complex interactions that occur among the terrestrial, atmospheric, aquatic, living, and anthropological systems that compose Earth and the surroundings that may affect living things.[3] It includes all the disciplines, such as chemistry, biology, ecology, sociology, and government, that affect or describe these interactions. For the purposes of this book, environmental science will be defined as the study of the earth, air, water, and living environments, and the effects of technology there on. To a significant degree, environmental science has evolved from investigations of the ways by which, and places in which, living organisms carry out their life cycles. This discipline used to be known as natural history, which later evolved into ecology, the study of environmental factors that affect organisms and how organisms interact with these factors and with each other.

1.3: Seeing Green

Given the dependence of humans upon a livable environment, it is essential that it be maintained in a healthy state. The maintenance of a healthy environment is commonly termed **sustainability**. In recent years there has been a lot of activity in the area of sustainability. Earlier efforts in the sustainability arena centered around pollution and its effects. Degradation of the environment has been a concern of thoughtful people for many decades. Dating back to the early 1800s and even before, the widespread use of high-sulfur coal for fuel was noted as a cause of bad air quality and impaired visibility in urban areas such as London. Water polluted by pathogenic microorganisms sickened and killed millions of people for many centuries. By the end of World War II, the atmosphere of Los Angeles had become noxious, irritating, and unhealthy due to the presence of ozone and other chemical oxidants, aldehydes, and small particulate matter. In some respects, this condition resembled pollution of the London atmosphere observed earlier, which was a combination of smoke and fog which some called “smog.” So the condition afflicting Los Angeles and a number of similar cities came to be known as smog, but a kind of smog that developed in air having low humidity and exposed to intense sunlight, conditions opposite of those under which London smog was formed. Chemically, the two kinds of smog were totally different in that London smog was in a reducing atmosphere with high concentrations of chemically reducing SO_2 whereas the Los Angeles smog is oxidizing and any SO_2 emitted to it is rapidly oxidized to sulfuric acid.

Concern over deterioration of the environment increased with the 1962 publication of Rachel Carson’s classic book *Silent Spring*,[4] the theme of which was that DDT and other mostly pesticidal chemicals were becoming concentrated through the food chain with the result that birds at the top of the chain, such as eagles and hawks, were producing eggs with soft shells that failed to produce viable baby birds. The implication was that substances harming bird populations might harm humans as well.

By about 1970 it was generally recognized that air, water, and land pollution was reaching intolerable levels. As a result, various countries passed and implemented laws designed to reduce pollutants and to clean up waste chemical sites at a cost that has easily exceeded one trillion dollars globally.

More recently concern over environmental pollution has extended beyond a narrow focus upon pollution and its effects to include the broader area of sustainability. The achievement of sustainability certainly requires avoiding pollution and counteracting its effects. But it also mean maintaining flows of essential materials, energy, food, safe water, healthy air, and the other things that humans and other organisms on Planet Earth require for their survival and well-being.

The term “green” has come to stand for sustainability in its various forms and is used throughout this book. Most of sustainability has to do with matter, and chemistry is the science of matter. It is only natural, therefore, that sustainable chemistry is now known as green chemistry, a discipline that has developed rapidly since about the mid-1990s. This book is about green chemistry. But the practice of green chemistry involves more broadly green science and technology, which are discussed in this book and related to green chemistry.

1.4: Natural Capital of the Earth

All of that very small group of humans who have been privileged to view Earth from outer space have been struck with a sense of awe at the sight. Photographs of Earth taken at altitudes high enough to capture its entirety reveal a marvelous sphere, largely blue in color, white where covered by clouds, with desert regions showing up in shades of brown and red. But Earth is far more than a beautiful globe that inspires artists and poets. In a very practical sense it is a source of the life support systems that sustain humans and all other known forms of life. Earth obviously provides the substances required for life including water, atmospheric oxygen, carbon dioxide from which billions of tons of biomass are made each year by photosynthesis, and ranging all the way down to the trace levels of micronutrients such as iodine and chromium that organisms require for their metabolic processes. But more than materials are involved. Earth provides temperature conditions conducive to life and a shield against incoming ultraviolet radiation, its potentially deadly photons absorbed by molecules in the atmosphere, their energy dissipated as heat. Earth also has a good capacity to deal with waste products that are discharged to the atmosphere, into water, or into the geosphere.

The capacity of Earth to provide materials, protection, and conditions conducive to life is known as its **natural capital,** which can be regarded as the sum of two major components: **natural resources** and **ecosystem services**. These conditions are giving rise to a new business model termed **natural capitalism**. Early hunter-gatherer and agricultural human societies made few demands upon Earth's natural capital. As the industrial revolution developed from around 1800, natural resources were abundant and production of material goods was limited largely by labor and the capacity of machines to process materials. But now population is in excess, computerized machines have an enormous capacity to process materials, and the availability of natural capital is the limiting factor in production including availability of natural resources, the vital life-support ability of ecological systems, and the capacity of the natural environment to absorb the byproducts of industrial production, most notably greenhouse gas carbon dioxide.

Rather than the adversarial relationship that has prevailed between the traditional business community and environmentalists with regard to economic development, a functioning system of natural capitalism properly values natural and environmental resources. The goal of natural capitalism is to increase well-being, productivity, wealth, and capital while reducing waste, consumption of resources, and adverse environmental effects. The traditional capitalist economic system has proven powerful in delivering consumer goods and services using the leverage of individual and corporate incentives. A functional system of natural capitalism retains these economic drivers while incorporating sustainable practices such as recycling wastes back into the raw material stream and emphasizing the provision of services rather than just material goods. In so doing a system of natural capitalism emulates nature's systems through the practice of industrial ecology, discussed in detail in Chapter 14, and the application of the principles of green chemistry (see Chapter 2).

The development of a functional system of natural capitalism requires several important changes in business practices. These include the following:

1. Implement technologies that are highly productive with greatly reduced use of nonrenewable minerals and energy.
2. Develop systems in which waste materials and energy from one sector are utilized by another sector (a functioning system of industrial ecology).
3. Change business models from those that emphasize selling goods to those that concentrate upon providing services, for example, by selling fewer automobiles and providing better mass transportation systems.
4. Reinvest in natural capital to increase production of ecosystem services. An example is the provision of constructed wetlands as part of wastewater treatment systems to provide wildlife breeding grounds along with finishing of treated wastewater effluent.

Evolution of the Utilization of Natural Capital

Figure 1.4.1 shows the burden on Earth's natural capital as a function of the progression of economic development. During pre-industrial times the capacity of humans to deplete natural capital was minimal, largely because of limitations on the rates at which energy could be used. As the industrial revolution developed and humans learned how to harness energy sources, particularly from fossil fuels, Earth's natural capital was increasingly consumed in areas such as exploitation of depleting resources and utilization of the hydrosphere, geosphere, and atmosphere for the disposal of wastes. As industrialization progressed, it became increasingly obvious that it was causing problems in areas such as air and water pollution, soil erosion exacerbated by the capabilities of fossil-fueled tillage machinery to disturb soil, and depletion of rich ore sources necessitating the mining of much larger amounts of less rich ores to obtain needed quantities of

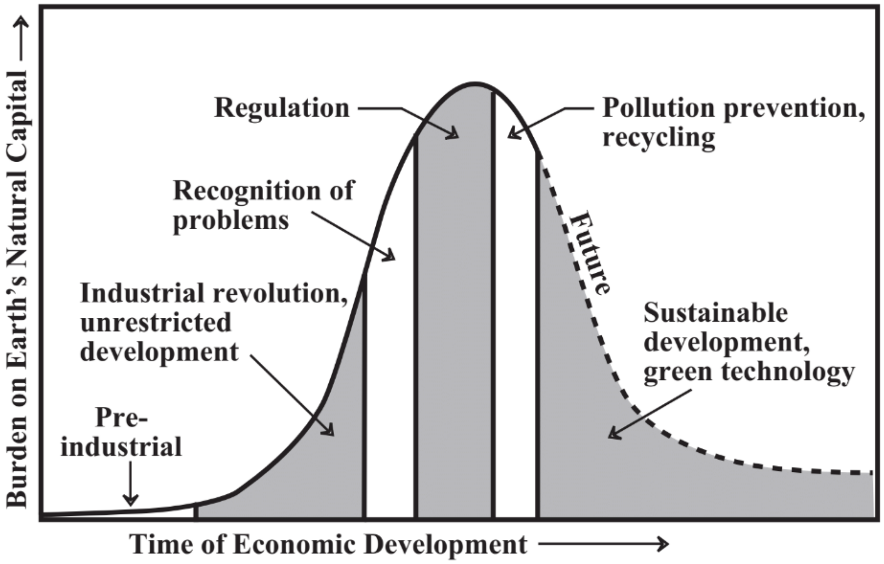

Figure 1.4.1. Stages of economic development with respect to utilization of Earth's natural capital.

metals and other geospheric resources. As a consequence, laws were passed and regulations put into place to reduce pollution and to conserve resources. Particularly after the devastating Dust Bowl years of the 1930s in which much productive topsoil was lost to wind erosion, the U.S.government initiated programs of soil conservation with incentives to preserve the essential soil resource. Efforts to reduce air and water pollution concentrated initially on the most obvious pollutants, such as particles emitted from smokestacks, followed by greater emphasis upon more insidious pollutants, such as heavy metals in water. The regulatory approach has been evolving into one that emphasizes pollution prevention, recycling, and conservation of energy and materials. A final phase is sustainable development and utilization of green technology that can support growing economic development while substantially reducing exploitation of Earth's natural capital.

1.5: Sustainability as a Group Effort- It Takes a (Very Big) Village

The achievement of sustainability and preservation of natural capital requires intense efforts by both individuals and groups. This was illustrated centuries ago in England by “the tragedy of the commons”[5]. The commons consisted of a pasture shared by village residences to provide forage for their cows, sheep, and horses. An individual family could increase its wealth (in meat, milk, or horsepower) by adding an animal. For example, a one-cow family could double its wealth in cows by buying another and putting it to graze in the pasture. If the pasture was accommodating 100 cows, for example, this would have an apparent cost of only about 1% for the small community as a whole. The natural tendency was for families to keep on adding cows until a point was reached at which the pasture became exhausted and unproductive due to overgrazing, the animals died or had to be slaughtered, and the entire support system to provide milk and meat based upon the natural capital of the pasture in the commons collapsed. During the fourteenth century this unfortunate circumstance became so widespread that the economies of many villages collapsed with whole populations no longer able to provide for their basic food needs.

History has many examples of the tragedy of the commons. As an example, when the settlers began to cultivate what was formerly open rangeland in Edwards County, Texas, in the 1880s the ranchers who had used it for pasture met and proclaimed the following: “Resolved that none of us know, or care to know, anything about grasses, native or otherwise, outside of the fact that for the present, there are lots of them, the best on record, and we are getting the most of them while they last.”[6] Soon the combined effects of overgrazing and drought reduced the yield of grass such that the ranchers’ livelihoods were threatened and the newly cultivated land became unproductive. Shortsighted attitudes towards Earth’s natural capital similar to those expressed by the ranchers continue to lead to many tragedies of the commons. In modern times heavy cultivation of marginal land is turning large areas to desert (desertification), the Amazon rain forest is being cut down and burned to provide a one-time harvest of wood and a few years of crop production (deforestation), severe deterioration of the global ocean fisheries resource is occurring, congested freeways at times become great linear parking lots and, of much direct concern to many university students and faculty, some parking facilities have become so oversold that their utility is seriously curtailed as paying customers cannot find parking space.

The logic of the commons holds true in modern times in which the global commons consist of the air humans must breathe, water resources, agricultural lands, mineral resources, capacity of the natural environment to absorb wastes, and all other facets of natural capital. According to the logic of the commons, each consumer has the right to acquire a segment of natural capital, the cost of which is distributed throughout the commons and shared by all. The natural competition among consumers results in some consumers acquiring relatively more of Earth’s natural capital and becoming wealthier. Within limits this is a healthy consequence of capitalist systems. However, if enough consumer units use too much natural capital, it becomes exhausted and unsustainable, therefore unable to support the society as a whole, so that all suffer, including those on top of the consumer food chain.

Automotive transportation illustrates a modern tragedy of the commons. Acquisition of an automobile adds to an individual’s possessions and mobility. The materials required to make a single automobile, the fuel to run it, and its exhaust pollutants make a minuscule impression on Earth’s natural capital. However, when millions of people acquire automobiles, the demand on Earth’s natural capital of materials, fuel, and ability to absorb pollutants becomes severely stressed, heavy traffic turns the automobile from a convenience into a burden, and, in some places at some times, the whole transportation system collapses.

These “tragedies of the commons” illustrate the limitations of unregulated “free-for-all” capitalist economic systems in achieving sustainable development and make a strong case for collective actions in the public sector to ensure that humankind can exist within the limits of Earth’s natural capital. However, the collapse of Communist economic systems around 1990 left a legacy of abandoned, inefficient factories, poverty, and environmental degradation showing the adverse effects from discouraging private enterprise. In addition to enlightened regulations that ensure preservation of Earth’s essential support systems, successful economic systems require human ingenuity, initiative, and even greed. Getting these and other incentives to work well on a planet in which natural capital is the major limiting economic factor is the huge challenge facing modern and developing economies.

There is an old African proverb that translates to, “It takes a village to raise a child.” The idea is of course that successful child-rearing requires the efforts of more than just parents, but requires the efforts of an entire village. The same principle applies to Planet Earth except that in this case billions of children are being raised and it will take the efforts of a very large village — the population of the entire world — to preserve the planet and its resources upon which those billions of children must depend for their existence.

1.6: Sustainable Energy- Away from the Sun and Back Again

As discussed in more detail in Chapter 15, the key to sustainability is abundant, environmentally safe energy. The evolution of humankind's utilization of energy is illustrated in Figure 1.6.1. Until very recently in the history of humankind we have depended upon the sun to meet our energy needs. The sun has kept most of the land mass of Earth at a temperature that enables human life to exist. Solar radiation has provided the energy for photosynthesis to convert atmospheric carbon dioxide to plant biomass providing humans with food, fiber, and wood employed for dwelling construction and fuel. Animals feeding on this biomass provided meat for food and hides and wool that humans used for clothing. Eventually humans developed means of indirectly using solar energy. This was especially true of wind driven by solar heating of air masses and used to propel sailing vessels and eventually to power windmills employed for power. The solar-powered hydrologic cycle provided flowing water, the energy of which was harnessed by water wheels. Virtually all the necessities of life came from utilization of solar energy.

The Brief Era of Fossil Fuels

Dating from around 1800, humankind began to exploit fossil fuels for their energy needs. Initially, coal was burned for heating and to power newly developed steam engines for mechanical energy used in manufacturing and steam locomotives. After about 1900 petroleum developed rapidly as a source of fuel and, with the development of the internal combustion engine, became the energy source of choice for transportation needs. Somewhat later natural gas developed as an energy source. The result was a massive shift from solar and biomass energy sources to fossil fuels. Utilization of fossil carbon-based materials resulted in a revolution that went far beyond energy utilization. One important example was the invention by Carl Bosch and Fritz Haber in Germany in the early 1900s, of a process for converting atmospheric elemental nitrogen from air to ammonia, NH_3 by the reaction of N_2 with H_2. This high-pressure, high-temperature process required large amounts of fossil fuel to provide energy and to react with steam to produce elemental hydrogen. The discovery of synthetic nitrogen fixation enabled the production of huge quantities of relatively inexpensive nitrogen fertilizer and the resulting increase in agricultural production may well have saved Europe, with a rapidly developing population at the time, from widespread starvation. (It also enabled the facile synthesis of great quantities of nitrogen-based explosives that killed millions of people in World War I and subsequent conflicts.) Fossil fuel, which has been described as "fossilized sunshine,"[7] resulted in an era of unprecedented material prosperity and an increase in human population from around 1 billion to over 6 billion.

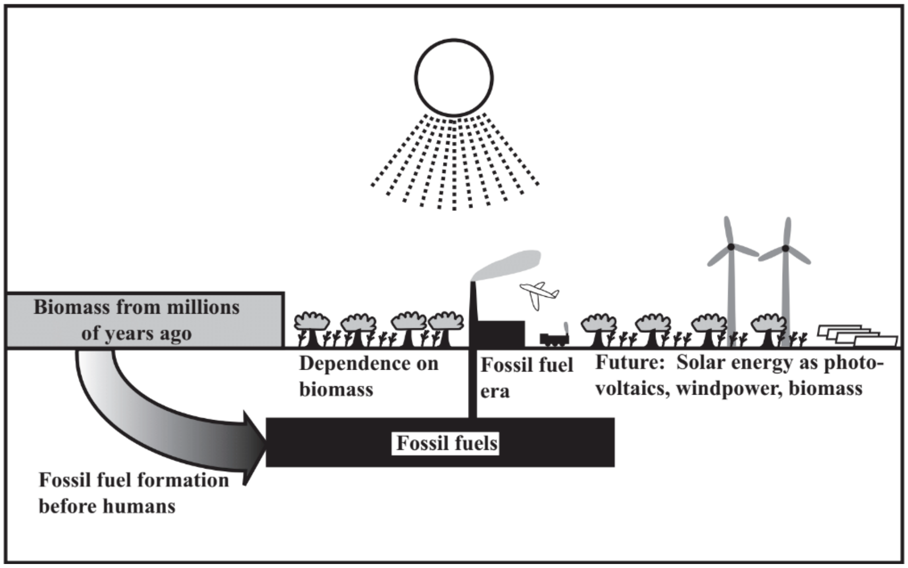

Figure 1.6.1, Evolution of the use of energy from solar and biomass sources through the brief, but spectacular, era of fossil fuels and on to renewable solar-based sources

By the year 2000 it had become obvious that the era of fossil fuels was not sustainable. One reason is that fossil fuel is a depleting resource that cannot last indefinitely as the major source of energy for the industrial society to which it has led. Approximately half of the world's total petroleum resource has already been consumed so that petroleum will continue to become more scarce and expensive and can last for only a few more decades as the dominant fuel and organic chemicals raw material. Coal is much more abundant, but its utilization leads to the second reason that the era of fossil fuels must end because it is the major source of anthropogenic atmospheric carbon dioxide, greatly increased levels of which will almost certainly lead to global warming and massive climate change. Natural gas (methane, CH_4) is an ideal, clean-burning fossil fuel that produces the least amount of carbon dioxide per unit energy generated. Rapidly expanding new discoveries of natural gas largely from previously inaccessible tight shale formations means that it can serve as a "bridging fuel" for several decades until other sources can be developed. Nuclear energy, properly used with nuclear fuel reprocessing, can take on a greater share of energy production, especially for base load electricity generation. But clearly drastic shifts must occur in the ways in which energy is obtained and used.

Back to the Sun

With the closing of the brief but spectacular era of fossil hydrocarbons, the story of humankind and its relationship to Planet Earth is becoming one of "from the sun to fossil fuels and back again" as humankind returns to the sun as the dominant source of energy and photosynthetic energy to convert atmospheric carbon dioxide to biomass raw materials. In addition to direct uses for solar heating and for photovoltaic power generation, there is enormous potential to use the sun for the production of energy and material. Arguably the fastest-growing energy source in the world is wind-generated electricity. The wind is produced when the sun heats masses of air causing the air to expand. Once the dominant source of energy and materials, biomass produced by solar-powered photosynthesis is beginning to live up to its potential as a source of feedstocks to replace petroleum in petrochemicals manufacture and of energy in synthetic fuels (see Chapter 14,"Chapter 14 Feeding the Anthrosphere: Utilizing Renewable and Biological Materials" and Chapter 15, "Sustainable Energy: The Essential Basis of Sustainable Systems"). Biomass is still evolving as a practical source of liquid fuels. The two main ones of these are fermentation to produce ethanol and synthesis of biodiesel fuel made from plant lipid oils. Unfortunately, although ethanol made from sugar derived from sugar cane that grows prolifically in some areas such as Brazil is an economical gasoline substitute, the net energy gain from ethanol derived from cornstarch relies on the grain, the most valuable part of the plant otherwise used for food and animal feed; the net energy gain is marginal. The economics of producing synthetic biodiesel fuel from sources such as soybeans may be somewhat better. However, production of this fuel from oil palm trees in countries such as Malaysia is resulting in destruction of rain forests and diversion of palm oil from the food supply.

Practical means do exist to utilize biomass for energy and materials without seriously disrupting the food supply. Arguably the best way to do that is to thermochemically convert biomass to synthesis gas, a mixture of CO and H_2 that can be combined chemically by long-established synthetic routes to produce methane, larger-molecule hydrocarbons, alcohols and other products (see Chapter 15). The main pathway for so doing is to utilize biomass from renewable non-food biosources, which include crop byproducts (wheat straw, rice straw, cornstalks produced in surplus during the production of grain) and dedicated crops among which are highly productive hybrid poplar trees and sawgrass. Microscopic algae are especially promising as a biomass source because of their much higher productivity than terrestrial plants, their ability to grow in brackish(somewhat saline) water in containments in desert areas, and their ability to utilize sewage as a nutrient source. When biomass is used to produce synthesis gas, the essential nutrients, especially potassium and phosphorus, can be reclaimed from the biomass residues and used as fertilizer material to promote the growth of additional biomass.

Future scientific discoveries and technological advances will play key roles in the achievement of energy sustainability. Three areas in which Nobel-level breakthroughs are needed in the achievement of energy sustainability were expressed in a February 2009 interview by Dr.Steven Chu, a Nobel Prize winning physicist who had just been appointed Secretary of Energy inU.S. President Barack Obama's new administration. The first of these is in solar power in which the efficiency of solar energy capture and conversion to electricity needed to improve several-fold. A second area of need is for improved electric batteries to store electrical energy generated by renewable means and to enable practical driving ranges in electric vehicles. A third area in need of a quantum leap is for improved crops capable of converting solar energy to chemical energy in biomass by photosynthesis at much higher efficiencies than the current levels of less than 1%achieved by many crops. In this case the potential for improvement is enormous because most plants convert less than 1% of the solar energy falling on them to chemical energy through photosynthesis. Through genetic engineering, it is likely that this efficiency could be improved several-fold leading to vastly increased generation of biomass. Clearly, the achievement of sustainability employing high-level scientific developments will be an exciting development in decades to come

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1.7: Green Science

As shown in Figure 1.7.1, science, engineering, and technology are closely interrelated. Science refers to a set of rigorously organized bodies of knowledge and their acquisition based upon several criteria. Dealing with the discovery, explanation, and development of theories pertaining to interrelated natural phenomena of energy, matter, time, and space, science consists of an organized body of facts consistent with a number of general laws that are verifiable by rigorously defined systematic experimental processes composing the **scientific method**. Although science seeks to avoid value judgements, scientific methods are used for worthy goals, such as development of genetically based cures for disease, as well as for more sinister purposes, such as the synthesis of more deadly military poisons. **Pure science** is conducted to extend knowledge without defined practical goals and **applied science** is directed toward practical, usually commercial, objectives; these two aspects of science are commonly applied together. Especially with the explosive growth of the internet, which allows dissemination of both information and misinformation, it is important to beware of "junk science" often used to attempt to support political, economic, or theological agendas in areas such as climate change and evolution.

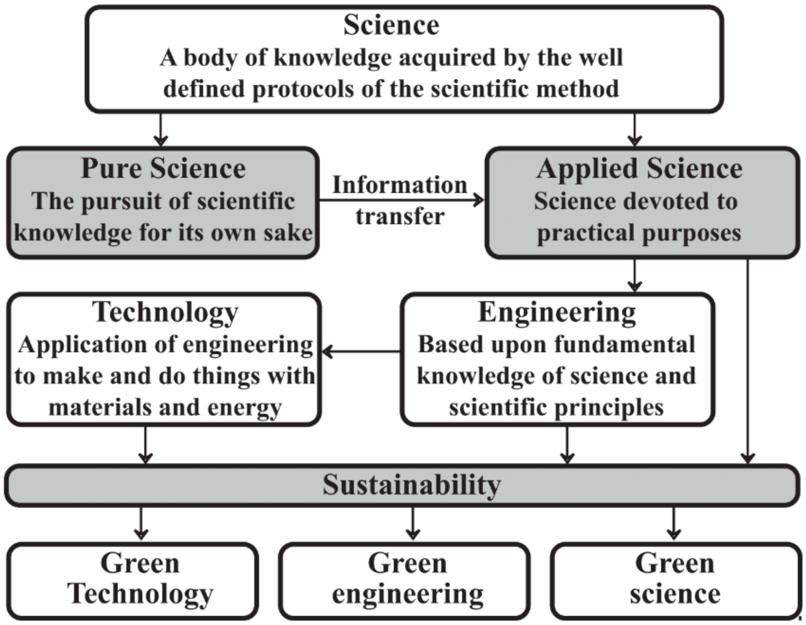

Figure 1.7.1, . Scientific principles are the basis of engineering which guides the development of technologies to make and dothings with materials and energy. As Earth's natural capital becomes more limiting, green technology, green engineering, and green science have become crucial to maintaining the planet's environment in a livable state.

The practice of science dedicated to sustainability including the maintenance of environmental quality, the reduction of hazards, the efficient use of environmentally benign sources of energy, and the minimization of consumption of non-renewable resources is the basis of **green science**, which is one of the main themes of this book. Chemical science, the science of matter, has great accomplishments to its credit in improving human welfare but it has also led to environmental pollution, exposure to hazardous substances, consumption of resources such as petroleum feedstocks, and other unpleasant aspects of modern industrialized societies. These problems can be mitigated by the constructive application of chemical science known as **green chemistry** defined as the *practice of chemistry in a manner that maximizes its benefits while eliminating or at least greatly reducing its adverse impacts.*[8] Based upon "twelve principles of green chemistry,"9since the mid-1990s the science of green chemistry has spawned a number of books, journal articles, and symposia as well as journals devoted to the topic and centers and societies of green chemistry. This book is primarily about green chemistry and how it relates to sustainability, green science, and green technology.

1.8: Green Technology

Humans direct **technology** toward practical ends to make things they need with materials and to utilize energy in manufacturing, transportation, and the maintenance of hospitable living conditions. Long a matter of applied human ingenuity, technology is now mostly the product of engineering based on the fundamental knowledge of science and application of scientific principles. Technology uses the plans and means to achieve specific practical objectives provided by engineering to carry out desired objectives. Technology obviously has enormous importance in determining how human activities affect Earth and its life support systems.

Three great “growth spurts” in human populations that have taken place since modern humans first appeared on Earth have been enabled by developments in technology that enabled successively higher levels of human populations to exist. The first of these culminating about 10,000 years ago with a human population of perhaps 2 or 3 million was enabled by the primitive, but remarkably effective tools that early humans developed. One such technology was the bow and arrow which allowed for killing game at a much safer distance from the unwilling and often dangerous source of meat than that required for spearing or clubbing the quarry. The technology for making garments from animal hides allowed humans to avoid potentially fatal hypothermia from exposure to Ice Age climates.

About 10,000 years ago a second population growth spurt got underway as the “hunter/gatherer” societies that had sustained humans evolved into more reliable agricultural societies when humans learned to cultivate crops and domesticate animals used for meat, milk, and wool. These societies ensured a generally dependable food supply in smaller areas. As a result, humans were able to gather food from relatively small agricultural fields rather than having to scout large expanses of forest or grasslands for game to kill or berries to gather. Agricultural economic systems were based upon newly evolved technologies for cultivating soil, utilizing irrigation, and transporting food for trade by primitive sailing vessels. Ancillary technologies such as spinning wheels and looms for turning wool and plant fibers into cloth and water-powered mills for grinding grain also appeared. The development of agricultural systems had the major effect of allowing humans to remain in one place in settlements and, freed from the necessity of having to constantly hunt and gather food from their natural surroundings, humans could apply their ingenuity in areas such as developing more sophisticated tools. The agricultural revolution allowed a second large increase in numbers of humans and enabled the development of a human population of around 100 million 1000 years ago.

The third great growth spurt in human populations came with the industrial revolution, beginning slowly several centuries ago and made possible by the ability to utilize energy other than that provided by human labor and animal power. Initially wind power and water power were harnessed for mills and factories to use to produce goods. After about 1800 this power potential was multiplied many-fold with the steam engine and later the internal combustion engine, turbines, nuclear energy, and electricity, enabling current world population of almost 7 billion and growing at an eventually unsustainable rate (though not as fast as some of the more pessimistic projections from past years).

Unintended Consequences and the Need for Green Technology

According to the **law of unintended consequences**, the predicted benefits of new technologies are often accompanied by substantial problems, sometimes called revenge effects, due to the unforeseen ways in which people interact with new technologies. The individual freedom of movement and huge economic boost that resulted from the nascent automobile industry were accurately predicted by visionaries in the early 1900s, but they did not foresee the millions of deaths from automobile accidents, unhealthy polluted air in urban areas, urban sprawl, and depletion of petroleum resources that occurred in the following century. The tremendous educational potential of personal computers was visualized when the first of these came on the market. Less predictable were the mind-numbing hours that young people (and some not so young) would waste playing senseless computer games or viewing questionable content on the internet.

Defined as technology applied in a manner that minimizes environmental impact and resource consumption and maximizes economic output relative to materials and energy, **green technology** is designed to foresee and avoid revenge effects. Aided by increasingly sophisticated computer methodologies, the practitioners of green technology attempt to predict undesirable consequences of new technologies and put in place preventative measures before revenge effects have a chance to develop and cause major problems. A key component of the implementation of green technology is careful consideration of the practice of **industrial ecology**, which integrates the principles of science, engineering, and ecology in industrial systems through which goods and services are provided in a way that minimizes environmental impact and optimizes utilization of resources, energy, and capital. Above all a sustainable means of providing goods and services, industrial ecology considers every aspect of so doing from concept, through production, and to the final fate of products remaining after use. It is most successful in its application when it mimics natural ecosystems, which are inherently sustainable by nature. Rather than organisms and populations of organisms working in natural ecosystems, industrial ecology works through **industrial ecosystems** consisting of groups of industrial concerns, distributors, and other enterprises functioning to mutual advantage, using each others' products, recycling each others' potential waste materials, and utilizing energy as efficiently as possible. Industrial ecology is discussed in some detail in Chapter 13, "The Anthrosphere, Green Chemistry, and Industrial Ecology."

1.9: Sustainability and the Eco-Economy

An important component of green technology is **life-cycle analysis** (assessment) which considers process and product design in the management of materials from their source through manufacturing, distribution, use, reuse (recycle), and ultimate fate. The objective of life-cycle analysis is to determine, quantify, and minimize adverse resource, environmental, economic, and social impacts. The four major facets of life-cycle analysis are(1)determination of the scope of the assessment; (2) inventory analysis of materials mass and energy to enable development of mass and energy balances; (3) analysis of impact on the environment, human health, and other impacted areas; and (4) improvement analysis to determine ways in which greater efficiencies maybe achieved.

Life-cycle analysis is summarized in Figure $1.9.1$. Note that there are several possible recycling loops ranging from simple product reuse through material reprocessing and fabrication to waste mining in which wastes are processed to reclaim useful materials that can go back into the manufacturing process.

The **eco-economy** is one in which the production of goods and services is totally integrated with the natural world. The practice of **eco-efficiency** (Figure $1.9.2$) enables provision of affordable goods and services to satisfy human needs sustainably, doing so with the minimum consumption of Earth's natural capital and with most efficient utilization of energy. The practice of eco-efficiency has several major aspects related to sustainability. Dematerialization seeks to meet economic needs with minimum amounts of material using renewable and recycled sources wherever possible. Analogous to dematerialization is "de-energyization" which uses only minimum amounts of energy and takes energy from renewable sources. Service and knowledge flows are substituted for material flows wherever possible. Using natural ecosystems as models, production loops are closed to the maximum extent possible. Sustainability is enhanced by shifting from a supply-driven to a demand-driven economy. Rather than manufacturing large quantities of material goods that are then vigorously marketed, the emphasis is placed upon finding the real needsof consumers, then meeting them in the most efficient way possible. Functional extension is achieved by manufacturing products with enhanced functionality and selling services to increase product functionality. Eco-efficient products are designed to be as durable as possible consistent with their intended uses, to be long-lived, and designed for ease of recycling of components and materials. Dispersion of toxic materials is minimized or eliminated in eco-efficient systems.

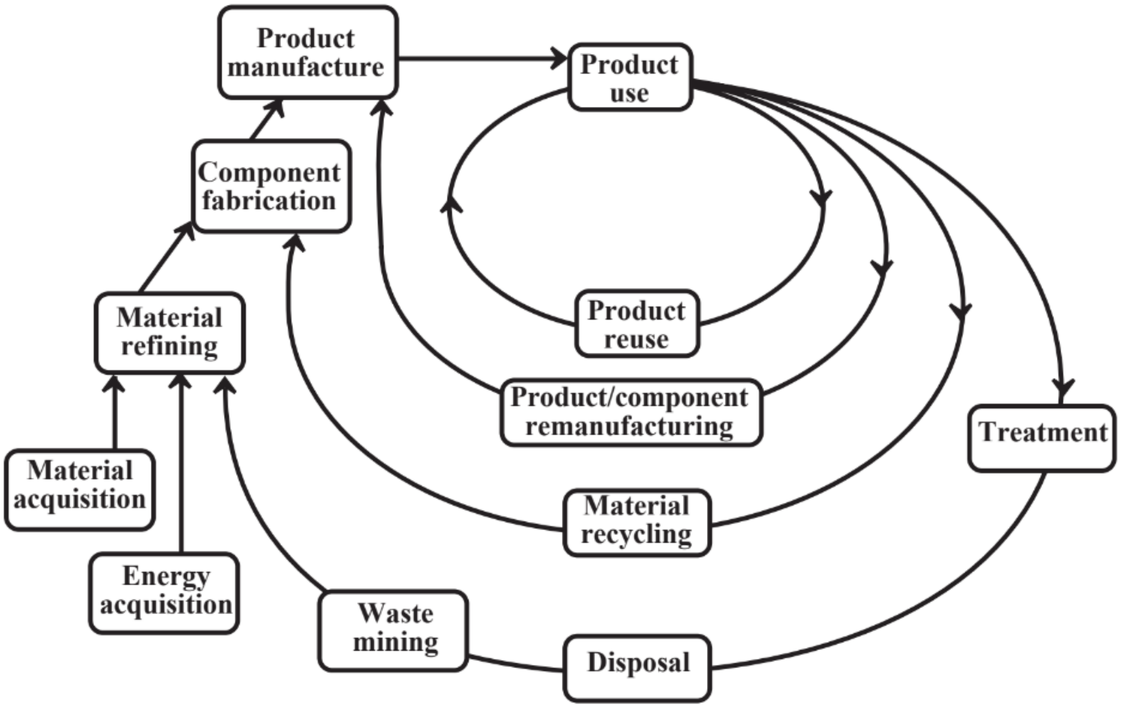

Figure $1.9.1$. Various levels of materials use employed in life-cycle analysis. The inner loops are most desirable from the viewpoint of sustainability

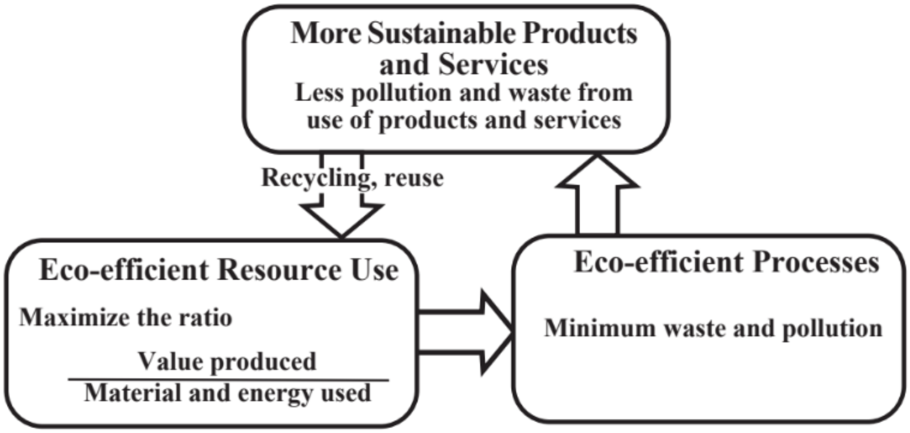

Figure 1.9.2 Achievement of sustainability with eco-efficient resource use and eco-efficient processes

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1.10: Green Products and Services- Design for Sustainability

Green products use relatively smaller amounts of material and energy and throughout their life cycles from manufacture to disposal minimize exposure of humans and the environment to hazardous substances, pollutants, and wastes. A **green service** fulfills these criteria in providing a service. A hybrid fuel/electric automobile with a capability of recharging its battery from the electrical grid has minimum environmental and sustainability impact so it is a green product. The function of such an automobile can be replaced by a green service consisting of efficient rail and bus transportation.

Green products have several characteristics in common. One is high durability so long as it does not pose undue disposal problems. Another characteristic is low potential for exposure to toxic substances. A green product comes with minimal, recyclable packaging and is generally reusable, repairable, and capable of being remanufactured. Green materials used in consumer applications are relatively more concentrated with minimum inert ingredients so that they are economical to transport (a concentrated liquid laundry detergent compared to detergent in a granular formulation containing a lot of filler). Business and governmental practices and infrastructures can determine product sustainability. For example, a sustainable product requires that it be easily repaired and that repair parts are readily available. The sustainability of electrical batteries requires dropoff points and infrastructure for recycling of the materials in the batteries. A good example is the need for facilities to reclaim and recycle the lithium in lithium ion batteries as these sources of electrical energy storage become more popular in a world where sources of lithium are limited. Efforts have been made in some countries to require product take-back to enforce recycling components and materials in spent products.

The practices of design **for environment and design for sustainability are** key aspects of eco-efficiency.[10]In the practice of design for environment, environmental performance and potential environmental impacts are given priority consideration in the earliest stages of product development including raw materials acquisition, manufacturing, packaging, distribution, installation, operation, and ultimate fate at the end of the useful product lifetime. Design for sustainability does much the same thing with emphasis upon minimizing impact upon Earth's natural capital.

The following is a list of some specific design characteristics that go into design for environment and design for sustainability:

- Material substitution to use readily available materials from renewable sources that require relatively less energy for processing and that are recyclable,nontoxic, and environmentally friendly
- Minimize packaging
- Products with long lifetimes
- Promote recycling and reuse with products designed for separability, disassembly, reuse, remanufacture and recyclability.
- Consumptive materials should be biodegradable or capable of being burned for energy without emitting harmful byproducts (avoid bound halogens and heavy metals in plastics)

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Questions and Problems

Access to and use of the internet is assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be "right."

1. According to some environmentalists, Earth is now entering the Anthropocene epoch. What is an epoch? In which epoch have humans lived until now? What are some of the past epochs that Earth has been through? Approximately when was the term Anthropocene coined and who is responsible for it?

2. It is noted in this chapter that the narrow layer between the geosphere and atmosphere where plants grow is an important environmental interface. The microclimate in this interface may vary significantly in its characteristics from the microclimate of the atmosphere just above it. What is microclimate? How does the microclimate in the narrow layer just described tend to vary from the climate just above it?

3. Thin layers and interfaces are very important in Earth's environment. Describe some of these layers.

4. The assertion has been made that if Earth were a classroom globe, the layer of soil covering it would be about as thick as the dimensions of a human cell. Assume that a classroom globe is 25 centimeters in diameter. Look up Earth's dimensions and using the assertion made above, calculate the average thickness of soil in cm.

5. What was the London smog disaster? When did it occur? What interaction between the atmosphere and anthrosphere caused it? Approximately how many people died as a result?

6. Approximately when did the steam engine become a practical machine? How did it enable the industrial revolution to occur? What are the analogies with current conditions in which increasingly large and sophisticated farm machinery are enabling an ongoing revolution in agriculture?

7. What was the Love Canal affair and how did it likely influence environmental laws and implementation of environmental regulations in the U.S.?

8. One of the most active areas in energy development in many nations including the U.S. is the development of new sources of natural gas. What is happening in the area of natural gas utilization? Does burning natural gas emit carbon dioxide to the atmosphere? How is it superior in that respect to coal and petroleum? What is meant by the term "bridging fuel" as applied to natural gas?

9. How are desertification and deforestation related to global warming? How do they contribute to each other? How does destruction of a rain forest contribute carbon dioxide to the atmosphere?

10. The process for chemical fixation of atmospheric nitrogen developed by Bosch and Haber in the early 1900s led to the ability to make huge quantities of explosives that subsequently took millions of lives in warfare. However, the initial product, NH_3, is not explosive. Look up the formulas of several common explosives and suggest what is done to use NH_3 to make explosives.

11. Secretary of Energy Steven Chu has suggested three areas in which Nobel-level breakthroughs are needed in the achievement of energy sustainability. Considering conditions on Earth and the rate of depletion of natural capital suggest other areas in the general area of sustainability in which breakthroughs are needed.

12. Of all nations, Brazil has been the most successful in using fuels from biological sources as renewable energy sources. What are the conditions in Brazil that have made that possible?

13. What are the major crops that enabled humans to transition from hunter/gatherer societies to agricultural societies? Where is it believed that this transition first took place and how long ago was it?

14. How does photochemical smog that plagues Los Angeles, Mexico City, and many other urban areas around the world illustrate the law of unintended consequences and revenge effects?

15. A basic premise of Green Science and Technology is that "human welfare must be measured interms of quality of life, not just acquisition of material possessions." Suggest how the dwellings of humans and their living surroundings in general might reflect such a transition.

16. Figure 1.5 reflects various levels of materials use in which the innermost loops are most desirable. The most efficient materials use is product reuse in which a product or component is put directly back into the manufacturing loop. Suggest how a high level of component reuse at the manufacturing site might in fact reflect a less than optimum manufacturing process.

17. Gross domestic product per unit of energy use is a measure of efficiency of the economic systems of various countries and probably reflects the degree to which needed goods and services are provided relative to burden on natural capital. Look up the rank of various nations with respect to this ratio. Are there any surprises in this list? Are there nations on this list with a high rank that are probably not very desirable in terms of living amenities and are there others in which the opposite is true? Suggest two or three nations that have both a high rank and a high quality of life in general?

18. Much concern is being expressed over deteriorating infrastructure in the U.S. What is infrastructure and how may its degeneration contribute to a lack of sustainability?

19. Are paper grocery bags necessarily “green?” After doing some research on paper manufacture suggest ways in which they may not be ideal for sustainability. What is a greener alternative?

20. One recipe for sustainability may be expressed as “electrons, not paper.” Suggest what is meant by this expression and how it may be implemented for sustainability

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CHAPTER OVERVIEW

2: The Key Role of Chemistry and Making Chemistry Green

“We have no choice but to deal with chemistry because all things are chemical. The human body itself is a remarkably complex chemical system composed of thousands of chemicals, the main one of which is water.”

2.1: Chemistry is Good (and Unavoidable)
2.2: The Environment and its Chemistry
2.3: What is Environmental Chemistry?
2.4: Environmental Pollution
2.5: Practice of Green Chemistry
2.6: Green Chemistry and Synthetic Chemistry
2.7: Reduction of Risk- Hazard and Exposure
2.8: The Risks of No Risks
2.9: Waste Prevention
2.10: Basic Principles of Green Chemistry
2.11: Some Things to Know About Chemistry before You Even Start
2.12: Combining Atoms to Make Molecules and Compounds
2.13: The process of making and breaking chemical bonds- chemical reactions
2.14: The Nature of Matter and States of Matter
References and Questions

2.1: Chemistry is Good (and Unavoidable)

Chapter 1 has provided an overview of environmental science and sustainability in general. Sustainability is all about the way that we deal — often poorly and wastefully — with matter and energy. As the science of matter and how it interacts with energy, **chemistry** is a crucial science in sustainability. Most of this book is about the sustainable practice of chemistry.

Many people are freaked out by the idea of chemistry and try to avoid it. But avoiding chemistry is impossible. That is because all matter, all things, the air we must breathe, the water we must drink, and all living organisms are made of chemicals. People who try to avoid all things that they regard as chemical may fail to realize that chemical processes are continuously being carried out in their own bodies. These are processes that far surpass in complexity and variety those that occur in chemical manufacturing operations. So, even those people who want to do so cannot avoid chemistry; they are, themselves, complex chemical factories. The best course of action with anything that cannot be avoided and that might have an important influence on our lives (one's chemistry professor may come to mind) is to try to understand it, to deal with it. To gain an understanding of chemistry is probably one of the main reasons why you are reading this book.

As one of its major functions, this book seeks to present a body of chemical knowledge from the most fundamental level within a framework of the relationship of chemical science to human beings, their surroundings, and their environment. Face it, the study of chemistry-based upon facts about elements, atoms, compounds, molecules, chemical reactions, and other fundamental concepts needed to understand this science, though enticing to some, is found by many to be less than exciting. However, these concepts and many more are essential to a meaningful understanding of chemistry. Anyone interested in green chemistry clearly wants to know how chemistry influences people in the world around us. So this book discusses real-world chemistry, introducing chemical principles as needed.

During the approximately two centuries that chemical science has been practiced on an ever-increasing scale, it has enabled the production of a wide variety of goods that are valued by humans. These include such things as pharmaceuticals that have improved health and extended life, fertilizers that have greatly increased food productivity and prevented widespread starvation, and semiconductors that have made possible computers and other electronic devices. Without the persistent efforts of chemists and the enormous productivity of the chemical industry, nothing approaching the high standard of living enjoyed in modern industrialized societies would be possible.

But there can be no denying that in years past, and even at present, chemistry has been misused in many respects, such as the release of pollutants and toxic substances and the production of nonbiodegradable materials, resulting in harm to the environment and living things, including humans. It is now obvious that chemical science must be turned away from emphasis upon the exploitation of limited resources and the production of increasing amounts of products that ultimately end up as waste and toward the application of chemical science in ways that provide for human needs without damaging the Earth support system and depleting its natural capital (defined in Chapter 1) upon which all living things depend. Fortunately, the practice of chemical science and industry is moving steadily in the direction of environmental friendliness and resource sustainability. The practice of chemistry in a manner that maximizes its benefits while eliminating or at least greatly reducing its adverse impacts has come to be known as green chemistry, the central theme of this book.

As will be seen in later chapters of this book, the practice of chemistry is divided into several main categories. Most elements other than carbon are involved with **inorganic chemistry**. Common examples of inorganic chemicals are water, salt (sodium chloride), air pollutant sulfur dioxide, and lime. Carbon occupies a special place in chemistry because it is so versatile in the kinds of chemical species (compounds) that it forms. Most of the tens of millions of known chemicals are substances based on carbon. These compounds are organic chemicals and addressed by the subject of organic **chemistry**. The unique chemistry of carbon is addressed specifically in Chapter 6, “The Wonderful World of Carbon: Organic Chemistry and Biochemicals.” The underlying theory and physical phenomena that explain chemical processes are explained by physical **chemistry**. Living organisms carry out a vast variety of chemical processes that are important in green chemistry and environmental chemistry. The chemistry that living organisms perform is biochemistry, which is addressed specifically in Chapters 7, “Chemistry of Life andGreen Chemistry.” It is always important to know the identities and quantities of various chemical species present in a system, including various environmental systems. Often, significant quantities of chemical species are very low, so sophisticated means must be available to detect and quantify such species. The branch of chemistry dealing with the determination of kinds and quantities of chemical species is analytical **chemistry**.

As the chemical industry developed and grew during the early and mid-1900s, most practitioners of chemistry remained unconcerned with and largely ignorant of the potential for harm — particularly damage to the outside environment — of their products and processes. Environmental chemistry was essentially unknown and certainly not practiced by most chemists. Incidents of pollution and environmental damage, which were many and severe, were commonly accepted as a cost of doing business or blamed upon the industrial or commercial sectors. The unfortunate attitude that prevailed is summarized in a quote from a standard book on industrial chemistry from 1954 (*American Chemical Industry—A History*, W. Haynes, Van Nostrand Publishers, 1954): “By sensible definition any by-product of a chemical operation for which there is no profitable use is a waste. The most convenient, least expensive way of disposing of said waste — up the chimney or down the river — is best."

Despite their potential to cause harm, nobody is more qualified to accept responsibility for environmental damage from chemical products or processes than are chemists who have the knowledge to understand how such harmful effects came about. As the detrimental effects of chemical manufacture and use became more obvious and severe, chemists were forced, often reluctantly, to deal with them. At present, enlightened chemists and chemical engineers do not view the practice of environmentally beneficial chemistry and manufacturing as a burden, but rather as an opportunity that challenges human imagination and ingenuity.

2.2: The Environment and its Chemistry

It was noted in Section 1.2 that, the *environment* consists of our surroundings, which may affect us and which, in turn, we may affect. Obviously the chemical nature and processes of matter in the environment are important. Compared to the generally well defined processes that chemists study in the laboratory, those that occur in the environment are rather complex and must be viewed in terms of simplified models. A large part of this complexity is due to the fact that the environment consists of the five overlapping and interacting spheres — the atmosphere, the hydrosphere, the geosphere, the biosphere, and the anthrosphere mentioned in Section 1.2 and shown from the viewpoint of their chemical interactions in Figure 2.2.1. In order to better understand the chemistry that occurs in these spheres they are briefly described here.

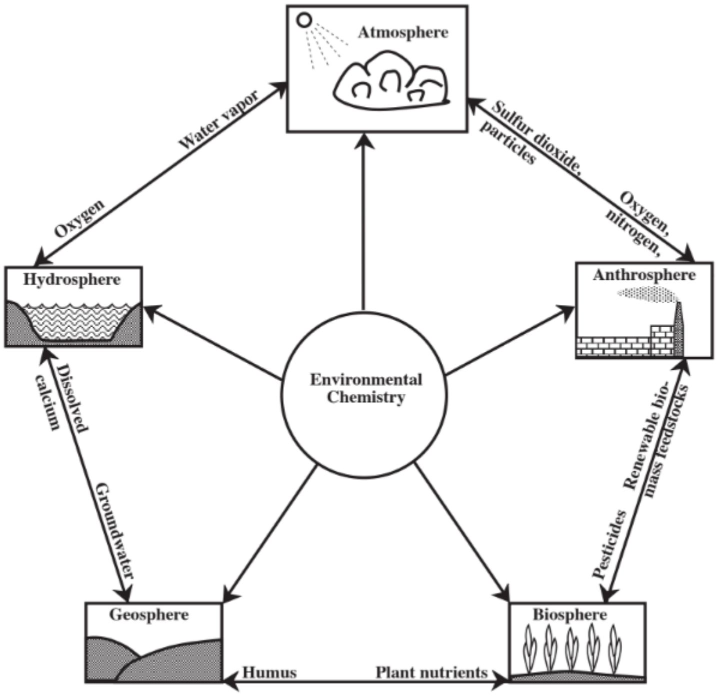


Figure 2.2.1. Illustration of the five major spheres of the environment and some of their chemical interactions. These spheres are closely tied together, interact with each other, and exchange materials and energy. A meaningful examination of environmental sciences must include all five of these spheres, including the anthrosphere.

The atmosphere is a very thin layer compared to the size of Earth, with most atmospheric gases lying within a few kilometers of sea level. In addition to providing oxygen for living organisms, the atmosphere provides carbon dioxide required for plant photosynthesis, and nitrogen that organisms use to make proteins. The atmosphere serves a vital protective function in that it absorbs highly energetic ultraviolet radiation from the sun that would kill living organisms exposed to it. A particularly important part of the atmosphere in this respect is the stratospheric layer of ozone, an ultraviolet-absorbing form of elemental oxygen. Because of its ability to absorb infrared radiation by which Earth loses the energy that it absorbs from the sun, the atmosphere stabilizes Earth’s surface temperature. The atmosphere also serves as the medium by which the solar energy that falls with greatest intensity in equatorial regions is redistributed away from the Equator. It is the medium in which water vapor evaporated from oceans as the first step in the hydrologic cycle is transported over land masses to fall as rain over land.

Earth’s water is contained in the hydrosphere. Although frequent reports of torrential rainstorms and flooded rivers produced by massive storms might give the impression that a large fraction of Earth’s water is fresh water, more than 97% of it is seawater in the oceans. Most of the remaining fresh water is present as ice in polar ice caps and glaciers. A small fraction of the total water is present as vapor in the atmosphere. The remaining liquid fresh water is that available for growing plants and other organisms and for industrial uses. This water may be present on the surface as lakes, reservoirs, and streams, or it may be underground as groundwater.

The solid part of earth, the geosphere, includes all rocks and minerals. A particularly important part of the geosphere is soil, which supports plant growth, the basis of food for all living organisms. The **lithosphere** is a relatively thin solid layer extending from Earth’s surface to depths of 50–100 km. The even thinner outer skin of the lithosphere known as the **crust** is composed of relatively lighter silicate-based minerals. It is the part of the geosphere that is available to interact with the other environmental spheres and that is accessible to humans.

The biosphere is composed of all living organisms. For the most part, these organisms live on the surface of the geosphere on soil, or just below the soil surface. The oceans and other bodies of water support high populations of organisms. Some life forms exist at considerable depths on ocean floors. In general, though, the biosphere is a very thin layer at the interface of the geosphere with the atmosphere. The biosphere is involved with the geosphere, hydrosphere, and atmosphere in *biogeochemical cycles* through which materials such as nitrogen and carbon are circulated.

Through human activities, the anthrosphere, that part of the environment made and operated by humans, has developed strong interactions with the other environmental spheres. Many examples of these interactions could be cited. By cultivating large areas of soil for domestic crops, humans modify the geosphere and influence the kinds of organisms in the biosphere. Humans divert water from its natural flow, use it, sometimes contaminate it, then return it to the hydrosphere. Emissions of particles to the atmosphere by human activities affect visibility and other characteristics of the atmosphere. The emission of large quantities of carbon dioxide to the atmosphere by combustion of fossil fuels may be modifying the heat-absorbing characteristics of the atmosphere to the extent that global warming is almost certainly taking place. The anthrosphere perturbs various biogeochemical cycles.

The effect of the anthrosphere over the last two centuries in areas such as burning large quantities of fossil fuels is especially pronounced upon the atmosphere and has the potential to change the nature of Earth significantly. According to Nobel Laureate Paul J. Crutzen of the Max Planck Institute for Chemistry, Mainz, Germany, this impact is so great that it will lead to a new global epoch to replace the halocene epoch that has been in effect for the last 10,000 years since the last Ice Age. Dr. Crutzen has coined the term *anthropocene* (from anthropogenic) to describe the new epoch that is upon us.

2.3: What is Environmental Chemistry?

The practice of green chemistry must be based upon **environmental chemistry**. This important branch of chemical science is defined as *the study of the sources, reactions, transport, effects, and fates of chemical species in water, soil, air, and living environments and the effects of technology thereon*.[1] Figure 2.2 illustrates this definition of environmental chemistry with an important type of environmental chemical species. In this example, two of the ingredients required for the formation of photochemical smog — nitric oxide and hydrocarbons — are emitted to the atmosphere from vehicles and transported through the atmosphere by wind and air currents. In the atmosphere, energy from sunlight brings about photochemical reactions that convert nitric oxide and hydrocarbons to ozone, noxious organic compounds, and particulate matter, all characteristic of photochemical smog. Various harmful effects are manifested, such as visibility-obscuring particles in the atmosphere, or ozone, which is unhealthy when inhaled by humans, or toxic to plants. Finally, the smog products end up on soil, deposited on plant surfaces, or in bodies of water.

Figure 2.2.1 showing the five environmental spheres may provide an idea of the complexity of environmental chemistry as a discipline. Enormous quantities of materials and energy are continually exchanged among the five environmental spheres. In addition to variable flows of materials, there are variations in temperature, intensity of solar radiation, mixing, and other factors, all of which strongly influence chemical conditions and behavior.

Throughout this book the role of environmental chemistry in the practice of green chemistry is emphasized. Green chemistry is practiced to minimize the impact of chemicals and chemical processes upon humans, other living organisms, and the environment as a whole. It is only within the framework of a knowledge of environmental chemistry that green chemistry can be successfully practiced.

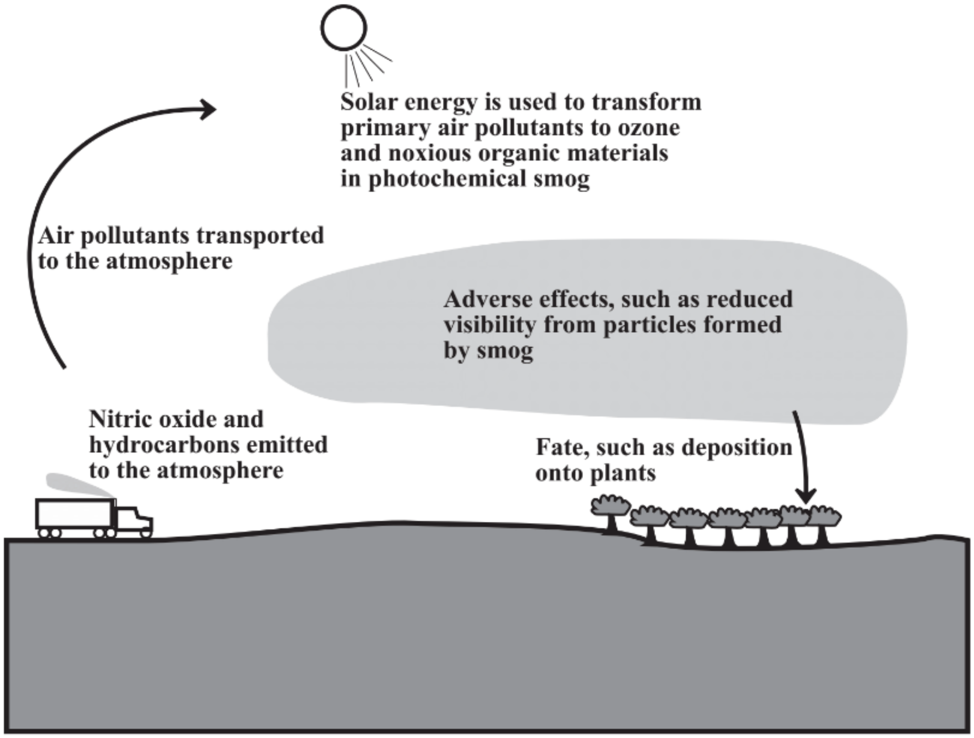


Figure 2.3.1 Illustration of the definition of environmental chemistry with a common environmental contaminant

There are several highly interconnected and overlapping categories of environmental chemistry. **Aquatic chemistry** deals with chemical phenomena and processes in water. Aquatic chemical processes are very strongly influenced by microorganisms in the water, so there is a strong connection between the hydrosphere and biosphere insofar as such processes are concerned. Aquatic chemical processes occur largely in "natural waters" consisting of water in oceans, bodies of fresh water, streams, and underground aquifers. These are places in which the hydrosphere can interact with the geosphere, biosphere, and atmosphere and is often subjected to anthrospheric influences. Aspects of aquatic chemistry are considered in various parts of this book and are addressed specifically in Chapter 9, "Water, the Ultimate Green Substance."

Atmospheric chemistry is the branch of environmental chemistry that considers chemical phenomena in the atmosphere. Two things that make this chemistry unique are the extreme dilution of important atmospheric chemicals and the influence of photochemistry. Photochemistry occurs when molecules absorb photons of high-energy visible light or ultraviolet radiation, become energized ("excited"), and undergo reactions that lead to a variety of products, such as photochemical smog. In addition to reactions that occur in the gas phase, many important atmospheric chemical phenomena take place on the surfaces of very small solid particles suspended in the atmosphere and in droplets of liquid in the atmosphere. Although no significant atmospheric chemical reactions are mediated by organisms in the atmosphere, microorganisms play a strong role in determining species that get into the atmosphere. As examples, bacteria growing in the absence of oxygen, such as in cows' stomachs and under water in rice paddies, are the single greatest source of hydrocarbon in the atmosphere because of the large amounts of methane that they emit. The greatest source of organic sulfur compounds in the atmosphere consists of microorganisms in the oceans that emit dimethyl sulfide. Atmospheric chemistry is addressed specifically in Chapter 10, "Blue Skies for a Green Environment."

Chemical processes that occur in the geosphere involving minerals and their interactions with water, air, and living organisms are addressed by the topic of **geochemistry**. A special branch of geochemistry, soil chemistry, deals with the chemical and biochemical processes that occur in soil. Aspects of geochemistry are explained in Chapter 11, "The Geosphere and a Green Earth," and soil and agricultural chemistry are covered in Chapter 12, "The Biosphere and Feeding a Hungry World.

Environmental biochemistry addresses biologically mediated processes that occur in the environment. Such processes include, as examples, the biodegradation of organic waste materials in soil or water and processes within biogeochemical cycles, such as denitrification, which returns chemically bound nitrogen to the atmosphere as nitrogen gas. The basics of biochemistry are presented in Chapter 7, "The Chemistry of Life and Green Chemistry," and other aspects of biochemistry are presented in Chapter 12, "The Biosphere and Feeding a Hungry World." Chapter 14, "Feeding the Anthrosphere: Utilizing Renewable and Biological Materials," discusses how chemical processes carried out by organisms can produce material feedstocks needed for the practice of green chemistry. The toxic effects of chemicals are of utmost concern to chemists and the public. Chapter 16, "Terrorism, Toxicity, And Vulnerability: Green Chemistry and Technology in Defense of Human Welfare," deals with aspects of these toxic effects and discusses **toxicological chemistry.**

Although there is not a formally recognized area of chemistry known as "anthrospheric chemistry," most of chemical science and engineering developed to date deals with chemistry carried out in the anthrosphere. Included is industrial chemistry, which is very closely tied to the practice of green chemistry. A good way to view "anthrospheric chemistry" from a green chemistry perspective is within the context of **industrial ecology**. Industrial ecology considers industrial systems in a manner analogous to natural ecosystems. In a system of industrial ecology, various manufacturing and processing operations carry out "industrial metabolism" on materials.A successful industrial ecosystem is well balanced and diverse, with various enterprises that generate products for each other and use each other's products and potential wastes. A well-functioning industrial ecosystem recycles materials to the maximum extent possible and produces little — ideally no — wastes. Therefore, a good industrial ecosystem is a green chemical system. Industrial ecology and anthrospheric environmental chemistry are addressed in Chapter 13, "TheAnthrosphere, Green Chemistry, and Industrial Ecology."

2.4: Environmental Pollution

Environmental chemistry has developed in response to problems and concerns regarding environmental pollution. Although awareness of chemical pollution had increased significantly in the two decades following World War II, the modern environmental movement dates from the 1962 publication of Rachel Carson's classic book *Silent Spring*. The main theme of this book was the accumulation of DDT and other persistent, mostly pesticidal, chemicals through the food chain, which caused birds at the end of the chain to produce eggs with soft shells that failed to produce viable baby birds. The implication was that substances harming bird populations might harm humans as well.

Around the time of the publication of Silent Spring another tragedy caused great concern regarding the potential effects of chemicals. This was the occurrence of approximately 10,000 births of children with badly deformed or missing limbs as a result of their mothers having taken the pharmaceutical thalidomide to alleviate the effects of morning sickness at an early stage of pregnancy.

The 1960s were a decade of high concern and significant legislative action in the environmental arena aimed particularly at the control of water and air pollutants. By around 1970, it had become evident that the improper disposal of chemicals to the geosphere was also a matter of significant concern. Although many incidents of such disposal were revealed, the one that really brought the problem into sharp focus was the Love Canal site in Niagara Falls, New York. This waste dump was constructed in an old abandoned canal in which large quantities of approximately 80 waste chemicals had been placed for about two decades starting in the 1930s. It had been sealed with a clay cap and given to the city. A school had been built on the site and housing constructed around it. By 1971 it became obvious that the discarded chemicals were leaking through the cap. This problem led eventually to the expenditure of many millions of dollars to remediate the site and to buy out and relocate approximately one thousand households. More than any other single incident the Love Canal problem was responsible for the passage of legislation in the U.S., including Superfund, to clean up hazardous waste sites and to prevent their production in the future.

By about 1970 it was generally recognized that pollution of air, water, and land was reaching intolerable levels. As a result, various countries passed and implemented laws designed to reduce pollutants and to clean up waste chemical sites at a cost that has easily exceeded one trillion dollars globally. In many respects, this investment has been strikingly successful. Streams that had deteriorated to little more than stinking waste drainage ditches (the Cuyahoga River in Cleveland, Ohio, once caught on fire from petroleum waste floating on its surface) have been restored to a healthy and productive condition. Despite a much increased population, the air quality in smog-prone Southern California has improved markedly. A number of dangerous waste disposal sites have been cleaned up. Human exposure to toxic substances in the workplace, in the environment, and in consumer products has been greatly reduced. The measures taken and regulations put in place have prevented devastating environmental problems from occurring.

Initially, serious efforts to control pollution were based on a **command and control** approach, which specifies maximum concentration guideline levels of substances that can be allowed in the atmosphere or water and places limits on the amounts or concentrations of pollutants that can be discharged in waste streams. Command and control efforts to diminish pollution have resulted in implementation of various technologies to remove or neutralize pollutants in potential waste streams and stack gases. These are so-called end-of-pipe measures. As a result, numerous techniques, such as chemical precipitation of water pollutants, neutralization of acidic pollutants, stack gas scrubbing, and waste immobilization have been developed and refined to deal with pollutants after they are produced.

Release of chemicals to the environment is now tracked in the U.S. through the Toxics Release Inventory TRI, under requirements of the Emergency Planning and Community Right to Know Act, which requires that information be provided regarding the release of more than 300 chemicals. The release of as much as one billion kilograms of these chemicals has been reported in the U.S. during a single year. Not surprisingly, the chemical industry produces the most such substances, followed by primary metals and paper manufacture. Significant amounts are emitted from transportation equipment, plastics, and fabricated metals, with smaller quantities from a variety of other enterprises. Although the quantities of chemicals released are high, they are decreasing, and the publicity resulting from the required publication of these releases has been a major factor in decreasing the amounts of chemicals released.

Although much maligned, various pollution control measures implemented in response to command and control regulation have reduced wastes and improved environmental quality. Regulation-based pollution control has clearly been a success and well worth the expense and effort. However, it is much better to prevent the production of pollutants rather than having to deal with them after they are made. This was recognized in United States with the passage of the 1990 Pollution Prevention Act, which recognized that source reduction is fundamentally different and more desirable than waste management and pollution control. This act explicitly states that, wherever possible, wastes are not to be generated and their quantities are to be minimized. The means for accomplishing this objective can range from very simple measures, such as careful inventory control and reduction of solvent losses due to evaporation, to much more sophisticated and drastic approaches including complete redesign of manufacturing processes with waste minimization as a top priority. The means for preventing pollution are best implemented through the practice of green chemistry, which is discussed in detail in the following section.

2.5: Practice of Green Chemistry

The limitations of a command and control system for environmental protection have become more obvious even as the system has become more successful. In industrialized societies with good, well-enforced regulations, most of the easy and inexpensive measures that can be taken to reduce environmental pollution and exposure to harmful chemicals have been implemented. Therefore, small increases in environmental protection now require relatively large investments in money and effort. Is there a better way? There is, indeed. The better way is through the practice of green chemistry.

Green chemistry can be defined as the practice of chemical science and manufacturing in a manner that is sustainable, safe, and non-polluting and that consumes minimum amounts of materials and energy while producing little or no waste material. This definition of green chemistry is illustrated in Figure 2.5.1. The practice of green chemistry begins with recognition that the production, processing, use, and eventual disposal of chemical products may cause harm when performed incorrectly. In accomplishing its objectives, green chemistry and green chemical engineering may modify or totally redesign chemical products and processes with the objective of minimizing wastes and the use or generation of particularly dangerous materials. Those who practice green chemistry recognize that they are responsible for any effects on the world that their chemicals or chemical processes may have. Far from being economically regressive and a drag on profits, green chemistry is about increasing profits and promoting innovation while protecting human health and the environment.

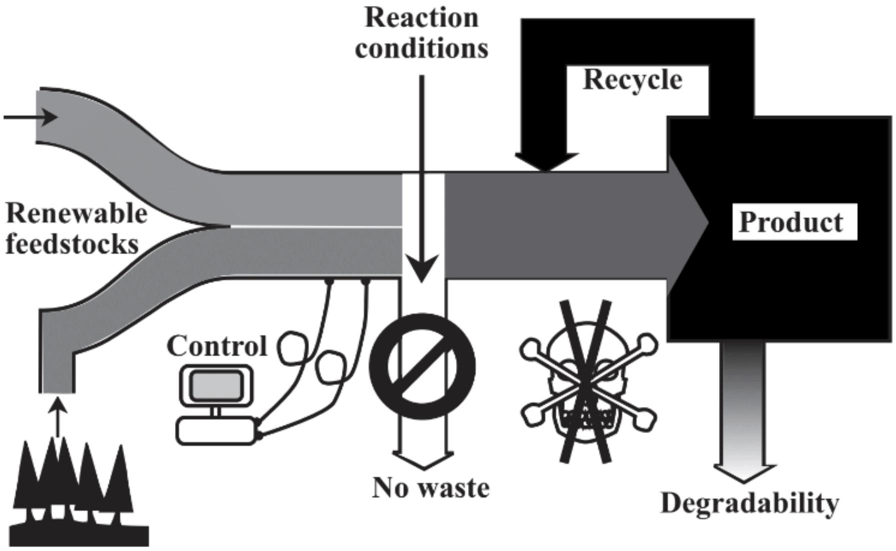


Figure 2.5.1. Illustration of the definition of green chemistry, which emphasizes renewable feedstocks, exacting control, mild reaction conditions, maximum recycling of materials, minimal wastes, and degradability of products that might enter the environment.

To a degree, we are still finding out what green chemistry is. That is because it is a rapidly evolving and developing subdiscipline in the field of chemistry. And it is a very exciting time for those who are practitioners of this developing science. Basically, green chemistry harnesses a vast body of chemical knowledge and applies it to the production, use, and ultimate disposal of chemicals in a way that minimizes consumption of materials, exposure of living organisms, including humans, to toxic substances, and damage to the environment. And it does so in a manner that is economically feasible and cost effective. In one sense, green chemistry is the most efficient possible practice of chemistry and the least costly when all of the costs of doing chemistry, including hazards and potential environmental damage are taken into account.

Green chemistry is sustainable chemistry. There are several important respects in which green chemistry is sustainable:

- Economic: At a high level of sophistication green chemistry normally costs less in strictly economic terms (to say nothing of environmental costs) than chemistry as it is normally practiced.
- Materials: By efficiently using materials, maximum recycling, and minimum use of virgin raw materials, green chemistry is sustainable with respect to materials.
- Waste: By reducing insofar as possible, or even totally eliminating their production, green chemistry is sustainable with respect to wastes

2.6: Green Chemistry and Synthetic Chemistry

Synthetic chemistry is the branch of chemical science involved with developing means of making new chemicals and developing improved ways of synthesizing existing chemicals. A key aspect of green chemistry is the involvement of synthetic chemists in the practice of environmental chemistry. Synthetic chemists, whose major objective has always been to make new substances and to make them cheaper and better, have come relatively late to the practice of environmental chemistry. Other areas of chemistry have been involved much longer in pollution prevention and environmental protection. From the beginning, analytical chemistry has been a key to discovering and monitoring the severity of pollution problems. Physical chemistry has played a strong role in explaining and modeling environmental chemical phenomena. The application of physical chemistry to atmospheric photochemical reactions has been especially useful in explaining and preventing harmful atmospheric chemical effects including photochemical smog formation and stratospheric ozone depletion. Other branches of chemistry have been instrumental in studying various environmental chemical phenomena. Now the time has arrived for the synthetic chemists, those who make chemicals and whose activities drive chemical processes, to become intimately involved in making the manufacture, use, and ultimate disposal of chemicals as environmentally friendly as possible.

Before environmental and health and safety issues gained their current prominence, the economic aspects of chemical manufacture and distribution were relatively simple and straightforward. The economic factors involved included costs of feedstock, energy requirements, and marketability of product. Now, however, costs must include those arising from regulatory compliance, liability, end-of-pipe waste treatment, and costs of waste disposal. By eliminating or greatly reducing the use of toxic or hazardous feedstocks and catalysts and the generation of dangerous intermediates and byproducts, green chemistry eliminates or greatly reduces the additional costs that have come to be associated with meeting environmental and safety requirements of conventional chemical manufacture.

As illustrated in Figure 2.6.1, there are two general and often complementary approaches to the implementation of green chemistry in chemical synthesis, both of which challenge the imaginations and ingenuity of chemists and chemical engineers. The first of these is to use existing feedstocks but make them by more environmentally benign, “greener,” processes. The second approach is to substitute other feedstocks that are made by environmentally friendly means. In some cases, a combination of the two approaches is used.

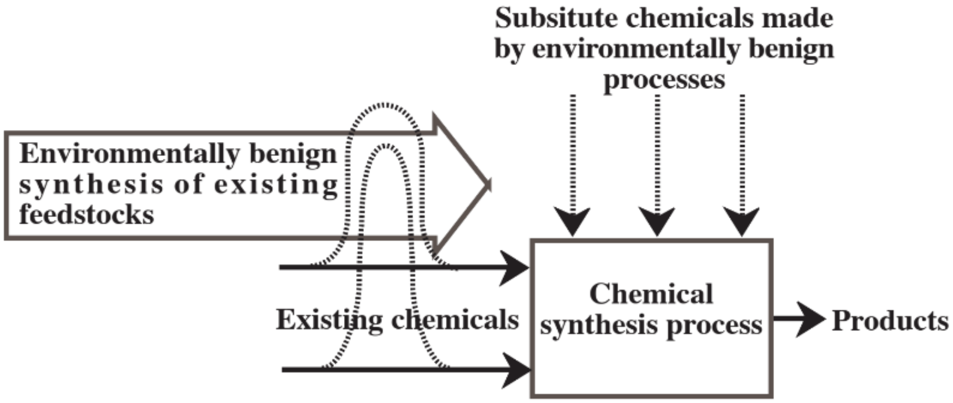


Figure 2.4. Two general approaches to the implementation of green chemistry. The dashed loops on the left represent alternative approaches to environmentally benign means of providing chemicals already used for chemical synthesis. A second approach, where applicable, is to substitute entirely different, environmentally safer raw materials.

Yield and Atom Economy

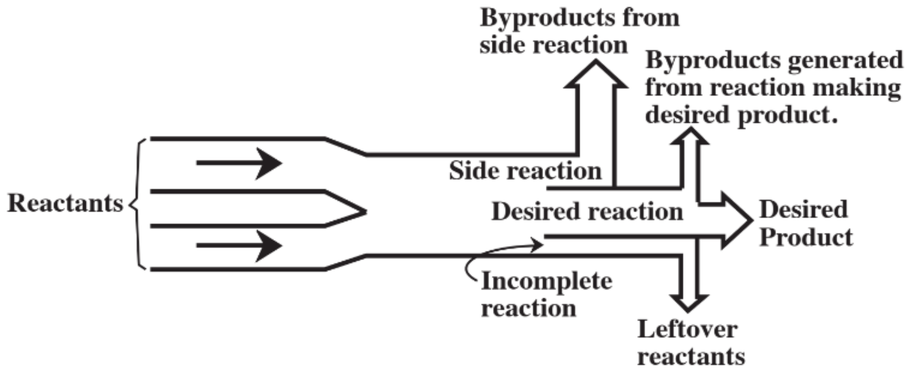
Traditionally, synthetic chemists have used **yield**, defined as a percentage of the degree to which a chemical reaction or synthesis goes to completion to measure the success of a chemical synthesis. For example, if a chemical reaction shows that 100 grams of product should be produced, but only 85 grams is produced, the yield is 85%. A synthesis with a high yield may still generate significant quantities of useless byproducts if the reaction does so as part of the synthesis process. Instead of yield, green chemistry emphasizes **atom economy**, the fraction of reactant material that actually ends up in final product. With 100 percent atom economy, all of the material that goes into the synthesis process is incorporated into the product. For efficient utilization of raw materials, a 100% atom economy process is most desirable. Figure 2.7.1 illustrates the concepts of yield and atom economy.

2.7: Reduction of Risk- Hazard and Exposure

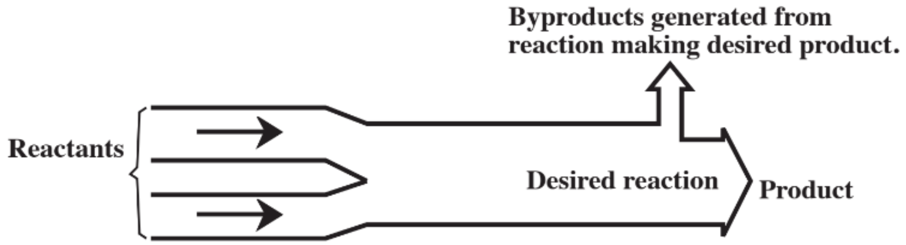
A major goal in the manufacture and use of commercial products, and, indeed, in practically all areas of human endeavor, is the reduction of risk. There are two major aspects of risk — the hazard presented by a product or process and exposure of humans or other potential targets to those hazards.

$$\text{Risk} = \text{F}\{\text{hazard x exposure}\} \tag{2.7.1}$$

This relationship simply states that risk is a function of hazard times exposure. It shows that risk can be reduced by a reduction of hazard, a reduction of exposure, and various combinations of both.



(a) Typical reaction with less than 100% yield and with byproducts



(b) Reaction with 100% yield, but with byproducts inherent to the reaction

(c) Reaction with 100% atom economy, no leftover reactants, no byproducts

Figure 2.7.1 Illustration of percent yield and atom economy.

The command and control approach to reducing risk has concentrated upon reduction of exposure. Such efforts have used various kinds of controls and protective measures to limit exposure. The most common example of such a measure in the academic chemistry laboratory is the wearing of goggles to protect the eyes. Goggles will not by themselves prevent acid from splashing into the face of a student, but they do prevent the acid from contacting fragile eye tissue. Explosion shields will not prevent explosions, but they do retain glass fragments that might harm the chemist or others in the vicinity.

Reduction of exposure is unquestionably effective in preventing injury and harm. However, it does require constant vigilance and even nagging of personnel, as any laboratory instructor charged with making laboratory students wear their safety goggles at all times will attest. It does not protect the unprotected, such as a visitor who may walk bare-faced into a chemical laboratory ignoring the warnings for required eye protection. On a larger scale, protective measures may be very effective for workers in a chemical manufacturing operation but useless to those outside the area or the environment beyond the plant walls who do not have protection. Protective measures are most effective against acute effects, but less so against long-term chronic exposures that may cause toxic responses over many years period of time. Finally, protective equipment can fail and there is always the possibility that humans will not use it properly.

Where feasible, hazard reduction is a much more certain way of reducing risk than is exposure reduction. The human factors that play so prominently in successfully limiting exposure and that require a conscious, constant effort are much less crucial when hazards have been reduced. Compare, for example, the use of a volatile, flammable, somewhat toxic organic solvent used for cleaning and degreasing of machined metal parts with that of a water solution of a nontoxic cleaning agent used for the same purpose. To safely work around the solvent requires an unceasing effort and constant vigilance to avoid such hazards as formation of explosive mixtures with air, presence of ignition sources that could result in a fire, and excessive exposure by inhalation or absorption through skin that might cause peripheral neuropathy (a nerve disorder) in workers. Failure of protective measures can result in a bad accident or serious harm to worker health. The water-based cleaning solution, however, would not present any of these hazards so that failure of protective measures would not create a problem.

Normally, measures taken to reduce risk by reducing exposure have an economic cost that cannot be reclaimed in lower production costs or enhanced value of product. Of course, failure to reduce exposure can have direct, high economic costs in areas such as higher claims for worker compensation. In contrast, hazard reduction often has the potential to substantially reduce operating costs. Safer feedstocks are often less costly as raw materials. The elimination of costly control measures can lower costs overall. Again, to use the comparison of an organic solvent compared to a water-based cleaning solution, the organic solvent is almost certain to cost more than the aqueous solution containing relatively low concentrations of detergents and other additives. Whereas the organic solvent will at least require purification for recycle and perhaps even expensive disposal as a hazardous waste, the water solution may be purified by relatively simple processes, and perhaps even biological treatment, then safely discharged as wastewater to a municipal wastewater treatment facility. It should be kept in mind, however, that not all low-hazard materials are cheap, and may be significantly more expensive than their more hazardous alternatives. And, in some cases, nonhazardous alternatives simply do not exist.

2.8: The Risks of No Risks

There are limits to the reduction in risk beyond which efforts to do so become counterproductive. As in other areas of endeavor, there are circumstances in which there is no choice but to work with hazardous substances. Some things that are inherently dangerous are rendered safe by rigorous training, constant attention to potential hazards, and understanding of hazards and the best way to deal with them. Consider the analogy of commercial flight. When a large passenger aircraft lands, typically 100 tons of aluminum, steel, flammable fuel, and fragile human flesh traveling at a speed of twice the legal interstate speed limits for automobiles come into sudden contact through air-filled rubber tires with an unforgiving concrete runway. That procedure is inherently dangerous! But it is carried out millions of times per year throughout the world with but few injuries and fatalities, a tribute to the generally superb design, construction, and maintenance of aircraft and the excellent skills and training of aircrew. The same principles that make commercial air flight generally safe also apply to the handling of hazardous chemicals by properly trained personnel under carefully controlled conditions.

So, although much of this book is about risk reduction as it relates to chemistry, we must always be mindful of the risks of not taking risks. If we become so timid in all of our enterprises that we refuse to take risks, scientific and economic progress will stagnate. The U.S. space program is an example of an area in which progress has been made only by a willingness to take risks. However, progress has probably been slowed because of risk aversion resulting from previous accidents, especially the 1987 Challenger space shuttle tragedy. If we get to the point that no chemical can be made if its synthesis involves the use of a potentially toxic or otherwise hazardous substance, the progress of chemical science and the development of such beneficial products as new life-saving drugs or innovative chemicals for treating water pollutants may be held back. It may be argued that thermonuclear fusion entails significant risks as an energy source and that research on controlled thermonuclear fusion must therefore be stopped. But when that potential risk is balanced against the virtually certain risk of continuing to use fossil fuels that produce greenhouse gases that cause global climate warming, it seems sensible to at least continue research on controlled thermonuclear fusion energy sources. Another example is the use of thermal processes for treating hazardous wastes, somewhat risky because of the potential for the release of toxic substances or air pollutants, but still the best way to convert many kinds of hazardous wastes to innocuous materials.

2.9: Waste Prevention

Waste prevention is better than having to treat or clean up wastes. In the earlier years of chemical manufacture the direct costs associated with producing large quantities of wastes were very low because such wastes were simply discarded into waterways, onto the ground, or in the air as stack emissions. With the passage and enforcement of environmental laws after about 1970, costs for waste treatment increased steadily. For example, General Electric announced in April, 2010, that it had spent $561 in the first phase of dredging and removing PCBs from deposits in Hudson River sediments produced decades earlier when the extremely persistent PCBs were discarded to the river as wastes from the company's manufacture of electrical equipment. The cost of the second phase of cleanup of these wastes was projected to be much more than the $561million already spent. The cleanup of pollutants including asbestos, dioxins, pesticide manufacture residues, perchlorate and mercury are costing various concerns hundreds of millions of dollars. The eventual cleanup costs from the 2010 BP Deepwater Horizon oil well blowout in the Gulf of Mexico may eventually exceed the $20 billion that the company initially set aside for the project. By the year 2000 in the United States, costs of complying with environmental and occupational health regulations had grown to a magnitude similar to that of research and development for industry as a whole. From a purely economic standpoint, therefore, a green chemistry approach that avoids these costs is very attractive, in addition to its large environmental benefits.

Although the costs of such things as engineering controls, regulatory compliance, personnel protection, wastewater treatment, and safe disposal of hazardous solid wastes have certainly been worthwhile for society and the environment, they have become a large fraction of the overall expense of doing business. Companies must now do **full cost accounting**, taking into account the total costs of emissions, waste disposal, cleanup, and protection of personnel and the environment, none of the proceeds of which go into the final product.

2.10: Basic Principles of Green Chemistry

From the preceding discussion, it should be obvious that there are certain basic principles of green chemistry. Some publications recognize “the twelve principles of green chemistry.”[2] This section addresses the main ones of these.

As anyone who has ever spilled the contents of a food container onto the floor well knows, it is better to not make a mess than to clean it up once made. As applied to green chemistry, this basic rule means that *waste prevention is much better than waste cleanup*. Failure to follow this simple rule has resulted in most of the troublesome hazardous waste sites that are causing problems throughout the world today.

One of the most effective ways to prevent generation of wastes is to make sure that insofar as possible *all materials involved in making a product should be incorporated into the final product*. Therefore, the practice of green chemistry is largely about incorporation of all raw materials into the product, if at all possible. We would not likely favor a food recipe that generated a lot of inedible byproduct. The same idea applies to chemical processes. In that respect, the concept of atom economy discussed in Section 2.6 is a key component of green chemistry.

The use or generation of substances that pose hazards to humans and the environment should be avoided. Such substances include toxic chemicals that may be hazardous to workers. They include substances that are likely to become air or water pollutants and harm the environment or organisms in the environment. Here the connection between green chemistry and environmental chemistry is especially strong.

Chemical products should be as effective as possible for their designated purpose, but with minimum toxicity. The practice of green chemistry is making substantial progress in designing chemicals and new approaches to the use of chemicals such that effectiveness is retained and even enhanced while toxicity is reduced.

Chemical synthesis as well as many manufacturing operations make use of auxiliary substances that are not part of the final product. In chemical synthesis, such a substance consists of solvents in which chemical reactions are carried out. Another example consists of separating agents that enable separation of product from other materials. Since these kinds of materials may end up as wastes or (in the case of some toxic solvents) pose health hazards, *the use of auxiliary substances should be minimized and preferably totally avoided.*

Energy consumption poses economic and environmental costs in virtually all synthesis and manufacturing processes. In a broader sense, the extraction of energy, such as fossil fuels pumped from or dug out of the ground, has significant potential to damage the environment. Therefore, *energy requirements should be minimized*. One way in which this can be done is through the use of processes that occur near ambient conditions, rather than at elevated temperature or pressure. One successful approach to this has been the use of biological processes, which, because of the conditions under which organisms grow, must occur at moderate temperatures and in the absence of toxic substances. Such processes are discussed further in Chapters 13 and 14.

Raw materials extracted from earth are depleting in that there is a finite supply that cannot be replenished after they are used. So, wherever possible, *renewable raw materials should be used instead of depletable feedstocks*. As discussed further in Chapter 14, biomass feedstocks are highly favored in those applications for which they work. For depleting feedstocks, recycling should be practiced to the maximum extent possible.

In the synthesis of an organic compound (see Chapter 6), it is often necessary to modify or protect groups on the organic molecule during the course of the synthesis. This often results in the generation of byproducts not incorporated into the final product, such as occurs when a protecting group is bonded to a specific location on a molecule, then removed when protection of the group is no longer needed. Since these processes generate byproducts that may require disposal, *the use of protecting groups in synthesizing chemicals should be avoided insofar as possible.*

Reagents should be as selective as possible for their specific function. In chemical language, this is sometimes expressed as a preference for selective catalytic reagents over nonselective stoichiometric reagents.

Products that must be dispersed into the environment should be designed to break down rapidly into innocuous products. One of the oldest, but still one of the best, examples of this is the modification of the surfactant in household detergents 15 or 20 years after they were introduced for widespread consumption to yield a product that is biodegradable. The poorly biodegradable surfactant initially used caused severe problems of foaming in wastewater treatment plants and contamination of water supplies. Synthesis of a biodegradable substitute solved the problem.

Exacting “real-time” control of chemical processes is essential for efficient, safe operation with minimum production of wastes. This goal has been made much more attainable by modern computerized controls. However, it requires accurate knowledge of the concentrations of materials in the system measured on a continuous basis. Therefore, *the successful practice of green chemistry requires real-time, in-process monitoring techniques coupled with process control.*

Accidents, such as spills, explosions, and fires, are major hazards in the chemical industry. Not only are these incidents potentially dangerous in their own right, they tend to spread toxic substances into the environment and increase exposure of humans and other organisms to these substances. For this reason, it is best to *avoid the use or generation of substances that are likely to react violently, burn, build up excessive pressures, or otherwise cause unforeseen incidents in the manufacturing process*.

The principles outlined above are developed to a greater degree in the remainder of the book. They should be kept in mind in covering later sections.

2.11: Some Things to Know About Chemistry before You Even Start

Chapters 3-7 explain the basic principles of chemistry as they relate to green chemistry. For even greater detail on the basics of chemistry the reader is referred to a book on that subject.3However, at this point, it is useful to have a brief overview of chemistry, in a sense a minicourse in chemistry that provides the basic definitions and concepts of chemistry such as chemical compounds, chemical formulas, and chemical reactions before they are covered in detail in the later chapters.

All chemicals are composed of fewer than 100 naturally-occurring fundamental kinds of matter called elements. Humans have succeeded in making about 30 artificial elements since the late 1930s, but the amounts of these are insignificant compared to the total of known chemicals. Elements, in turn, are composed of very small entities called atoms. Atoms of the same element may differ a bit in their masses, but all atoms of the same element behave the same chemically. So we can logically begin the study of chemistry with the atoms that make up the elements of which all matter is composed.

Each atom of a particular element is chemically identical to every other atom. Each element is given an atomic number specific to the element, ranging from 1 to more than 100. The atomic number of an element is equal to the number of extremely small, positively charged protons contained in the nucleus located in the center of each atom of the element. Each electrically neutral atom has the same number of electrons as it has protons. The electrons are negatively charged and are in rapid motion around the nucleus, constituting a cloud of negative charge that makes up most of the volume of the atom. In addition to its atomic number, each element has a name and a chemical symbol, such as carbon, C; potassium, K (for its Latin name kalium); or cadmium, Cd. In addition to atomic number, name, and chemical symbol, each element has an atomic mass (atomic weight). The atomic mass of each element is the average mass of all atoms of the element so it is not a whole number. Atoms of most elements consist of two or more **isotopes**. All isotopes of the same element have identical chemical properties but differ in mass because of the presence in their nuclei of differing numbers of electrically neutral neutrons (see Chapter 3).

2.12: Combining Atoms to Make Molecules and Compounds

About the only atoms that exist alone are those of the noble gases, a group of elements including helium, neon, argon, and radon located on the far right of the periodic table. Even the simple hydrogen atom in the elemental state is joined together with another hydrogen atom. Two or more uncharged atoms bonded together are called a **molecule**. As illustrated in Figure 2.12.1, the hydrogen molecule consists of 2 hydrogen atoms as denoted by the chemical formula of elemental hydrogen, H_2. This formula states that a molecule of elemental hydrogen consists of 2 atoms of hydrogen, shown by the subscript of 2. The atoms are joined together by a chemical bond. As explained in Chapter 3, a hydrogen atom consists of a very small positively charged nucleus surrounded by a much larger cloud of negative charge from a single, rapidly moving, electron. But, hydrogen atoms are more “content” with 2 electrons. So two hydrogen atoms share their two electrons constituting the chemical bond in the hydrogen molecule. A bond composed of shared electrons is a **covalent bond**.

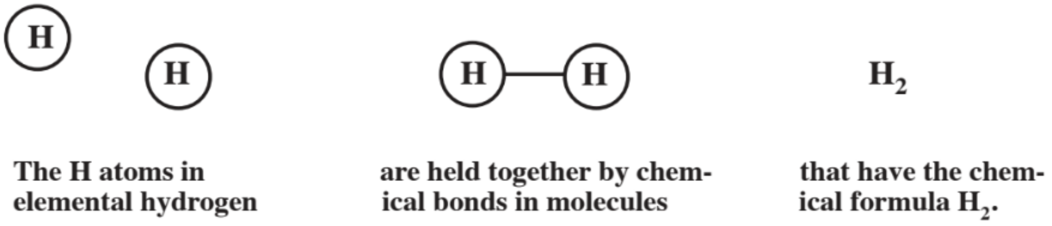


Figure 2.12.1. Molecule of H_2

Chemical Compounds

The example just discussed was one in which atoms of the same element, hydrogen, join together to form a molecule. Most molecules consist of atoms of different elements joined together. An example of such a molecule is that of **water**, chemical formula H_2O. This formula stands for the fact that the water molecule consists of *two* hydrogen atoms bonded to *one* oxygen atom, O, where the absence of a subscript number after the O indicates that there is 1 oxygen atom. The water molecule is shown in Figure 2.12.2. Each of the hydrogen atoms is held to the oxygen atom in the water molecule by two shared electrons in a covalent bond. A material such as water in which two or more elements are bonded together is called a **chemical compound**. It is because of the enormous number of combinations of two or more atoms of different elements that it is possible to make 20 million or more chemical compounds from fewer than 100 elements.

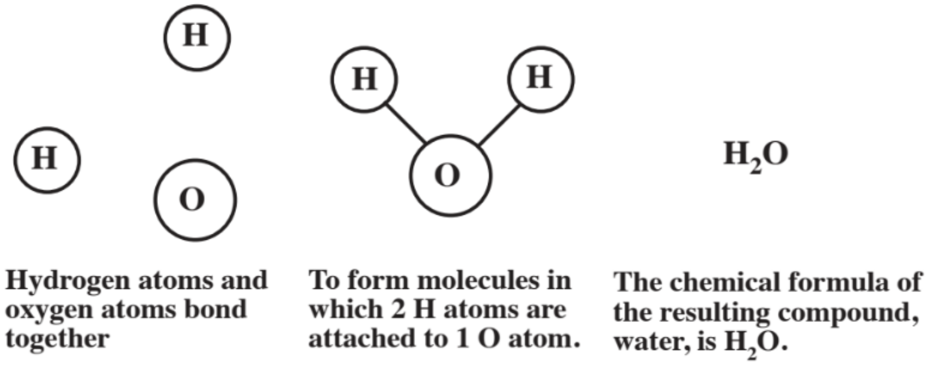


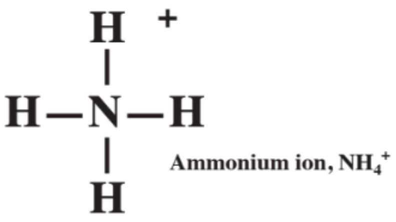
Figure 2.12.2. Atoms of hydrogen and oxygen join together by chemical bonds to form a molecule of water, chemical formula H_2O

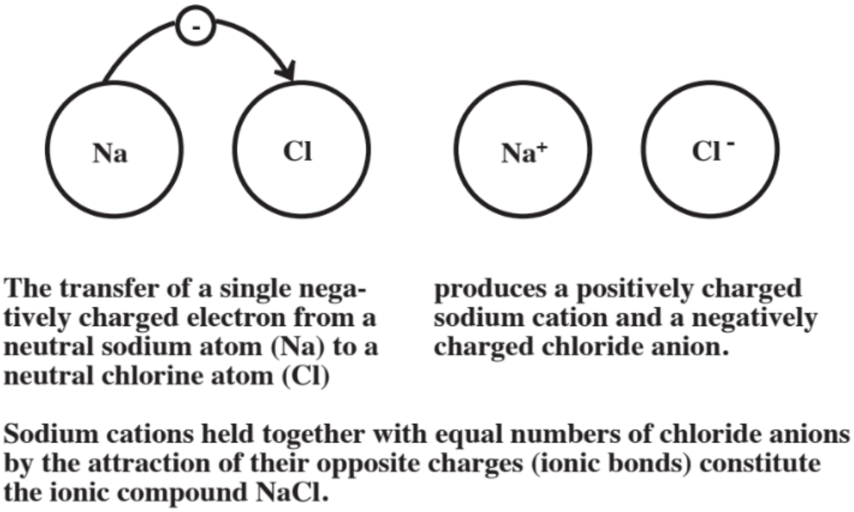
Ionic Bonds

Two different molecules have just been discussed in which atoms are joined together by *covalent bonds* consisting of *shared* electrons. Another way in which atoms can be joined together is by *transfer* of electrons from one atom to another. A single *neutral* atom has a number of electrons surrounding its nucleus that is the same as the number of protons in the nucleus of the atom. But, if the atom loses one or more negatively charged electrons, it ends up with a net *positive* electrical charge and the atom becomes a positively charged **cation**. An atom that has gained one or more negatively charged electrons attains a net *negative* charge and is called an **anion**. Cations and anions are attracted together in an **ionic compound** because of their opposite electrical charges. The oppositely charged ions are joined by **ionic bonds** in a **crystalline lattice**.

Figure 2.12.3 shows the best known ionic compound, sodium chloride, NaCl (common table salt). The chemical formula of NaCl implies that there is 1 Na for each Cl. In this case these consist of Na^+ cations and Cl^- anions. For ionic compounds such as NaCl, the first part of the name is simply that of the metal forming the cation, in this case sodium. The second part of the name is based upon the anion, but has the ending *ide*. So the ionic compound formed from sodium and chlorine is sodium chlor*ide*. As shown by the preceding example, ionic compounds may consist of ions composed of atoms that have lost electrons (producing positively charged cations) and other atoms that have gained electrons (producing negatively charged anions).

In addition to being charged atoms, ions may also consist of groups of several atoms with a net charge. Ammonium ion, NH_4^+, is such an ion. As shown below, the NH_4^+ cation consists of 4H atoms covalently bonded (by 2 shared electrons) to a central N atom, with the group of 5 total atoms having a net electrical charge of +1.





The transfer of a single negatively charged electron from a neutral sodium atom (Na) to a neutral chlorine atom (Cl) produces a positively charged sodium cation and a negatively charged chloride anion.

Sodium cations held together with equal numbers of chloride anions by the attraction of their opposite charges (ionic bonds) constitute the ionic compound NaCl.

Figure 2.12.3. Ionic bonds are formed by the transfer of electrons and the mutual attraction of oppositely charged ions in a crystalline lattice.

2.13: The process of making and breaking chemical bonds- chemical reactions

The preceding section has discussed chemical compounds and the two major kinds of bonds— covalent bonds and ionic bonds — that hold them together. Next is discussed the process of making and taking apart chemical compounds, **chemical reactions**. A chemical reaction occurs when chemical bonds are broken and formed and atoms are exchanged to produce chemically different species.

First consider two very simple chemical reactions involving only one element, oxygen. In the very thin air high in the stratosphere more than 10 kilometers above Earth's surface (above the altitudes where jet airliners normally cruise), high-energy ultraviolet radiation from the sun, represented by the symbol $h\nu$, splits apart molecules of elemental oxygen, O_2,

$$O_2 + h\nu \rightarrow 2O \tag{2.13.1}$$

to produce oxygen atoms. As with most single atoms, the O atoms are reactive and combine with oxygen molecules to produce ozone, O_3:

$$O + O_2 \rightarrow O_3 \tag{2.13.2}$$

Both of these processes are chemical reactions. In a chemical reaction, the substances on the left of the arrow (read as "yields") are the **reactants** and those on the right of the arrow are **products**. The first of these reactions states that the chemical bond holding together a molecule of O_2 *reactant* is split apart by the high energy of the ultraviolet radiation to produce two oxygen atom *products*. In the second reaction, an oxygen atom reactant, O, and an oxygen molecule reactant, O_2, form a chemical bond to yield an ozone product, O3. Are these very simple chemical reactions important to us? Emphatically yes. They produce a shield of ozone molecules in the stratosphere which in turn absorb ultraviolet radiation that otherwise would reach Earth's surface, destroying life, causing skin cancer and other maladies that would make our existence on Earth impossible. As discussed in Chapter 10, the use of chlorofluorocarbon refrigerants (Freons) has seriously threatened the stratospheric ozone layer. It is a triumph of environmental chemistry that this threat was realized in time to do something about it and an accomplishment of green chemistry to develop relatively safe substitutes for ozone-threatening chemicals.

Many chemical reactions are discussed in this book. At this point a very common chemical reaction can be considered, that of elemental hydrogen with elemental oxygen to produce water. A first approach to writing this reaction is

$$H_2 + O_2 \rightarrow H_2O \tag{2.13.3}$$

stating that elemental hydrogen and elemental oxygen react together to produce water. This is not yet a proper *chemical equation* because it is not balanced. A **balanced chemical equation** has the same number of each kind of atom on both sides of the equation. As shown above, there are 2 H atoms in the single H_2 molecule on the left and 2 H atoms in the single molecule H_2O product. That balances hydrogen, but leaves 2 O atoms in the O_2 molecule on the left with only 1 O atom in the single H_2O molecule product. But, writing the reaction a

$$2H_2 + O_2 \rightarrow 2H_2O \tag{2.13.4}$$

gives a balanced chemical equation with a total of 4 H atoms in 2 H_2 molecules on the left, 4 H atoms in 2 H_2O molecules on the right, and a total of 2 O atoms in the 2 H_2O molecules on the right, which balances the 2 O atoms in the O_2 molecule on the left. So the equation as now written is *balanced*. A **balanced** chemical equation always has the same number of each kind of atom on both sides of the equation.

2.14: The Nature of Matter and States of Matter

We are familiar with matter in different forms. We live in an atmosphere of gas that is mostly N_2 with about 1/4 as much oxygen, O_2, by volume. We only become aware of the gas in the atmosphere when something is wrong with it, such as contamination by irritating air pollutants. A person stepping into an atmosphere of pure N_2 would not notice anything wrong immediately, but would die within a few minutes, not because N_2 is toxic, but because the atmosphere lacks life-giving oxygen. The same atmosphere that we breathe contains water in the gas form as water vapor. And we are also familiar, of course, with liquid water and with solid ice.

he air that we breathe, like most substances, is a **mixture** consisting of two or more substances. Air is a **homogeneous mixture** meaning that the molecules of air are mixed together at a molecular level. There is no way that we can take air apart by simple mechanical means, such as looking at it under a magnifying glass and picking out its individual constituents. Another common substance that is a homogeneous mixture is drinking water, which is mostly H_2O molecules, but which also contains dissolved O_2 and N_2 from air, dissolved calcium ions (Ca^{2+}), chlorine added for disinfection, and other materials.

A **heterogeneous mixture** is one that contains discernible and distinct particles that, in principle at least, can be taken apart mechanically. Concrete is a heterogeneous mixture. Careful examination of a piece of broken concrete shows that it contains particles of sand and rock embedded in solidified Portland cement.

A material that consists of only one kind of substance is known as a **pure substance**. Absolutely pure substances are almost impossible to attain. Hyperpure water involved in semiconductor manufacturing operations approaches absolute purity. Another example is 99.9995% pure helium gas used in a combination gas chromatograph/mass spectrometer instrument employed for the chemical analysis of air and water pollutants.

Mixtures are very important in the practice of green chemistry. Among other reasons why this is so is that separation of impurities from mixtures in the processing of raw materials and in recycling materials is often one of the most troublesome and expensive aspects of materials utilization and may generate large quantities of wastes. Impurities may make mixtures toxic. For example, toxic arsenic, which is directly below phosphorus in the periodic table and has chemical properties similar to phosphorus, occurs as an impurity in the phosphate ores from which elemental phosphorus is extracted. This is not a problem for phosphorus used as fertilizer because the small amount of arsenic added to the soil is negligible compared to the arsenic naturally present in the soil. But, if the phosphorus is to be made into phosphoric acid and phosphate salts to be added to soft drinks or to food, impurity arsenic cannot be tolerated because of its toxicity requiring removal of this element at considerable expense.

Many byproducts of manufacturing operations are mixtures. For example, organochlorine solvents used to clean and degrease machined parts are mixtures that contain grease and other impurities. As part of the process for recycling these solvents, the impurities must be removed by expensive processes such as distillation. The separation of mixture constituents is often one of the most expensive aspects of the recycling of materials.

States of Matter

As shown in Figure $2.14.1$, the three common states of matter are gases, liquids, and solids. These are readily illustrated by water, the most familiar form of which is liquid water. Ice is a solid and water vapor in the atmosphere or in a steam line is a gas.

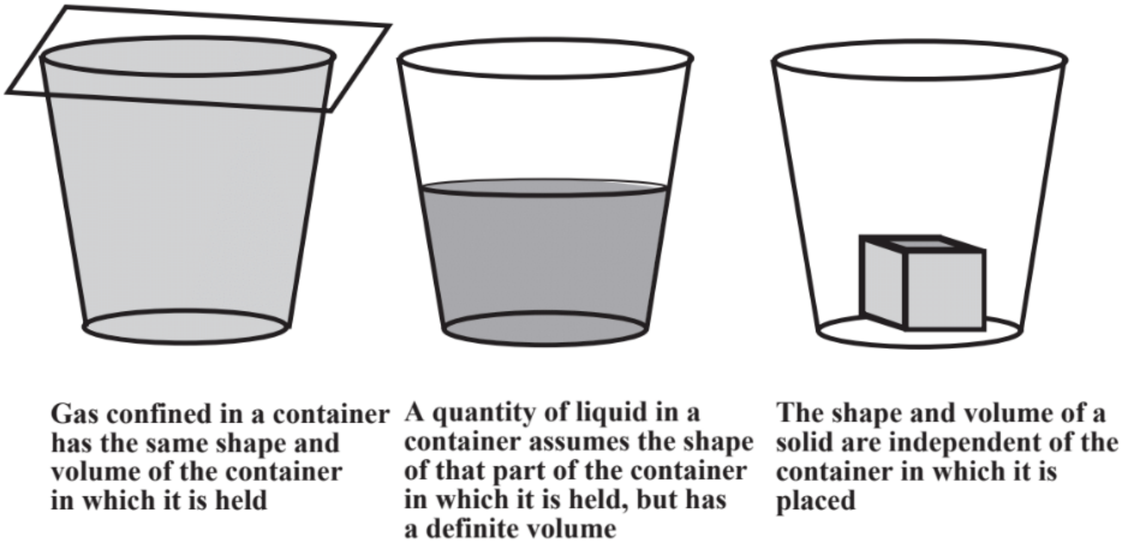


Figure 2.14.1 Illustration of the three states of matter.

Gases, such as those composing the air around us, are composed mostly of empty space through which molecules of the matter composing the gas move constantly, bouncing off each other or the container walls millions of times per second. A quantity of gas expands to fill the container in which it is placed. Because they are mostly empty space, gases can be significantly **compressed**; squeeze a gas and it responds with a decreased volume. Gas **temperature** is basically an expression of the tendency of the gas molecules to move more rapidly; higher temperatures mean faster molecular movement and more molecules bouncing off each other or container walls per second. The constant impact of gas molecules on container walls is the cause of gas **pressure**. Because of the free movement of molecules relative to each other and the presence of mostly empty space, a quantity of gas takes on the volume and shape of the container in which it is placed. The physical behavior of gases is described by several gas laws relating volumes of gas to quantities of the gas, pressure, and temperature. Calculations involving these laws are covered at the beginning of Chapter 10.

Molecules of **liquids** can move relative to each other, but cannot be squeezed together to a significant extent, so liquids are not compressible. Liquids do take on the shape of the part of a container that they occupy. Molecules of **solids** occupy fixed positions relative to each other. Therefore, solids cannot be significantly compressed and a solid object retains its shape regardless of the container in which it is placed.

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QUESTIONS AND PROBLEMS

Access to and use of the internet are assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be "right."

1. What is chemistry? Why is it impossible to avoid chemistry?

2. What is green chemistry?

3. Match the following pertaining to major areas of chemistry:

A. Analytical chemistry 1. Occurs in living organisms

B. Organic chemistry 2. Underlying theory and physical phenomena

C. Biochemistry 3. Chemistry of most elements other than carbon

D. Physical chemistry 4. Chemistry of most carbon-containing compounds

E. Inorganic Chemistry 5. Measurement of kinds and quantities of chemicals

4. What are the five environmental spheres? Which of these did not exist before humans evolved on Earth?

5. Discuss why you think the very thin "skin" of Earth ranging from perhaps two or three kilometers in depth below the surface to several kilometers (several miles) in altitude in the atmosphere has particular environmental importance.

6. What is environmental chemistry?

7. Which event may be regarded as the beginning of the modern environmental movement?

8. What is the command and control approach to pollution control?

9. What is the Toxics Release Inventory, TRI. How does it reduce pollution?

10. Why are incremental increases in regulations under the command and control approach to pollution control much less effective now than they were when pollution control laws were first enacted and enforced?

11. What is the special relationship of green chemistry to synthetic chemistry?

12. What does Figure 2.1 show with respect to environmental chemistry, green chemistry, and other topics discussed in this chapter?

13. In which important respects is green chemistry sustainable chemistry?

14. With respect to raw materials, what are two general and often complementary approaches to the practice of green chemistry?

15. What is the distinction between yield and atom economy?

16. For a chemical synthesis of a pharmaceutical compound, 100 kilograms (kg) of reactants mixed in the exact proportions that would give a 100% theoretical yield of product would give 65.2 kg of product, the rest being byproduct. In an actual chemical synthesis, an excess of 10kg of one of the reactants was added to the 100 kg of mixture to help push the reaction to completion. After the total of 110 kg of reactants was put through the process, an actual yield of 59.5 kg of product was obtained. What was the percent yield? What was the percent atom economy?

17. What are two factors that go into assessing risk?

18. What are the risks of no risks?

19. What are the major basic principles of green chemistry?

20. What is shown by the formula O_3? What about H_2O_2?

21. How does a covalent bond differ from an ionic bond?

22. What is the name given to a kind of material in which two or more different elements are bonded together?

23. Considering the compound shown in Figure 2.8, what is the name of the compound formed when a magnesium atom transfers two electrons to an oxygen atom giving a compound consisting of Mg^{2+} cations and O^{2-} anions?

24. Summarize the information given by $3H_2 + O_3 \rightarrow 3H_2O$.

25. In addition to showing the correct reactants and products, a correct chemical equation must be_____________________.

26. Name three kinds of matter based upon purity. Which of these is extremely rare?

27. In terms of molecules, how are gases, liquids, and solids distinguished?

28. Describe gas pressure and temperature in terms of molecular motion.

29.What is the Presidential Green Chemistry Challenge? What have been some of the winning ideas in this challenge?

30. Which elemental species mentioned in this chapter is present in photochemical smog?

CHAPTER OVERVIEW

3: The Elements - Basic Building Blocks of Green Chemicals

“More than fifty million unique chemical substances have been identified and the number is growing at a rapid pace. Essentially all of these are composed of the 92 naturally-occurring elements and the vast majority are from twenty or fewer of the most abundant elements.”

3.1: Elements, Atoms, and Atomic Theory
3.2: Hydrogen - The Simplest Atom
3.3: Helium - The First Noble Gas
3.4: Lithium, The First Metal
3.5: The Second Period of the Periodic Table
3.6: The Magic Octet of 8 Outer-Shell Electrons
3.7: Completing the 20-Element Periodic Table
3.8: The Brief Periodic Table is Complete
3.E: The Elements - Basic Building Blocks of Green Chemicals (Exercises)
3.R: References

Template:HideTOC

3.1: Elements, Atoms, and Atomic Theory

Chemistry is the science of matter. The fundamental building blocks of matter are the atoms of the various elements, which are composed of **subatomic particles**, the positively charged **proton** (+), the negatively charged **electron** (-), and the electrically neutral **neutron** (n). It is the properties of these atoms that determine matter's chemical behavior. More specifically, it is the arrangement and energy levels of electrons in atoms that direct how they interact with each other, thus dictating all chemical behavior. One of the most fundamental aspects of chemistry is that elemental behavior varies periodically with increasing atomic number. This has enabled placement of elements in an orderly arrangement with increasing atomic number known as the **periodic table**. The periodic behavior of elements' chemical properties is due to the fact that, as atomic number increases, electrons are added incrementally to atoms and occupy so-called shells, each filled with a specific number of electrons. After each shell is filled, a new shell is started, thus beginning a new period (row) of the periodic table. This sounds complicated, and indeed may be so, occupying the full-time computational activities of banks of computers to explain the behavior of electrons in matter. However, this behavior can be viewed in simplified models and is most easily understood for the first 20 elements using dots to represent electrons, enabling construction of an abbreviated 20-element periodic table. Although simple, this table helps understand and explain most of the chemical phenomena discussed in this book.

The chapter also emphasizes some of the green aspects of the first 20 elements and how they relate to sustainability. Included among these elements are the nitrogen, oxygen, carbon (contained in carbon dioxide), and hydrogen and oxygen (in water vapor) that make up most of the air in the "green" atmosphere; the hydrogen and oxygen in water, arguably the greenest compound of all; the sodium and chlorine in common table salt; the silicon, calcium, and oxygen that compose most mineral matter, including the soil that grows plants supplying food to most organisms; and the hydrogen, oxygen, carbon, nitrogen, phosphorus, and sulfur that are the predominant elements in all living material.

Long Before Subatomic Particles Were Known, There Was Dalton's Atomic Theory

Atomic theory describes the atoms in relation to chemical behavior. With the sophisticated tools now available to chemists, the nature of atoms, largely based upon the subatomic particles of which they are composed, especially the negatively charged electrons, is well known. But long before these sophisticated tools were even dreamed about, more than two centuries ago in 1808, an English schoolteacher named John Dalton came up with the atomic theory that bears his name. To a large extent, this theory is the conceptual basis of modern chemistry. Key aspects of Dalton's atomic theory are the following:

- The matter in each element is composed of extremely small particles called atoms. (Dalton regarded atoms as indivisible, unchanging bodies. We now know that they exchange and share electrons, which is the basis of chemical bonding.)
- Atoms of different elements have different chemical properties. (These differences may range from very slight, such as those between the noble gases neon and argon, to vastly different, such as those between highly metallic sodium and strongly nonmetallic chlorine.)
- Atoms cannot be created, destroyed, or changed to atoms of other elements. (In modern times, the provision is added that these things do not happen in ordinary chemical processes, since atoms can be changed to atoms of other elements by nuclear reactions, such as those that occur in nuclear reactors.)
- Chemical compounds are formed by the combination of atoms of different elements in definite, constant ratios that usually can be expressed as integers or simple fractions.
- Chemical reactions involve the separation and combination of atoms. (This phenomenon was surmised before anything was known about the nature of chemical bonds that are broken and formed as part of the process of chemical reactions.)

Three Important Laws

Dalton's atomic theory explains the three important laws listed below. Evidence for these laws had been found prior to the publishing of Dalton's atomic theory, and the atomic theory is largely based upon them.

1. **Law of Conservation of Mass**: *There is no detectable change in mass in an ordinary chemical reaction*. (This law, which was first stated in 1798 by "the father of chemistry," the Frenchman Antoine Lavoisier, follows from the fact that in ordinary chemical reactions no atoms are lost, gained, or changed; in chemical reactions, mass is conserved.)
2. **Law of Constant** Composition: *A specific chemical compound always contains the same elements in the same proportions by mass*.
3. **Law of Multiple Proportions**: *When two elements combine to form two or more compounds, the masses of one combining with a fixed mass of the other are in ratios of small whole numbers*. A common illustration of this law is provided by the simple

hydrocarbon compounds of carbon and hydrogen, which include $\mathrm{CH_4}$, $\mathrm{C_2H_2}$, $\mathrm{C_2H_4}$, and $\mathrm{C_2H_6}$. In these compounds the relative masses of C and H are in ratios of small whole numbers.

The Nature of Atoms

At this point it is useful to note several characteristics of atoms, which were introduced in Section 2.11. Atoms are extremely small and extremely light. Their individual masses are expressed by the minuscule atomic mass unit, u. The sizes of atoms are commonly expressed in picometers, where a picometer is 0.000 000 001 millimeters (a millimeter is the smallest division on the metric side of a ruler). Atoms may be regarded as spheres with diameters between 100 and 300 picometers.

As noted at the beginning of this chapter, atoms are composed of three basic *subatomic particles*, the positively charged *proton*, the electrically neutral *neutron*, and the much lighter negatively charged *electron*. Each proton and neutron has a mass of essentially 1 atomic mass unit, whereas the mass of the electron is only about 1/2000 as much The protons and neutrons are located in the *nucleus* at the center of the atom and the electrons compose a “fuzzy cloud” of negative charge around the nucleus. Essentially all the mass of an atom is in the nucleus and virtually all the volume is in the cloud of electrons. Each atom of a specific element has the same number of protons in its nucleus. This is the *atomic number* of the element. Each element has a name and is represented by a **chemical symbol** consisting of one or two letters. Atoms of the same element that have different numbers of neutrons and, therefore, different masses, are called **isotopes**. Isotopes may be represented by symbols such as $^{12}_{6}\mathrm{C}$ where the subscript is the atomic number and the superscript is the **mass number**, which is the sum of the numbers of protons and neutrons in an atom.

The average mass of all the atoms of an element is the **atomic mass**. Atomic masses are expressed relative to the carbon $^{12}_{6}\mathrm{C}$ the isotope, which contains 6 protons and 6 neutrons in its nucleus. The mass of this isotope is taken as exactly 12 u. Atomic masses normally are not integers, in part because atoms of most elements consist of two or more isotopes with different masses.

Electrons in Atoms

The behavior of electrons in the cloud of negative charge making up most of the volume of atoms, particularly their energy levels and orientations in space, are what determine chemical behavior. Arrangements of electrons are described by *electron configuration*. A detailed description of electron configuration is highly mathematical and sophisticated, but is represented in a very simplified fashion in this chapter. Because of their opposite charges, electrons are strongly attracted to positively charged nuclei, but they do not come to rest on it.

The placement of electrons in atoms determines the configuration of the periodic table, a complete version of which is printed at the end of this chapter. Elements are listed across this table in *periods* such that elements located in the same vertical *groups* have generally similar chemical behavior. The derivation of the complete periodic table showing more than 100 elements is too complicated for this book. So, in the remainder of this chapter, the first 20 elements will be discussed in order and the placement of electrons in the atoms of these elements will illustrate how these elements can be placed in the periodic table. From this information a brief 20-element periodic table will be constructed that should be very useful in explaining chemical behavior.

3.2: Hydrogen - The Simplest Atom

Hydrogen, **H**, is the element with atomic number 1. Most hydrogen atoms consist of a single proton forming the nucleus with 1 electron per hydrogen atom. Recall from Section 2.12 and Figure 2.6 that elemental hydrogen exists as molecules with 2 H atoms, chemical formula H2, in which the 2 H atoms are joined together by a *covalent bond* consisting of 2 shared electrons. Molecules consisting of 2 atoms so joined are called **diatomic** molecules. As will be seen, several important elements among the first 20 elements are gases that consist of diatomic molecules in their elemental forms.

Showing Electrons in Atomic Symbols and Molecular Formulas

In discussing chemical behavior related to atomic structure, it is particularly useful to have a means of showing the electrons in the atoms (more specifically, the less strongly held outer shell electrons). This is done with **Lewis symbols** (named after G. N. Lewis) also called **electron-dot symbols**. The Lewis symbol of the hydrogen at

Figure 3.1.

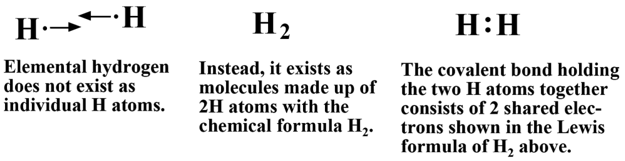


Figure 3.1. Elemental hydrogen exists as molecules each of which contains two H atoms.

Properties and Uses of Elemental Hydrogen

Pure elemental H2 under normal conditions is a colorless, odorless gas that has the lowest density of any pure substance. Liquified H2 boils at a very cold -253˚C and solidifies at -259˚ C. Hydrogen gas is widely used in the chemical industry to react chemically with a large number of substances. It burns readily with a large release of energy and mixtures of hydrogen with oxygen or air are extremely explosive. The chemical reaction for elemental hydrogen burning with oxygen (O2) in air is

$$2\,H_2 + O_2 \rightarrow 2\,H_2O + \text{energy} \tag{3.2.1}$$

The product of this reaction is water. Used as a fuel, elemental hydrogen is a very green element because when it is burned or otherwise reacted to provide energy, the reaction product is simply water, H2O. Furthermore, given a source of electrical energy, elemental hydrogen and elemental oxygen can be produced at two separate electrodes by passing a direct current through water in which an appropriate salt has been dissolved to make the water electrically conducting:

$2H2O \xrightarrow[\text{current}]{\text{Electrical}} 2H2 + O2$ (3.2.2)

So elemental hydrogen generated by the application of electrical energy to water provides a source of energy that can be moved from one place to another and utilized to produce electricity in fuel cells (see below) or for other beneficial purposes such as the synthesis of ammonia essential as a source of plant fertilizer nitrogen. The production of elemental hydrogen by electrolysis may be regarded as a green process because it does not require any reagents other than water. Furthermore, the electrolysis byproduct oxygen is harmless and has many uses whereas hydrogen made by the reaction of steam with carbon-containing compounds (see below) consumes fossil fuel and generates CO, which in some cases is burned producing greenhouse gas carbon dioxide. The main disadvantage of the electrolysis process for H2 generation is the relatively low efficiency by which the electricity is used in the process and improvements are needed in this area.

Elemental hydrogen is widely used for chemical synthesis and other industrial applications. Its preparation by electrolysis of water was mentioned above. It is now most commonly prepared from methane, CH4, the main ingredient of natural gas, by **steam reforming** at high temperatures and pressures:

$CH4 + H2O \xrightarrow[\text{30 atm P}]{\text{800°C T}} CO + 3H2$ (3.2.3)

Hydrogen is used to manufacture a number of chemicals. Two of the most abundantly produced chemicals that require hydrogen for synthesis are ammonia, NH_3, and methanol (methyl alcohol, CH_3OH). The latter is generated by the reaction between carbon monoxide and hydrogen:

$$CO + 2\,H_2 \rightarrow CH_3OH \tag{3.2.2}$$

Methanol used to be made by heating wood in the absence of air and condensing methanol from the vapor given off, a process known as destructive distillation. Generation of so-called wood alcohol made by this relatively green process from biomass has the potential to supply at least a fraction of the methanol now needed, thus reducing the consumption of natural gas.

Methanol has some important fuel uses. During the 1930s it was used instead of gasoline to run internal combustion engines to power a significant fraction of automobiles in France before Middle Eastern oil fields became such an abundant source of petroleum. At present it is blended with gasoline as an oxygenated additive; engines using this blended fuel produce less pollutant carbon monoxide. Now the most common use of methanol as a fuel is to break it down to elemental hydrogen and carbon dioxide to produce hydrogen used in fuel cells.

In addition to its uses in making ammonia and methanol, hydrogen is added chemically to hydrocarbon molecules in some fractions of gasoline to upgrade the fuel value of gasoline. Hydrogen can be added directly to coal or reacted with carbon monoxide to produce synthetic petroleum. It is also combined with unsaturated vegetable oils to make margarine and other hydrogenated fats and oils. This application is controversial and becoming less common because of suspected adverse long-term health effects of these products commonly called trans fats.

Hydrogen in Fuel Cells

Fuel cells, discussed further in Chapter 15, are devices that enable hydrogen to “burn” at around room temperature and to produce electricity directly without going through some sort of internal combustion engine and electricity generator. A fuel cell (Figure 3.2) consists of two electrically conducting electrodes, an anode and a cathode that are contacted with elemental H2 and O2, respectively. As shown in the diagram, at the anode H2 loses electrons (it is said to be oxidized) to produce H+ ion. At the cathode O2 gains electrons (it is said to be reduced) and reacts with H+ ions to produce water, H2O. The H+ ions required for the reaction at the cathode are those generated at the anode and they migrate to the cathode through a solid membrane permeable to protons (the H+ ion is a proton). The net reaction is

$$2\,H_2 + O_2 \rightarrow 2\,H_2O + \text{electricalenergy} \tag{3.2.3}$$

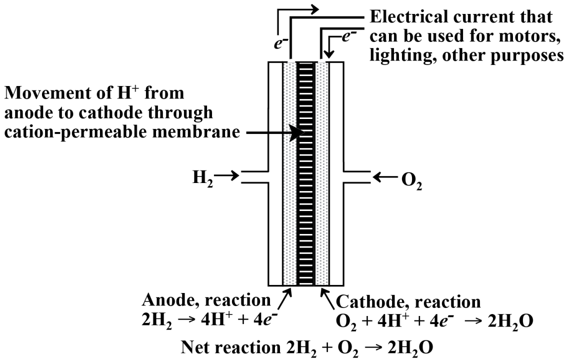


Figure 3.2. Cross-sectional diagram of a fuel cell in which elemental hydrogen can be reacted with elemental oxygen to produce electricity directly with water as the only chemical product.

3.3: Helium - The First Noble Gas

The second element in the periodic table is helium, He, atomic number 2. All helium atoms have 2 protons in their nuclei and 2 electrons. There are two isotopes of helium of which $^{4}_{2}\mathrm{He}$ that contains 2 neutrons in the nucleus is by far the predominant one, with much smaller numbers of the lighter isotope, $^{3}_{2}\mathrm{He}$ which has 2 protons and 1 neutron in its nucleus and a mass number of 3.

Helium is a *noble gas* meaning that it exists only as atoms of the elements that are never bonded to other atoms. Figure 3.3 is a representation of the helium atom showing its 2 electrons. The Lewis symbol of helium is simply He with 2 dots. This shows a very important characteristic of atoms. As electrons are added to atoms with increasing atomic number, they are added at various levels known as **electron shells**. The one electron in hydrogen, H, goes into the first electron shell, the one with the lowest possible energy. The second electron added to make the helium atom also goes into the first electron shell. This lowest electron shell can contain a maximum of only 2 electrons, so helium has a **filled electron shell**. Atoms with filled electron shells have no tendency to lose, gain, or share electrons and, therefore, do not become involved with other atoms through chemical bonding. Such atoms exist alone in the gas phase and the elements of which they consist are called noble gases. Helium is the first of the noble gases.

A helium atom has a filled electron shell containing 2 electrons.

It can be represented by the Lewis symbol above.

Figure 3.3. Two representations of the helium atom having a filled electron shell.

Helium gas has a very low density of only 0.164 g/L at 25˚C and 1 atm pressure. Elemental helium is the second least dense substance next to hydrogen gas. It is this low density characteristic that makes helium so useful in balloons, including weather balloons, which can stay aloft for days, reaching very high altitudes.

Helium is pumped from the ground with some sources of natural gas, some of which contain up to 10% helium by volume. Helium was first observed in the sun by the specific wavelengths of light emitted by hot helium atoms. Underground sources of helium were discovered by drillers searching for natural gas in southwestern Kansas who tried to ignite gas from a new well and were disappointed to find that it would not burn, since it was virtually pure helium!

Chemically unreactive, helium has no chemical uses, except to provide a chemically inert atmosphere. A nontoxic, odorless, tasteless, colorless gas, helium is used because of its unique physical properties. Applications in weather balloons and airships were mentioned previously. Because of its low solubility in blood, helium is mixed with oxygen for breathing by deep-sea divers and persons with some respiratory ailments. Use of helium by divers avoids the very painful condition called “the bends” caused by bubbles of nitrogen forming from nitrogen gas dissolved in blood.

The greatest use of helium is as the super-cold liquid, which boils at a temperature of only 4.2 K above absolute zero (-269˚C), especially in the growing science of **cryogenics**, which deals with very low temperatures. Some metals are superconductors at such temperatures so that helium is used to cool electromagnets enabling relatively small magnets to develop very powerful magnetic fields. Such magnets are components of the very useful chemical tool known as nuclear magnetic resonance (NMR). The same kind of instrument modified for clinical applications and called MRI is used as a medical diagnostic tool for scanning sections of the body for evidence of tumors and other maladies.

Hydrogen Wants to be Like Helium

Examination of the Lewis symbol of helium (right, Figure 3.3) and the Lewis formula of elemental hydrogen, H2, (Figure 3.1) shows that each of the two hydrogen atoms in the H2 molecule can lay claim to 2 electrons and thereby come to resemble the helium atom. Recall that helium is a noble gas that is very content with its 2 electrons. Each of the H atoms in H2 is satisfied with 2 electrons, though they are shared. This indicates a basic rule of chemical bonding that atoms of an element tend to acquire the same electron configuration as that of the nearest noble gas. In this case, hydrogen, which comes just before helium in the periodic table, gains the noble gas configuration of helium by sharing electrons.

3.4: Lithium, The First Metal

The element with atomic number 3 is lithium (Li), atomic mass 6.941. The most abundant lithium isotope is $^{7}_{3}\mathrm{Li}$ having 4 neutrons in its nucleus. A few percent of helium atoms are the $^{6}_{3}\mathrm{Li}$ isotope, which has only 3 neutrons. The third electron in lithium cannot fit in the lowest energy shell, which, as noted above, is full with only 2 electrons. Therefore, the third electron in lithium goes into a second shell, that is, an **outer shell**.

As a consequence of its electronic structure, lithium is the lowest atomic number element that is a **metal**. In a general sense, metals are elements that normally have only 1–3 electrons in their outer shells. These electrons can be lost from metals to produce positively charged *cations* with charges of +1, +2, or +3. In the pure elemental state metals often have a characteristic **luster** (shine), they are **malleable** (can be flattened or pushed into various shapes without breaking) and they **conduct electricity**. Although some metals, notably lead and mercury, are very dense, lithium is the least dense metal at only 0.531 g/cm3.

Two of lithium's 3 electrons are **inner electrons** contained in an **inner shell** as in the immediately preceding noble gas helium. Inner shell electrons such as these stay on average relatively close to the nucleus, are very tightly held, and are not exchanged or shared in chemical bonds. As mentioned above, the third electron in lithium is an **outer electron** farther from, and less strongly attracted to, the nucleus. The outer electron is said to be in the atom's *outer shell*. These concepts are illustrated in Figure 3.4.

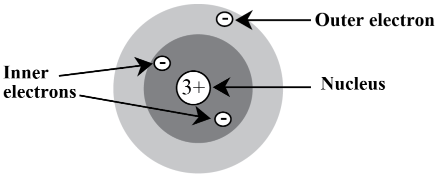
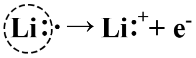


Figure 3.4. An atom of lithium, Li, has 2 inner electrons and 1 outer electron. The latter can be lost to another atom to produce the Li^{+} ion, which is present in ionic compounds (see Section 2.12).

The Lewis symbol for atoms such as lithium that have both inner shell and outer shell electrons normally shows just the latter. (Inner shell electrons can be shown on symbols to illustrate a point, but normally this takes too much space and can be confusing.) Since lithium has only one outer shell electron, its Lewis symbol is

$$\mathrm{Li}\cdot$$

Consider that the lithium atom has an inner shell of 2 electrons, just like helium. Being only 1 electron away from the helium noble gas structure, lithium has a tendency to lose its extra electron so it can be like helium as shown by the following:



$$\mathrm{Li}{:}\cdot \rightarrow \mathrm{Li}{:}^{+} + e^{-} \tag{3.4.1}$$

Note that the product of this reaction is no longer a neutral atom, but is a positively charged Li^{+} *cation*. In losing an electron to become a cation, the lithium atom is said to be **oxidized**. When lithium forms chemical compounds with other elements, it does so by losing an electron from each lithium atom to become Li^{+} cations. These, then, are attracted to negatively charged *anions* in ionic compounds.

Lithium compounds have a variety of uses. Lithium carbonate, Li2CO3, is widely prescribed as a pharmaceutical to alleviate the symptoms of mania in manic-depressive and schizo-affective mental disorders. Lithium carbonate is the most common starting material for the preparation of other lithium compounds and is an ingredient of specialty glasses and enamels and of ceramic ware that expands only minimally when heated. Lithium hydroxide, LiOH, is used to formulate some kinds of lubricant greases. In combination with iodine, lithium has been used to make cells that are sources of electricity for cardiac pacemakers. Implanted in the patient's chest, some of these pacemakers and their batteries have lasted for 10 years before having to be replaced.

Long an element with limited uses, lithium has become a rather "exciting" metal in the newly emerging sustainability economy because lithium-based storage batteries in which Li^{+} ion is a charge carrier have become the storage batteries of choice for computers, portable electric devices and, especially, electric and hybrid automobiles. Lithium storage batteries exhibit superior qualities with respect to charge held per unit mass, stability, and longevity. In addition, lithium dry cells in which Li metal is irreversibly converted to Li^{+} ion during discharge have become attractive (though expensive) options in the throwaway dry cell market because they are very long lived and carry much more charge per unit mass than standard alkaline dry cells.

The most common source of lithium is lithium brines where lithium has become concentrated by leaching of rock and evaporation of water from highland salt flats in South America and western China. Lithium salts are collected for processing from the evaporation of water from the brines in evaporation ponds. Bolivia is the largest producer of lithium and there is significant potential of production from Chile, Argentina, Australia, China, and perhaps even the state of Nevada. As use of lithium in batteries increases, recycled lithium from spent batteries will become an important source of the element.

3.5: The Second Period of the Periodic Table

The first period of the periodic table is a short one consisting of only two elements, hydrogen and helium. Lithium, atomic number 3 begins the second period, which has 8 elements. Elements with atomic numbers 4-10, which complete this period, are discussed in this section.

Beryllium, Atomic Number 4

Like atoms of all the elements in the second period of the periodic table, **beryllium**, atomic number 4, atomic mass 9.012, has 2 inner shell electrons. Beryllium also has 2 outer shell electrons, so its Lewis symbol is

$$\mathrm{Be}\!:$$

In addition to 4 protons in their nuclei, beryllium atoms also have 5 neutrons. When the beryllium atom is oxidized to form a beryllium cation, the reaction is

Be: → Be2+ + 2e- (lost to another atom) (3.5.1)

Since the beryllium atom needs to lose 2 electrons to reach the two-electron helium electron configuration, it produces doubly charged Be2+ cations.

Beryllium has some important uses in metallurgy. Melted together with other metals, a process that produces **alloys**, beryllium yields metal products that are hard and corrosion-resistant. Beryllium alloys can be blended that are good electrical conductors and that are nonsparking when struck, an important characteristic in applications around flammable vapors. Among the devices for which beryllium alloys are especially useful are various specialty springs, switches, and small electrical contacts. Beryllium has found widespread application in aircraft brake components where its very high melting temperature (about 1290˚C) and good heat absorption and conduction properties are very advantageous.

In a sense, beryllium is somewhat the opposite of a green element. This is because of its adverse health effects, including **berylliosis**, a disease marked by lung deterioration. Because of the extreme inhalation hazard of Be, allowable atmospheric levels are very low. Many workers were occupationally exposed to beryllium as part of the nuclear reactor and weapons industry in the U.S. in the decades following World War II. In recognition of the adverse health effects of occupational exposure to beryllium, in the late 1990s the U.S. Government agreed to compensate workers suffering occupational exposure to this metal.

Boron, a Metalloid

Boron, B, atomic number of 5, atomic mass 10.81, consists primarily of the isotope with 6 neutrons in addition to 5 protons in its nucleus; a less common isotope has 5 neutrons. Two of boron’s 5 electrons are in a helium core and 3 are outer electrons as denoted by

$$\dot{\mathrm{B}}\,:$$

Boron is the first example of an element with properties intermediate between those of metals and nonmetals called **metalloids**. In addition to boron, the metalloids include silicon, germanium, arsenic, antimony, and tellurium, of which the most notable, silicon, is among the first 20 elements. In the elemental state, metalloids have a luster like metals, but they do not readily form simple cations. Unlike metals, which generally conduct electricity well, metalloids usually conduct electricity poorly, if at all, but can become conductors under certain conditions. Such materials are called **semiconductors** and are of crucial importance because they form the basis of the world’s vast semiconductor industry, which has given us small, powerful computers and a huge array of other electronic products.

Boron is a high-melting substance (2190˚C) that is alloyed with copper, aluminum, and steel metals to improve their properties. As a good absorber of neutrons, boron is used in nuclear reactor control rods and as a neutron-absorbing additive to the water that circulates through a reactor core as a heat transfer medium. Boron nitride, BN, is extraordinarily hard, as are some other compounds of boron. Boron oxide, B2O3, is an ingredient of heat-insulating fiber glass and boric acid, H3BO3, is used as a flame retardant in cellulose insulation in houses.

The Element of Life, Carbon

Carbon, C, atomic number 6, brings us to the middle of the second period of the periodic table. In addition to its 2 inner electrons, the neutral carbon atom has 4 outer electrons as shown by the Lewis symbol

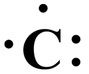


Figure 3.5 shows three organic compounds composed only of carbon and hydrogen (hydrocarbons), each containing 8 carbon atoms. These structures illustrate the bonding diversity of carbon.

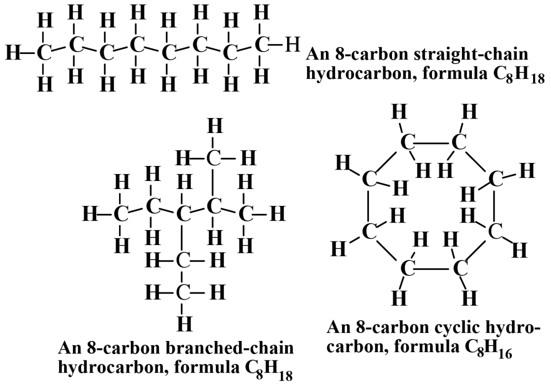


Figure 3.5. Illustration of the bonding versatility of carbon with three carbon-containing hydrocarbon compounds arranged as straight (continuous) chains, branched chains, and in a cyclic compound.

The ability of carbon atoms to bond with each other determines the properties of the several important and useful forms of elemental carbon. (Different forms of the same element are called allotropes.) Very fine carbon powder composes **carbon black**, which is used in tires, inks, and printer toner. Carbon atoms bonded in large flat molecules compose **graphite**, so soft and slick that it is used as a lubricant. Carbon treated with steam or carbon dioxide at elevated temperatures develops pores that give the carbon an enormous surface area. This product is **activated carbon** that is very useful in purifying foods, removing organic pollutants from water and removing pollutant vapors from air. Elemental carbon fibers are bonded together with epoxy resins to produce light composites so strong that they are used for aircraft construction. Bonded together in a different way that gives a very hard and rigid structure, carbon atoms produce diamond.

A particularly interesting class of carbon allotropes is that of **fullerenes** consisting of elemental carbon bonded in generally 5- and 6-membered rings to form spheres, ellipsoids, and tubes. The first of this class of elemental carbon discovered only in 1985 consists of aggregates of 60 carbon atoms bonded together in 5- and 6-membered rings that compose the surface of a sphere. This structure resembles the geodesic domes designed as building structures by Buckminster Fuller, a visionary designer. Therefore, the discoverers of this form of carbon named it buckminsterfullerene and the C60 balls, which resemble soccer balls in their structure, are commonly called “buckyballs.” Since the discovery of the C60 fullerene, many related forms have been synthesized, of which the most interesting may be very narrow carbon tubes called **carbon nanotubes**. (“Nano” is a prefix commonly assigned to materials in which the individual units have dimensions around 1 nanometer or 1 × 10-9 meters.) Carbon nanotubes have very interesting properties including some forms with an extraordinarily great length-to-diameter ratio of up to 132,000,000:1. Because of their unique dimensions, extraordinary strength, electrical properties, and ability to efficiently conduct heat, carbon nanotubes are of intense interest in materials science, nanotechnology, electronics, optics, and other high technology applications. However, special attention needs to be given to their potential toxicity.

Green Carbon from the Air

Carbon is present in the air as gaseous carbon dioxide, CO2. Although air is only about 0.04% CO2 by volume, it serves as the source of carbon for the growth of green plants. In so doing, the chlorophyll in plants captures solar energy in the form of visible light, represented *h*ν, and uses it to convert atmospheric carbon dioxide to high-energy glucose sugar, C6H12O6, as shown by the following reaction:

$$6\,CO_2 + 6\,H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6\,O_2 \tag{3.5.1}$$

The carbon fixed in the form of C6H12O6 and related compounds provides the basis of the food chains that sustain all organisms. Organic carbon produced by photosynthesis in eons past also provided the raw material for the formation of

> petroleum, coal, and other fossil fuels. Now, as supplies of these scarce resources dwindle and as the environmental costs of their extraction, transport, and utilization mount, there is much renewed interest in photosynthetically produced carbon compounds as raw materials and even fuels. Despite the low levels of carbon dioxide in the atmosphere and the relatively low efficiency of photosynthesis, rapidly growing plants, such as some varieties of hybrid poplar trees, can produce enormous quantities of carbon compounds very rapidly and in a sustainable manner.

Nitrogen from the Air

Nitrogen, N, atomic number 7, atomic mass 14.01, composes 78% by volume of air in the form of diatomic N2 molecules. The nitrogen atom has 7 electrons, 2 contained in its inner shell and 5 in its outer shell. So its Lewis symbol is the following:

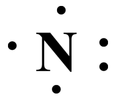


Figure 3.6.

Nitrogen gas does not burn and is generally chemically unreactive. Advantage is taken of the extreme chemical stability of nitrogen gas in applications where a nonreactive gas is needed to prevent fires and explosions. Although almost 80% of the air that people breathe consists of elemental nitrogen gas, people have died of asphyxiation by entering areas filled with nitrogen gas in which oxygen is absent. Since nitrogen gas has no odor, it does not warn of its presence.

Huge quantities of liquid nitrogen, which boils at a very cold -190˚C, are used in areas where cold temperatures are needed. This frigid liquid is employed to quick-freeze foods and for drying materials in freeze-drying processes, Biological materials, such as semen used in artificial breeding of animals, can be preserved in liquid nitrogen.

The atmosphere is an inexhaustible reservoir of nitrogen. However, it is very difficult to get nitrogen into the chemically combined form in which it occurs in simple inorganic compounds or proteins. This is because of the extreme stability of the N2 molecule, mentioned above. The large-scale chemical fixation of atmospheric nitrogen over a catalytic surface at high temperatures and pressure as represented by the reaction

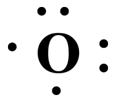
$$\mathrm{N_2 + 3\,H_2 \rightarrow 2\,NH_3} \tag{3.5.2}$$

was a major accomplishment of the chemical industry about a century ago. It enabled the large-scale production of relatively cheap nitrogen fertilizers that resulted in highly increased crop production, as well as the manufacture of enormous quantities of nitrogen-based explosives that made possible the unprecedented carnage of World War I. Despite the extreme conditions required for the preparation of nitrogen compounds by humans in the anthrosphere, humble bacteria accomplish the same thing under ambient conditions of temperature and pressure, converting N2 from the air into organically bound nitrogen in biomass. Prominent among the bacteria that do this are *Rhizobium* bacteria that grow symbiotically on the roots of legume plants, fixing atmospheric nitrogen that the plants need and drawing nutrients from the plants. Because of this ability, legumes, such as soybeans and clover grow well with less artificial nitrogen fertilizer than that required by other plants. One of the exciting possibilities with genetically modified plants is the potential to develop nitrogen-fixing varieties of corn, wheat, rice, and other crops that now lack the capability to fix nitrogen.

Nitrogen is an essential life element that is present in all proteins, hemoglobin, chlorophyll, enzymes, and other life molecules. It circulates through nature in the **nitrogen cycle** by which elemental nitrogen is incorporated from the atmosphere into biological material. Nitrogen-containing biomass is converted during biodegradation by bacteria to inorganic forms, which may be utilized as nutrient nitrogen by plants. Eventually, bacterial processes convert the nitrogen back to elemental N2, which is returned to the atmosphere to complete the cycle.

Oxygen, the Breath of Life

Oxygen, atomic number 8, atomic mass 16.00 is required by humans and many other living organisms. A diatomic nonmetal, elemental oxygen consists of O2 molecules and makes up 21% of the volume of air. Of its 8 electrons, the oxygen atom has 6 in the outer shell as represented by the Lewis formula:



Oxygen can certainly be classified as a green element for a number of reasons, not the least of which is that O in the atmosphere is there for the taking. Elemental oxygen is transferred from the atmosphere to the anthrosphere by liquifying air and distilling the liquid air, the same process that enables isolation of pure nitrogen. These two gases are also separated from air by adsorption onto solid surfaces under pressure followed by removal under vacuum. Pure oxygen has a number of applications including use as a gas to breathe by people with lung deficiencies, in chemical synthesis, and in oxyacetylene torches employed for welding and cutting metals.

Although the elemental oxygen molecule is rather stable, at altitudes of many kilometers in the stratosphere, it is broken down to oxygen atoms by the absorption of ultraviolet radiation from the sun as shown in Chapter 2, Reaction 2.13.1 As illustrated by Reaction 2.13.2, the oxygen atoms formed by the photochemical dissociation of O2 combine with O2 molecules to produce molecules of ozone, O3. The result is a layer of highly rarefied air containing some ozone over an altitude range of many kilometers located high in the stratosphere. There is not really much ozone in this layer. If it were pure ozone under the conditions of pressure and temperature that occur at ground level, the ozone layer would be only about 3 millimeters thick! This stratospheric ozone, sparse though it is, serves an essential function in protecting organisms on Earth’s surface from the devastating effects of ultraviolet radiation from the sun. Were it not for stratospheric ozone, life as it is now known could not exist on Earth.

Ozone has a split personality as a green form of oxygen. As discussed above, ozone in the stratosphere is clearly beneficial and essential for life. But it is toxic to inhale at levels less than even one part per million by volume. Ozone is probably the most harmful constituent of air polluted by the formation of photochemical smog in the atmosphere at ground levels.

The most notable chemical characteristic of oxygen is its ability to combine with other materials in energy-yielding reactions. One such reaction with which most people are familiar is the burning of gasoline in an automobile,

$$2\,\mathrm{C_8H_{18}} + 25\,\mathrm{O_2} \rightarrow 16\,\mathrm{CO_2} + 18\,\mathrm{H_2O} + \mathrm{energy} \tag{3.5.3}$$

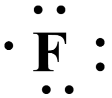
performed so efficiently that the combustion of only 1 gallon of gasoline can propel a full-size automobile more than 25 miles at highway speeds. Along with many other organisms, we use oxygen in our bodies to react with nutrient carbohydrates,

$$\mathrm{C_6H_{12}O_6(glucose)} + 6\,\mathrm{O_2} \rightarrow 6\,\mathrm{CO_2} + 6\,\mathrm{H_2O} + \mathrm{energy} \tag{3.5.4}$$

to provide energy that we use. Whereas the combustion of a fuel such as gasoline occurs at red-hot temperatures, the “burning” of carbohydrates in our body occurs through the action of enzymes in the body at body temperature of only 37˚C.

The Most Nonmetallic Element, Fluorine

Fluorine, F, atomic number 9, atomic mass 19.00 has 7 outer electrons as shown by its Lewis symbol



Elemental fluorine consists of diatomic F2 molecules constituting a greenish-yellow gas. Fluorine is the most nonmetallic of all the elements. It reacts violently with metals, organic matter, and even glass! Elemental fluorine is a very corrosive poison that attacks flesh and forms wounds that heal very poorly. Because of its hazards, the practice of green chemistry seeks to minimize the generation or use of F2.

Fluorine is used in chemical synthesis. It was once widely employed to make Freons, chlorofluorocarbon compounds such as dichlorodifluoromethane, Cl2CF2, that were used as refrigerant fluids, spray can propellants, and plastic foam blowing agents. As discussed in Chapter 10, these compounds were found to be a threat to the vital stratospheric ozone layer mentioned in the discussion of oxygen above. They have now been replaced with fluorine-containing substitutes such as HFC-134a, CH2FCF3, which either do not contain the chlorine (Cl) that destroys stratospheric ozone or undergo destruction by atmospheric chemical processes near Earth’s surface, and thus never reach the stratosphere.

3.6: The Magic Octet of 8 Outer-Shell Electrons

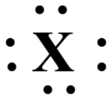
Only one element remains to complete the second period of the abbreviated periodic table. This element is **neon**, atomic number 10, atomic mass 20.18. Although most neon atoms have 10 neutrons in addition to the 10 protons in their nuclei, some have 12 neutrons, and very few have 11. Neon is a gas consisting of individual Ne atoms that constitutes about 2 parts per thousand of the volume of air. Neon is recovered by distillation of liquid air. Its most common use is as a gas in tubes through which an electrical discharge is carried in glowing neon signs.

The total of 10 electrons in the neon atom are contained in two shells with 8 in the outer shell. So the Lewis symbol of neon is

With 8 electrons, the second shell of electrons is a *filled electron shell*. (Recall that helium has a filled electron shell with only 2 electrons.) Because it has a filled outer electron shell, neon is a noble gas that exists as single gas-phase atoms and forms no chemical compounds.

The Special Significance of the Octet

In addition to helium and neon, there are four other noble gas elements. These are argon (atomic number 18), krypton (atomic number 36), xenon (atomic number 54), and radon (atomic number 86). Other than helium, these all share a common characteristic of 8 outer-shell electrons. Such an electron configuration can be shown by the general Lewis symbol,



and is known as an **octet** of electrons, where X is the chemical symbol of the noble gas.

Although only atoms of noble gases have octets as single atoms, many other atoms acquire octets by forming chemical bonds. This tendency of atoms to acquire stable octets through chemical bonding is the basis of the **octet rule**, which is used in this book to predict and explain the chemical bonding in a number of compounds, such as those discussed in Chapter 4. To see a simple application of the octet rule in chemical bonding, consider the bonds involved in molecular elemental nitrogen, N2. Recall the Lewis symbol of the N atoms showing 5 dots to represent the 5 outer-shell electrons in each N atom. Figure 3.6 shows bond formation between 2 N atoms.

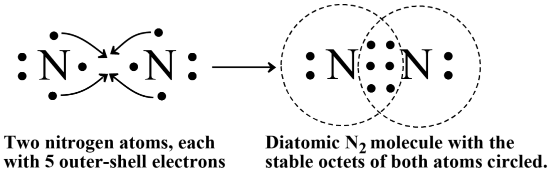


Figure 3.6. Illustration of the octet rule in the covalent bonding together of the 2 N atoms in N2. The six electrons in the bond connecting the two N atoms constitute a triple bond.

Each of the two N atoms in the N2 molecule needs 8 outer-shell electrons, but only 10 electrons are available to provide these electrons (the two inner-shell electrons in each N atom are not available to form bonds). This means that a lot of the electrons will have to be shared to form a bond between the N atoms in the N2 molecule, and, in fact, 6 of the 10 outer-shell electrons available in two N atoms are shared between the N atoms to give a *triple bond* consisting of 3 pairs of shared electrons as shown by the 3 pairs of dots between the 2 N atoms in the molecule of N2 in Figure 3.6.

3.7: Completing the 20-Element Periodic Table

So far in this chapter 10 elements have been defined and discussed. A total of 10 more are required to complete the 20-element abbreviated periodic table. Their names and properties are summarized briefly here. The periodic table is given in Figure 3.9.

Sodium, **Na**, atomic number 11, atomic mass 22.99, comes directly below lithium in the periodic table and is very similar to lithium in being a soft, chemically very reactive metal. There is one major isotope of sodium containing 12 neutrons in the atom's nucleus. Sodium has 10 inner-shell electrons contained in its first inner shell of 2 electrons and its second one of 8 electrons. The 11th electron in the sodium atom is in a third shell, which is an outer shell. This is shown as a single dot in the Lewis symbol of Na in Figure 3.7. The electrons in sodium can be represented as shown in Figure 3.7.

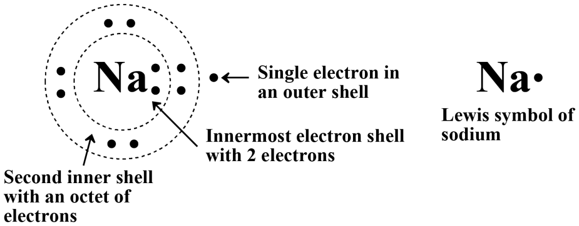


Figure 3.7. Representation of the electrons in 2 inner shells and 1 outer shell of sodium and the Lewis symbol of sodium.

Magnesium, **Mg**, atomic number 12, atomic mass 24.31, has 12 electrons per atom so it has 2 outer shell electrons. There are three isotopes of magnesium containing 12, 13, and 14 neutrons. Magnesium is a relatively strong, very lightweight metal that is used in aircraft, extension ladders, portable tools, and other applications where light weight is particularly important.

Aluminum, **Al**, atomic number 13, atomic mass 26.98, has 3 outer-shell electrons in addition to its 10 inner electrons. Aluminum is a lightweight metal used in aircraft, automobiles, electrical transmission lines, building construction and many other applications. Although it is chemically reactive, the oxide coating formed when aluminum on the surface of the metal reacts with oxygen in air is self-protecting and prevents more corrosion.

In some important respects aluminum can be regarded as a green metal. This is because aluminum enables construction of strong lightweight components which, when used in aircraft and automobiles, require relatively less energy to move. So aluminum is important in energy conservation. Aluminum cables also provide an efficient way to transmit electricity. Although the ores from which aluminum is made are an extractive resource dug from the earth, aluminum is an abundant element. And there are alternative resources that can be developed, including aluminum in the fly ash left over from coal combustion. Furthermore, aluminum is one of the most recyclable metals, and scrap aluminum is readily melted down and cast into new aluminum goods.

If an "element of the century" were to be named for the 1900s, humble **silicon**, **Si**, atomic number 14, atomic mass 28.09, would be a likely candidate. This is because silicon is the most commonly used of the semiconductor elements and during the latter 1900s provided the basis for the explosion in electronics and computers based upon semiconductor devices composed primarily of silicon. Despite the value of these silicon-based products, silicon is abundant in soil and rocks, ranking second behind oxygen as a constituent of Earth's crust. The silicon atom has 4 outer-shell electrons, half an octet, and it is a metalloid, intermediate in behavior between the metals on the left of the periodic table and the nonmetals on the right.

By vastly reducing the bulk of electronic components relative to performance, silicon has contributed to a huge saving of materials used in radios, televisions, communications equipment, and other electronic devices. Furthermore, the silicon-based semiconductor devices used in solid-state electronics consumes only a fraction of the electricity once used by vacuum tube based devices. The bulky wires made of relatively scarce copper formerly employed for transmitting communications signals electrically have been largely replaced by fiber optic devices consisting of transparent silica, SiO2, which transfer information as pulses of light. A hair-like optical fiber can transmit many times the amount of information per unit time as the thick copper wire that it replaces. And the energy required for transmission of a unit of information by a fiber optic cable is minuscule compared to that required to send the same information by electrical impulse over copper wire. So silicon is truly a green element that, although cheap and abundant, performs electronic and communications functions much faster and better than the copper and other metals that it has replaced.

Phosphorus, **P**, atomic number 15, atomic mass 30.97, has 5 outer-shell electrons. So it is directly below nitrogen in the periodic table and resembles nitrogen in its chemical behavior. Pure elemental phosphorus occurs in several forms, the most abundant of which is white phosphorus. White phosphorus is a chemically very reactive nonmetal that may catch fire spontaneously in the atmosphere. It is toxic and causes deterioration of bone. The jawbone is especially susceptible to the effects of phosphorus and develops a condition known as "phossy jaw" in which the bone becomes porous and weak and may break from the strain of chewing. Chemically combined phosphorus is an essential life element, however, and is one of the components of DNA, the basic molecule that directs molecular life processes. Phosphorus is also an essential plant fertilizer and is an ingredient of many industrial chemicals including some pesticides.

Arsenic is in the same group of the periodic table as phosphorus and occurs as an impurity with phosphorus processed from ore. If this phosphorus is to be used for food, the arsenic has to be removed.

Sulfur, **S**, atomic number 16, atomic mass 32.06, has 6 outer-shell electrons. It is a brittle, generally yellow nonmetal. It is an essential nutrient for plants and animals occurring in the amino acids that compose proteins. Sulfur is a common air pollutant emitted as sulfur dioxide, SO2, in the combustion of fossil fuels that contain sulfur. Much of the large quantities of sulfur required for industrial production of sulfuric acid and other sulfur-containing chemicals is reclaimed from the hydrogen sulfide, H2S, that contaminates much of the natural gas (methane, CH4) that is such an important fuel and raw material in the world today. In keeping with the best practice of green chemistry, the hydrogen sulfide is separated from the raw natural gas and about 1/3 of it is burned,

$$2\,H_2S + 3\,O_2 \rightarrow 2\,SO_2 + 2\,H_2O \tag{3.7.1}$$

producing sulfur dioxide, SO2. The sulfur dioxide produced is then reacted with the remaining hydrogen sulfide through the Claus reaction, below, yielding an elemental sulfur product that is used to synthesize sulfuric acid and other sulfur chemicals.

$$2\,H_2S + SO_2 \rightarrow 3\,S + 2\,H_2O \tag{3.7.2}$$

Chlorine, **Cl**, atomic number 17, atomic mass 35.453, has 7 outer-shell electrons, just 1 electron short of a full octet. Elemental chlorine is a greenish-yellow diatomic gas consisting of Cl2 molecules. In these molecules the Cl atoms attain stable octets of outer-shell electrons by sharing two electrons in a covalent bond as illustrated in Figure 3.8. The chlorine atom can also accept an electron to attain a stable octet in the Cl- anion as shown in the ionic compound sodium chloride, NaCl, in Figure 3.8.

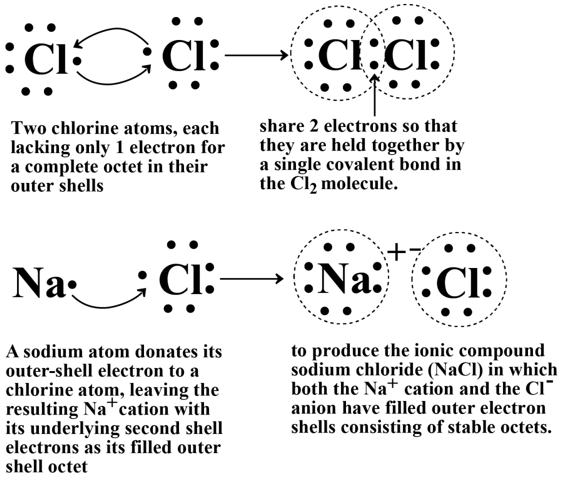


Figure 3.8. Chlorine atoms can attain a stable octet of outer-shell electrons by sharing electrons in covalent bonds, as shown for molecular diatomic elemental Cl2, or by accepting electrons to produce Cl- anion as shown for ionic sodium chloride, NaCl.

Elemental chlorine can be deadly when inhaled and was the first military poison gas used in World War I. Despite its toxic nature, chlorine gas has saved many lives because of its use for approximately the last 100 years as a drinking water disinfectant that has eradicated deadly water-borne diseases, such as cholera and typhoid. Chlorine is an important industrial chemical that is used to make plastics and solvents. There is no possibility of a shortage of chlorine and it can even be made by passing an electrical current through seawater, which contains chlorine as dissolved sodium chloride.

The green aspects of chlorine depend upon its application. Elemental chlorine is certainly a dangerous material whose manufacture and use are generally to be avoided where possible in the practice of green chemistry. But, as noted above, elemental chlorine has saved many lives because of its uses to disinfect water. A number of persistent pesticides including DDT are organic compounds composed of chlorine along with carbon and hydrogen. In addition to the ecological damage done by these pesticides, the waste byproducts of their manufacture and of the production of other organochlorine compounds are among the most abundant contaminants of troublesome hazardous waste chemical dumps. A common plastic, polyvinyl chloride (PVC), contains chlorine. This plastic is widely used in water pipe and drain pipe, in the former application replacing relatively scarce and expensive copper metal and toxic lead. But the material used to make PVC is volatile vinyl chloride. It is one of the few known human carcinogens, having caused documented cases of a rare form of liver cancer in workers formerly exposed to very high levels of vinyl chloride vapor in the workplace. Because of the dangers of elemental chlorine and the problems caused by organochlorine compounds, the practice of green chemistry certainly tries to minimize the production and use of elemental chlorine and generally attempts to minimize production of organochlorine compounds and their dispersion in the environment.

Element number 18, **argon**, **Ar**, atomic mass 39.95, brings us to the end of the third period of the abbreviated periodic table. It has a complete octet of outer-shell electrons and is a noble gas. No true chemical compounds of argon have been isolated and no chemical bonds involving this element were known until formation of a very unstable transient bond involving Ar atoms was reported in September, 2000. Argon composes about 1% by volume in the atmosphere. Largely because of its chemically inert nature, argon has some uses. It is employed as a gas to fill incandescent light bulbs. In this respect it helps prevent evaporation of white-hot tungsten atoms from the glowing lamp filament, thus significantly extending bulb life. It is also used as a plasma medium in instruments employed for inductively coupled plasma atomic emission analysis of elemental pollutants. In this application a radiofrequency signal is used to convert the argon to a gaseous plasma that contains positively charged Ar+ ions and negatively charged electrons and is heated to an incredibly hot 10,000˚C.

Completing the Periodic Table

The next element to be added to the abbreviated periodic table is element number 19. This begins a fourth period of the periodic table. This period actually contains 18 elements, but we will take it only as far as the first two. That is because element number 21 is the first of the transition metals and to explain their placement in the periodic table on the basis of the electrons in them gets a little more complicated and involved than is appropriate for this book. The reader needing more details is referred to other standard books on beginning chemistry.2,3

The element with atomic number 19 is **potassium**, **K**, having an atomic mass of 39.10. Most potassium consists of the isotope with 20 neutrons, ${}^{39}_{19}\mathrm{K}$. However, a small fraction of naturally occurring K is in the form of ${}^{40}_{19}\mathrm{K}$. This is a radioactive isotope of potassium and since we all have potassium (an essential element for life) in our bodies, we all are naturally radioactive! Muscle mass contains more potassium than adipose (fat) tissue, so more muscular people are more radioactive. But not to worry, the levels of radioactivity from potassium in the body are too low to cause concern and, under any circumstances, cannot be avoided. (One proponent of nuclear energy has pointed out that sleeping with a muscular person exposes one to more radioactivity than does living close to a nuclear power reactor.)

The same things that can be said of sodium, element number 11, are generally true of potassium. In the pure elemental state, potassium is a very reactive *alkali metal*. As an essential element for life, it is a common fertilizer added to soil to make crops grow well. Chemically, potassium loses its single outer-shell electron to produce K+ ion.

Calcium, **Ca**, atomic number 20, atomic mass 40.08, has 2 outer-shell electrons, two beyond a full octet. The calcium atom readily loses its 2 “extra” electrons to produce Ca2+ cation. Like other elements in its group in the periodic table, calcium is an alkaline earth metal. Elemental calcium metal is chemically reactive, though not so much so as potassium. Calcium has chemical properties very similar to those of magnesium, the alkaline earth metal directly above calcium in the periodic table.

Calcium is essential for life, although most soils contain sufficient calcium to support optimum crop growth. Calcium is very important in our own bodies because as hard mineral hydroxyapatite, Ca5OH(PO4)3, it is the hard material in teeth and bones. Calcium deficiency can cause formation of poor teeth and the development of disabling osteoporosis a condition characterized by weak bones that is especially likely to afflict older women.

3.8: The Brief Periodic Table is Complete

With element number 20, all of the elements required for the abbreviated periodic table have been described. As noted above, the placement of electrons in elements with atomic number 21 and higher is a little too complicated to explain here. However, these elements are important and they are all shown in the complete periodic table at the end of this chapter. Among the heavier elements in the complete periodic table are the transition metals, including the important metals chromium, manganese, iron, cobalt, nickel, and copper. Also included are the lanthanides and the actinides. Among these elements are thorium, uranium, and plutonium, which are important in nuclear energy and nuclear weaponry.

The abbreviated periodic table with the first 20 elements is illustrated in Figure 3.9. In addition to atomic number and atomic mass, this table shows the Lewis symbol of each element. It is seen that the symbols of the elements in the same vertical columns have the same number of dots showing identical configurations for their outer-shell electrons. This very simple, brief table contains much useful information, and it is recommended that the reader become familiar with it and be able to reproduce the Lewis symbols for each of the 20 elements. As will be seen in later chapters, the chemistry of the first 20 elements tends to be straightforward and easily related to the atomic structures of these elements.

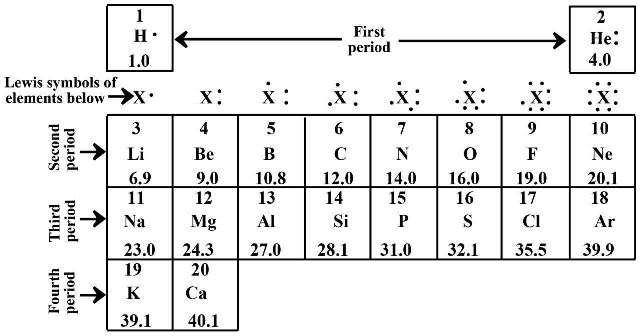


Figure 3.9. Abbreviated 20-element version of the periodic table showing Lewis symbols of the elements.

In examining the periodic table, hydrogen should be regarded as having unique properties and not belonging to a specific group. Otherwise, the elements in vertical columns belong to *groups* with similar chemical properties. Excluding hydrogen, the elements in the first group on the left of the table — lithium, sodium, and potassium — are *alkali metals*. In the elemental state alkali metals have a very low density and are so soft that they can be cut with a knife. Freshly cut, an alkali metal surface has a silvery-white color which almost instantaneously turns to a coating of gray metal oxide with exposure to air. The alkali metals (represented by M, below) react violently with water,

$$2M + 2H_2O \rightarrow 2MOH + H_2 \quad (3.5.4)$$

to produce the metal hydroxides, strongly basic substances that can be very destructive to flesh that they contact. The alkali metals react with elemental chlorine to produce the ionic chloride salts including, in addition to NaCl shown in Figure 3.8, LiCl and KCl. The second group of the abbreviated periodic table contains beryllium, magnesium, and calcium, all known as *alkaline earth* metals. Freshly exposed surfaces of these metals have a grayish-white luster. These metals are highly reactive to form doubly charged cations (Be^{2+}, Mg^{2+}, Ca^{2+}) by the loss of 2 electrons per atom. The second group from the right, which in the abbreviated periodic table consists of fluorine and chlorine, is known as the **halogens**. These elemental halogens are diatomic gases in which the two atoms of F_2 or Cl_2 are held together by a single covalent bond consisting of two shared electrons. These elements are the most nonmetallic of the elements. Rather than losing electrons to produce positively charged cations, as is common with metals, the halogens readily gain electrons to complete their outer shell electron octets, producing F^- and Cl^- anions. The far right group of the abbreviated periodic table is composed of the *noble gases*, helium, neon, and argon. These elements have complete outer shells, exhibit no tendency to enter into chemical bonds, and consist of individual gas-phase atoms.

3.E: The Elements - Basic Building Blocks of Green Chemicals (Exercises)

Access to and use of the internet is assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be "right."

1. Match the law or observation denoted by letters below with the portion of Dalton's atomic theory that explains it denoted by numbers:

A. Law of Conservation of Mass B. Law of Constant Composition

C. The reaction of C with O_2 does not produce SO_2

D. Law of Multiple Proportions

1. Chemical compounds are formed by the combination of atoms of different elements in definite constant ratios that usually can be expressed as integers or simple fractions

2. During the course of ordinary chemical reactions, atoms are not created or destroyed

3. During the course of ordinary chemical reactions, atoms are not changed to atoms of other elements

4. Illustrated by groups of compounds such as $CHCl_3$, CH_2Cl_2, or CH_3Cl

2. Explain why it is incorrect to say that atomic mass is the mass of any atom of an element. How is atomic mass defined?

3. Define what is meant by the notation ${}^{y}_{x}\mathrm{A}$? What do y, x, and A mean?

4. What is the Lewis symbol of hydrogen and what does it show? What is the Lewis formula of H2 and what does it show?

5. Why should hydrogen be considered in a separate category of the periodic table?

6. Consider the Lewis symbol of helium and explain how the helium atom illustrates the concepts of electron shell, filled electron shell, and noble gases.

7. What does helium have to do with cyrogenics?

8. Use three dots to show all the electrons in the lithium atom, Li. What does this show about inner and outer electrons and why Li produces Li+ cation?

9. In what respect may it be argued that beryllium is definitely not a green element?

10. What are two elemental oxygen species other than molecular O_2 found at very high altitudes in the stratosphere? How do they get there?

11. In what respects may carbon be classified as the "element of life"?

12. How are a specific kind of fluorine compounds related to stratospheric ozone? What does this have to do with green chemistry?

13. How does neon illustrate important points about the octet and the octet rule?

14. Of the following, the **untrue** statement pertaining to matter, atoms, and elements is

A. All matter is composed of only about a hundred fundamental kinds of matter called elements.

B. Each element is made up of very small entities called atoms

C. All atoms of the same element have the same number of protons and neutrons and the same mass

D. All atoms of the same element behave identically chemically

E. All atoms of the same element have the same number of protons

15. Given that in the periodic table elements with atomic numbers 2, 10, and 18 are gases that do not undergo chemical reactions and consist of individual molecules, of the following, the statement most likely to be true is

A. Elements with atomic numbers 3, 11, and 19 are also likely to be gases.

B. Elements with atomic numbers 3, 11, and 19 would not undergo chemical reactions.

C. Elements with atomic numbers 10 and 18 would be at opposite ends of the table.

D. The element with atomic number of 11 may well be a highly reactive metal.

E. The properties of elements with atomic number 3, 11, and 19 would have chemical properties that are much different from each other.

16. The two atoms represented below

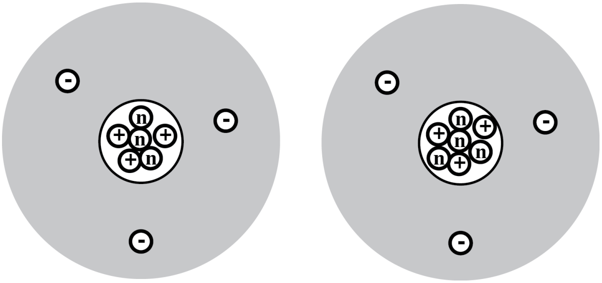
A. Are of different elements.

B. Are atoms of deuterium, a form of hydrogen, H.

C. Are of the same element.

D. Are **not** isotopes of the same element.

E. Are of two elements with atomic numbers 6 and 7.



17. Of the following, the statement that is **untrue** regarding chemical bonding and compounds is

A. Chemical bonds occur only in compounds, not in pure elements.

B. Molecules of H2 are held together by bonds consisting of shared electrons.

C. Ionic compounds consist of charged atoms or groups of atoms.

D. Both pure elemental hydrogen, H_2, and the compound water, H_2O, have covalent bonds.

E. An atom that has more electrons than protons is an anion.

18. Suggest a material that is a source of electrons in a fuel cell used to generate electricity. What may accept electrons?

19. What are semiconductors? What is the most important semiconductor discussed in this chapter.

20. What is the most notable chemical characteristic of elemental oxygen?

21. What are some reasons that aluminum can be regarded as a green metal?

22. What are some of the toxic elements or elemental forms among the first 20 elements?

23. What is a common air pollutant gas that contains sulfur?

24. Why does the abbreviated periodic table stop at atomic number 20?

25. Suggest why calcium might be particularly important in the diet of (A) children and (B) older people?

26. Which elements among the first 20 are commonly present in fertilizers used to enhance the growth of food crops?

27. What is the special significance of the carbon isotope with 6 neutrons in its nucleus?

28. What is the single exception to the rule that all atoms contain at least 1 neutron?

29. What is the single exception to the rule that noble gases contain stable octets of electrons?

30. What is the outer-shell electron configuration of metals? What does this have to do with their chemical behavior?

31. What is it about the carbon atom that enables millions of organic compounds to exist?

32. What are some of the forms of elemental carbon and their uses? Which of these was discovered only relatively recently?

33. What is the major chemical characteristic of elemental nitrogen? What is a major advantage afforded by this characteristic? In what respect is this a problem?

34. What are two applications that elemental magnesium and aluminum have in common?

35. How do copper and silica differ in the way that they transfer communications signals?

36. Using the octet rule, propose a Lewis formula for O_2.

3.R: References

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CHAPTER OVERVIEW

4: Compounds- Safer Materials for a Safer World

“The millions of known chemical compounds vary tremendously in their properties. For example, some are so unstable that just touching them with a steel spatula will cause them to explode spontaneously. Others are so stable and persistent that they last practically forever in the environment”

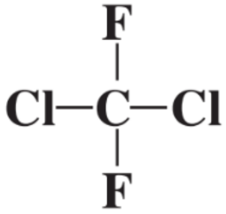
4.1: Chemical Bonds and Compound Formation
4.2: Electrons Involved in Chemical Bonds and Octets of Electrons
4.3: Sodium Chloride and Ionic Bonds
4.4: Covalent Bonds in H2 and Other Molecules
4.5: Covalent Bonds in Compounds
4.6: Covalent Bonds and Green Chemistry
4.7: Predicting Formulas of Covalently Bound Compounds
4.8: Chemical Formulas, the Mole, and Percentage Composition
4.9: What Are Chemical Compounds Called?
4.10: Acids, Bases and Salts
Questions and Problems

4.1: Chemical Bonds and Compound Formation

Chemical compounds consist of molecules or aggregates of ions composed of two or more elements held together by chemical bonds. Several examples of chemical compounds including water (H_2O), ammonia (NH_3), and sodium chloride (NaCl) were given in earlier chapters. This chapter addresses chemical compounds in more detail, including aspects of their green chemistry.

A crucial aspect of chemical compounds consists of the kinds of bonds that hold them together. As noted earlier, these may be covalent bonds composed of shared electrons or ionic bonds consisting of positively charged cations and negatively charged anions. The strengths of these bonds vary and are important in determining compound behavior. For example, chlorofluorocarbons, such as dichlorodifluoromethane, Cl_2CF_2, are so stable that they persist in the atmosphere and do not break down until reaching very high altitudes in the stratosphere, where the release of chlorine atoms destroys stratospheric ozone. The extreme stabilities of the chlorofluorocarbons are due to the very high strengths of the C-Cl and C-F bonds by which chlorine and fluorine are bonded to a central carbon atom. The proper practice of green chemistry requires that substances that get released to the environment break down readily. Since Cl_2CF_2 is so stable when released to the atmosphere, it cannot be regarded as being a very good green chemical.

Another important aspect of the way in which chemical compounds are put together is molecular structure, which refers to the shape of molecules. Consider the Cl_2CF_2 compound just mentioned in which the Cl and F atoms are bonded to a single carbon atom. To represent this molecule as the flat structure (below)



is not totally correct because not all of the 5 atoms in the compound lie in the same plane. Instead, the F and Cl atoms can be visualized as being distributed as far apart as possible in three dimensions around a sphere, at the center of which is the C atom. This can be represented as

where the two Cl atoms are visualized as being above the plane of the book page toward the reader and the two F atoms are represented as being below the plane of the page away from the reader. The shape of molecules is very important in determining the ways in which they interact with other molecules. For example, the molecules of enzymes that enable metabolism to occur in living organisms recognize the substrate molecules upon which they act by their complementary shapes.

What Are Green Chemical Compounds?

Chemical compounds vary markedly in the degree to which they are “green.”Dichlorodifluoromethane, Cl_2CF_2, the chlorofluorocarbon discussed above, is definitely not green. That is not because it is toxic — it is one of the least toxic synthetic compounds known — but because it is so extremely stable and persistent in the atmosphere and can cause stratospheric ozone destruction. The compounds that have replaced it, the hydrofluorocarbons and hydrochlorofluorocarbons, are much more green because they do not last long when released in the atmosphere or do not contain ozone-damaging chlorine.

There are several characteristics of compounds that meet the criteria of being green. These are the following:

- Preparation from renewable or readily available resources by environmentally friendly processes
- Low tendency to undergo sudden, violent, unpredictable reactions such as explosions that may cause damage, injure personnel, or cause release of chemicals and byproducts to the environment.

- Nonflammable or poorly flammable
- Low toxicity
- Absence of toxic or environmentally dangerous constituents, particularly heavymetals
- Facile degradability, especially biodegradability, in the environment.
- Low tendency to undergo bioaccumulation in food chains in the environment

An example of a green compound is sodium stearate, common hand soap. This common substance is prepared by reacting byproduct animal fat with sodium hydroxide, which is prepared by passing an electrical current through saltwater. Flushed down the drain, sodium stearate reacts with calcium in water to form a solid, calcium stearate, the white solid that composes “bathtub ring.” This removes the soap from the water and the nontoxic calcium stearate readily undergoes biodegradation so that it does not persist in the environment.

4.2: Electrons Involved in Chemical Bonds and Octets of Electrons

The electrons in the *outermost shell* of atoms are those that become involved in chemical bonds. These are called **valence electrons**. Refer back to the *Lewis symbols* of the elements shown in Figure 3.9. Note that the three elements on the right of the table are *noble gases* that are chemically content with their filled outer electron shells containing 2 electrons in the case of helium and 8 each for neon and argon. As a basis for the understanding of chemical bonds consider that the other elements tend to attain the filled electron shells of their nearest-neighbor noble gases by sharing, losing, or gaining electrons. Of these elements, the only one that we will consider in detail that attains a helium-like electron configuration is hydrogen, H, each atom of which almost always has access to 2 electrons shared in covalent bonds. The other elements that we will consider, carbon and higher, attain 8 electrons in their outer shells by chemical bonding. This is the basis of the **octet rule**, the tendency of atoms to attain stable outer shells of 8 electrons by forming chemical bonds. The octet rule is immensely useful in explaining and predicting chemical bonds and the formulas and structures of chemical compounds and will be emphasized in this chapter.

Some examples of the kinds of bonding arrangements discussed above have already been illustrated in Chapter 3. Figure 3.1 illustrates that, even in the elemental form, H2, hydrogen atoms have 2 valence electrons in the diatomic molecule. Examples of elements that have 8 valence electrons as the result of chemical bonding were also shown. Figure 3.6 illustrates the two N atoms in the N_2 molecule sharing 6 electrons in a covalent bond so that each of the atoms may have an octet. Figure 3.8 shows that 2 Cl atoms, each with 7 valence electrons, share 2 electrons in the covalent bond of the Cl_2 molecule to attain octets. The same figure shows that Na loses its single valence electron in forming ionic NaCl to produce the Na^+ ion, which has an octet of electrons in its outer shell. In forming the same ionic compound, Cl gains an electron to become the Cl^- anion, which also has a stable octet of outer-shell electrons.

In the remainder of this chapter, the octet rule will be used in explaining the formation of chemical compounds consisting of two or more different elements bonded together. It was already used to show the bonding in ionic sodium chloride in Figure 3.8. One of the best compounds for showing the octet rule in covalent compounds is methane, CH_4, shown in Figure 4.1. The molecule of CH_4 is produced when an atom of carbon with 4 outer electrons (see Figure 3.9) attains an octet of 8 electrons by sharing with H atoms.

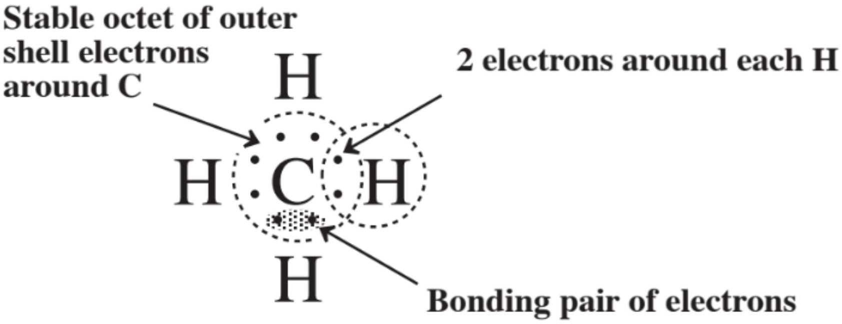


Figure 4.1. Stable outer electron shells from covalent bonding in compounds

Each H atom has 1 electron to donate to the sharing arrangement, so by each of 4 H atoms contributing an electron the carbon atom can gain an octet. Each of the H atoms has access to 2 electrons in the single covalent bond that connects it to the C atom. Examination of Figure 4.1 implies that the 4 H atoms and the C atom all lie in the same plane in a flat structure. But that is not the case because of the tendency for the 4 electron pairs composing the 4 covalent bonds to be oriented as far as possible from each other around the sphere of the carbon atom. The resulting structure is a little hard to illustrate on paper, but one way to approximate it is with a ball and stick model that represents the atoms as balls and the chemical bonds as sticks connecting the atoms. Figure 4.2 is an illustration of the ball and stick model of CH_4.

4.3: Sodium Chloride and Ionic Bonds

Many atoms and groups of atoms in chemical compounds are **ions** that have an electrical charge because of their unequal numbers of protons and electrons. **Cations** are positively charged ions and **anions** are negatively charged ions. Compounds consisting of ions are **ionic compounds** and the bonds holding them together are **ionic bonds**. Ionic bonds depend upon the mutual attraction between positive cations and negative anions for their bond strength (oppositely charged bodies attract each other, whereas negatively charged bodies repel each other).

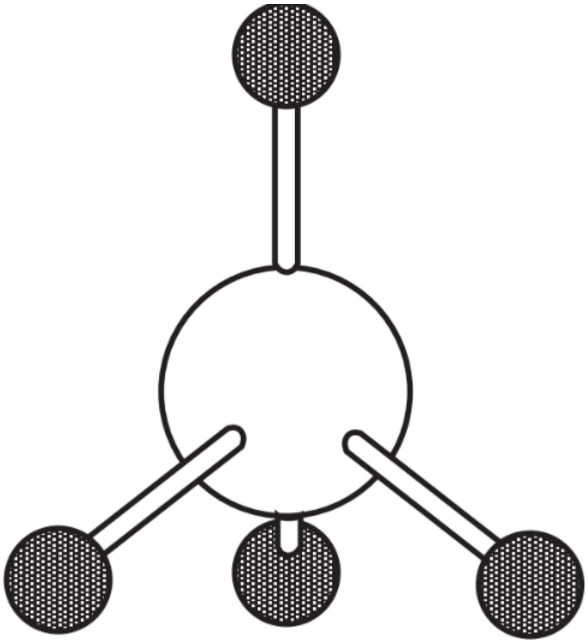


Figure 4.2. Ball and stick model of CH_4 in which 4 H atoms (shaded balls) are arranged in three dimensions around a carbon atom.

The formation of ions based upon the octet rule is readily seen for the well-known ionic compound, sodium chloride, NaCl, as illustrated in Figure 4.3. By losing an electron to become the Na^+ cation, sodium's underlying shell of 8 electrons becomes the ion's outer shell with a stable octet. Chlorine attains a stable octet of 8 outer-shell electrons by gaining 1 electron per atom to produce Cl^- ion.

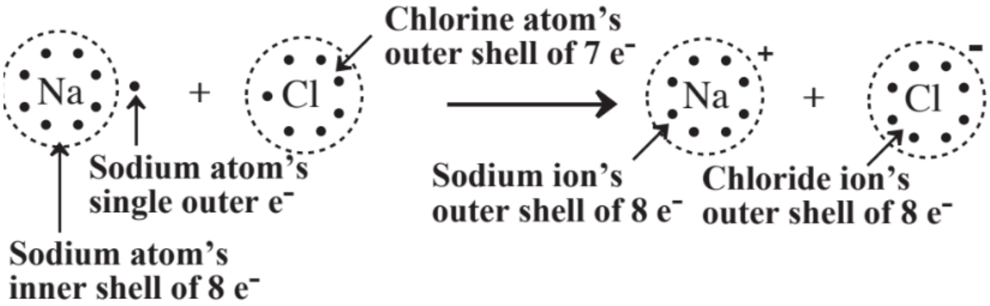


Figure 4.3. Formation of ionic sodium chloride from neutral Na and Cl atoms.

Sodium chloride is a very stable compound because of the mutual attraction of oppositely charged ions. But the ions have to be arranged in an optimum manner for this attraction to be effective. Since oppositely charged ions attract each other, but ions with the same charge are mutually repulsive, the ions in an ionic compound such as sodium chloride have to be packed to maximize attraction and minimize repulsion. The arrangement that does this for NaCl is shown by a ball and stick model in Figure 4.4.

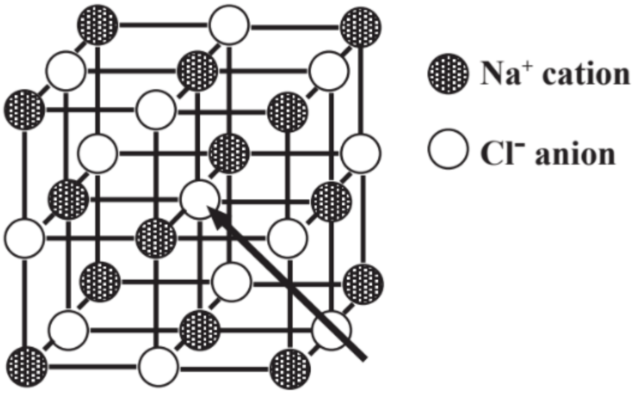


Figure 4.4. Representation of the structure of NaCl. This structure can be visualized in three dimensions as “balls” with interconnecting “sticks.” The balls are Na^+ and Cl^- ions. The closest neighbors to the Cl^- ion marked with an arrow are 6 Na^+ ions. The 6 closest neighbors to the Cl^- ion marked with an arrow are 6 Na^+ ions.

Although it may be a little hard to imagine for a model represented on paper, the six nearest neighbors of each negatively charged Cl^- anion are Na^+ cations. And the six nearest neighbors of each positively charged Na^+ cation are negatively charged Cl^- anions

In reality, ions are more accurately represented in an ionic structure as spheres that touch. The Na^+ cation is significantly smaller than the Cl^- anion, so a more accurate representation of NaCl than that shown in Figure 4.4 would show rather large Cl- spheres between which are nestled barely visible Na+spheres. But the imperfect ball and stick model shown in Figure 4.4 shows several important points regarding ionic NaCl. It illustrates the relative positions of the ions. These positions, combined with ionic charge and size, determine the **crystal structure** of the solid crystal of which the ionic compound is composed. Furthermore, examination of the figure shows that no single Cl^- anion belongs to a specific Na^+ cation, and no single Na^+ cation belongs to a specific Cl^- anion. So, although the chemical formula NaCl accurately represents the relative numbers of Na and Cl atoms in sodium chloride it *does not* imply that there are discrete molecules consisting of 1 Na and 1 Cl. For this reason it is not correct to refer to a *molecule* of sodium chloride because distinct molecules of ionic compounds do not exist as such. Instead, reference is made to **formula units** of ionic compounds, where a formula unit of NaCl consists of 1 Na^+ ion and 1 Cl^- ion, the smallest quantity of a substance that can exist and still be sodium chloride.

The stabilities of chemical compounds are all about energy. In general, the more energy released when a compound forms, the more stable the compound is. Sodium chloride could be formed by reacting elemental solid sodium with elemental Cl_2 gas,

$$2\,\mathrm{Na(solid)} + \mathrm{Cl_2(gas)} \rightarrow 2\,\mathrm{NaCl(solid)} \tag{4.3.1}$$

to produce solid sodium chloride. This reaction releases a large amount of energy and elemental sodium burns explosively in chlorine gas. The reaction can be viewed in terms of the following steps.

1. The atoms in solid Na are taken apart, which requires energy.
2. Each molecule of Cl_2 is taken apart, which requires energy.
3. An electron is taken from each Na atom to produce Na^+ ion, which requires energy.
4. An electron is added to each Cl atom to produce a Cl^- ion, which releases energy.
5. All the Na^+ cations and 1 Cl^- anion are assembled in a 1/1 ratio in a crystal lattice to produce NaCl, which releases a very large quantity of energy.

The very large amount of energy involved in Step 5 is called the **lattice energy** and is primarily responsible for the high stability of ionic compounds. A general picture of the energy involved is shown in Figure 4.5.

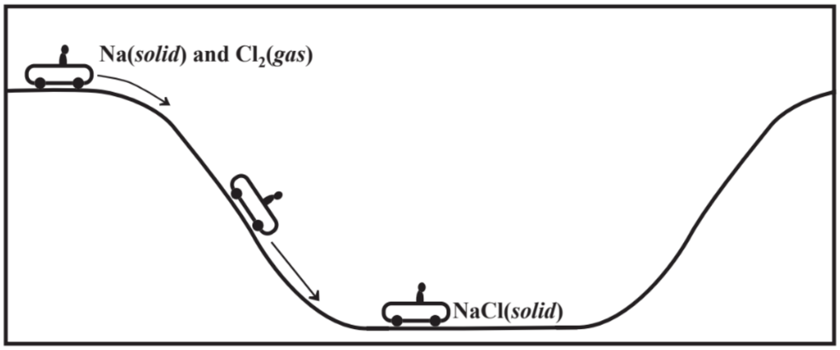


Figure 4.5. The energy involved in forming a compound is much like that involved in rolling a cart down a hill. In the case of sodium chloride, a lot of energy is released in forming solid crystalline ionic NaCl from solid Na metal and gaseous Cl_2

The differences in ionic size noted above are represented in Figure 4.6 for several monatomic (1-atom) ions from elements close to each other in the periodic table. The figure shows that negative monatomic ions are generally larger than positive monatomic ions formed from elements that are nearby in the periodic table. Thus, the negative F^- ion is larger than the positive Na+ion, although both ions have the same number of electrons (10) and the atomic number of Na is higher than that of F. It is seen that for ions in the same group of elements that have the same charge, the ion from the element with higher atomic number is larger. Figure 4.6 shows the Cl^-ion larger than the F^- ion and the K^+ ion is larger than the Na^+ ion. As electrons are removed from elements in the same period of the periodic table to produce progressively more highly charged cations, ion size shrinks notably as shown by the order of ion sizes $Na^+ > Mg^{2+} > Al^{3+}$, each of which has 10 e-. This occurs because as the charge of the nucleus becomes larger relative to the charge of the negative electron cloud around it, the cloud is drawn closer to the nucleus, shrinking ion size. As electrons are added to atoms to produce more highly charged anions, the anion size increases because more electrons occupy more space. So S^{2-} ion is larger than Cl^- ion.

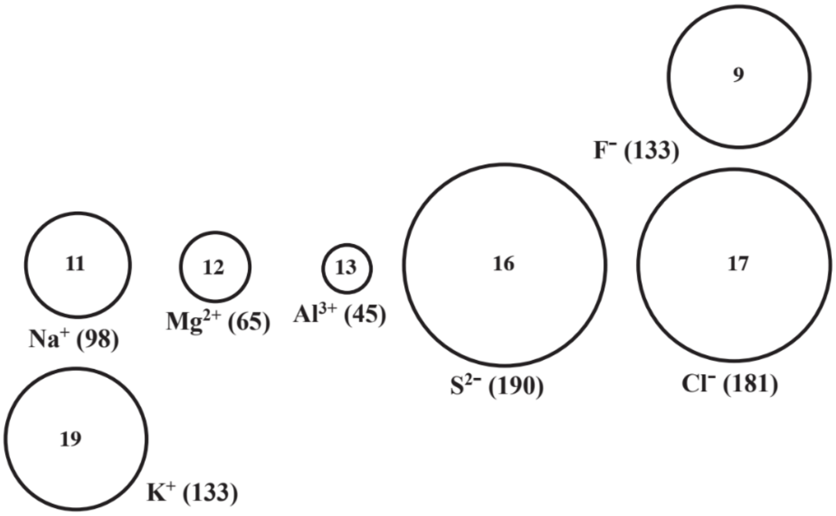
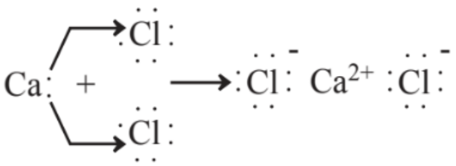


Figure 4.6. Relative sizes of several ions formed by removing electrons from or adding electrons to several elements shown in the abbreviated periodic table. The ion diameters are given in picometers (pm) in parentheses after the symbol for each ion. The atomic numbers of the elements from which each ion has been formed are shown inside the circles representing the ions.

In order to further understand ion formation, several more examples can be considered. Calcium and chlorine react,

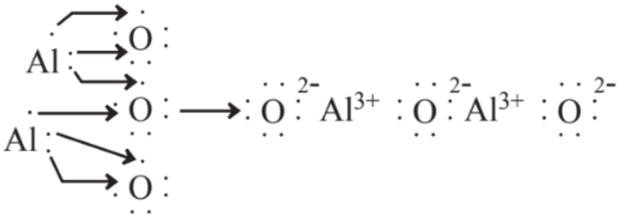


to form calcium chloride, $CaCl_2$. This compound is a byproduct of some industrial processes, from which its disposal can be a problem. It is commonly used as road salt to melt ice and snow on streets and highways. Although calcium chloride is effective in this respect, it is corrosive to automobiles and calcium chloride is a pollutant salt that can contribute to excess salt levels in bodies of water. A “greener,” though more costly substitute is calcium acetate, $Ca(C_2H_3O_2)_2$. This compound is composed of Ca^{2+} ions and acetate ($C_2H_3O_2^{2-}$) anions. Its advantage is that bacteria on soil and in water readily cause biodegradation of the acetate anion as shown by the reaction,

$$\mathrm{Ca(C_2H_3O_2)_2 + 4\,O_2} \xrightarrow{\mathit{Bacteria}} \mathrm{CaCO_3 + 3\,CO_2 + 3\,H_2O} \tag{4.3.2}$$

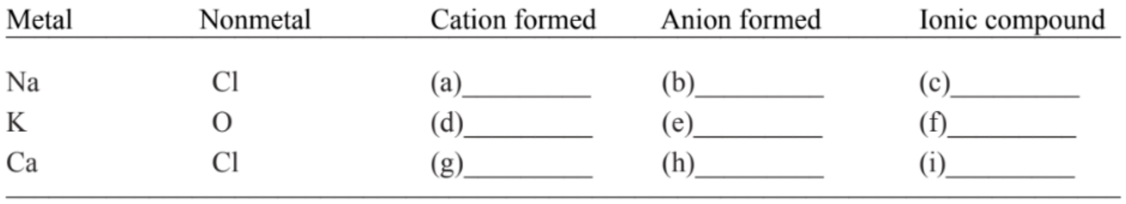
from which the calcium ends up as calcium carbonate, a common component of rock and soil.

Another example of the formation of an ionic compound is the following reaction of aluminum metal with elemental oxygen,



This reaction produces aluminum oxide for which the chemical formula is Al_2O_3. This compound is the source of aluminum in bauxite, the ore from which aluminum is produced and is an important industrial chemical. Called alumina, aluminum oxide itself has many applications including its use for abrasives and sandpaper, as a raw material for ceramics, and as an ingredient of antacids and antiperspirants.

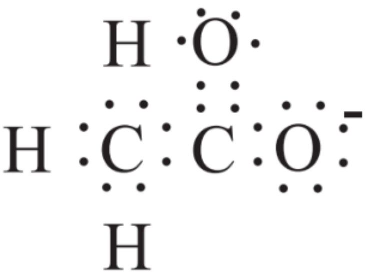
Exercise: Show the ionic products of the reaction of the metal and nonmetal indicated



Metal	Nonmetal	Cation formed	Anion formed	Ionic compound
Na	Cl	(a)__________	(b)__________	(c)__________
K	O	(d)__________	(e)__________	(f)__________
Ca	Cl	(g)__________	(h)__________	(i)__________

Answers: (a) Na^+, (b) Cl^-, (c) NaCl, (d) K^+, (e) O^{2-}, (f) K_2O, (g) Ca^{2+}, (h) Cl^-, (i) $CaCl_2$

In addition to ions formed from single atoms losing or gaining electrons, many ions consist of groups of atoms covalently bound together, but having a net electrical charge because of an excessor a deficiency of electrons. An example of such an ion is the acetate ion shown above in the formula of calcium acetate, $Ca(C_2H_3O_2)_2$. The structural formula of the acetate anion, $C_2H_3O_2^-$, is shown below in which the two carbon atoms are joined with a single covalent bond consisting of two shared electrons, each of the three H atoms are joined to one of the carbon atoms by a single covalent bond and the other carbon atom is joined to one oxygen with a single covalent bond and to the other by a double covalent bond consisting of 4 shared electrons. The net charge on the ion is -1.



Ionic Liquids and Green Chemistry

Most common ionic compounds such as sodium chloride are hard solids because the ions of which they are composed are relatively small and packed tightly together in the crystalline lattice. These ionic compounds must be heated to very high temperatures before they melt, 801°C for NaCl, for example. In recent years, ionic compounds have been developed that are liquids under ordinary conditions. The ions in these **ionic liquids** are composed of large organic molecules composed of skeletons of numerous carbon atoms bonded to other atoms and having a net charge. The charges on the ions in such compounds is much less concentrated than in simple inorganic compounds like NaCl, the large ions move readily relative to each other in the ionic crystal, and the compound is liquid at low temperatures. A common example of an ionic liquid compound is decylmethylimidazolium hexafluorophosphate, which is a liquid at temperatures above 40°C, the temperature of a very hot summer's day.

There has been a lot of interest in the application of ionic liquids to green chemistry. This is because many chemical reactions including those for preparing polymers used in synthetic fabrics or pharmaceutical compounds are carried out in liquid solvents, which tend to evaporate and contaminate air and to pose disposal problems. Furthermore, although the solvent properties in chemical synthesis often play a strong role in determining the course of the synthesis, the number of available solvents is very limited. In the case of ionic liquids, however, there is a vast variety of both cations and liquids which, combined together, could give as many as a trillion (!) different ionic liquids. This versatility enables fine-tuning the properties of the ionic liquids for specialized uses in synthesis and other applications. The ionic liquids are rather easy to recycle, adding to their green character. In addition to their applications as solvents for chemical synthesis media, ionic liquids may be useful for isolating pollutants. For example, an appropriate ionic liquid may be shaken with water contaminated with toxic heavy metals, such as lead or cadmium, which bind with the ionic liquid. Since such a liquid is normally not soluble in water, it can be physically separated from the water, carrying the heavy metals with it and leaving purified water.

4.4: Covalent Bonds in H2 and Other Molecules

Lewis symbols can be used to show how some atoms of elements on the left side of the table with only one or two outer-shell electrons can lose those electrons to form cations such as Na^+ or Ca^{2+}. It is also easily seen that atoms from groups near the right side of the periodic table can accept one or two electrons to gain stable octets and become anions such as Cl^- or O^{2-}. But, it is difficult to impossible to take more than two electrons away from an atom to form cations with charges greater than +2 or to add 3 or more electrons to form anions with charges of -3 or even more negative, although ions such as Al^{3+} and N^{3-} do exist. So atoms of elements in the middle of the periodic table and the nonmetals on the right have a tendency to share electrons in covalent bonds, rather than becoming ions.

It is readily visualized how mutually attracting ions of opposite charge are held together in a crystalline lattice. Shared electrons in covalent bonds act to reduce the forces of repulsion between the positively charged nuclei of the atoms that they join together. That is most easily seen for the case of the hydrogen molecule, H_2. The nuclei of H atoms consist of single protons, and the two H atom nuclei in the H_2 molecule repel each other. However, their 2 shared electrons compose a cloud of negative charge between the two H nuclei, shielding the nuclei from each other's repelling positive charge and enabling the molecule to exist as a covalently bound molecule (Figure 4.7).

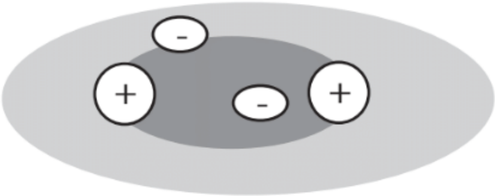


Figure 4.7. Electrons in motion between and around mutually repelling H nuclei shield the nuclei from each other constituting a single covalent bond that holds the H_2 molecule together

4.5: Covalent Bonds in Compounds

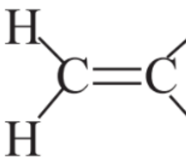
Consider next some example covalent bonds between atoms of some of the lighter elements. These are best understood in reference to Figure 3.9, the abbreviated version of the periodic table showing the Lewis symbols (outer shell valence electrons) of the first 20 elements. As is the case with ions, atoms that are covalently bonded in molecules often have an arrangement of outer shell electrons like that of the noble gas with an atomic number closest to the element in question. It was just seen that covalently bonded H atoms in molecules of H_2 have 2 outer shell electrons like the nearby noble gas helium. For atoms of many other elements, the tendency is to acquire 8 outer shell electrons— an octet— in sharing electrons through covalent bonds. This tendency forms the basis of the *octet rule* discussed in Section 4.2. In illustrating the application of the octet rule to covalent bonding Section 4.7 considers first the bonding of atoms of hydrogen to atoms of elements with atomic numbers 6 through 9 in the second period of the periodic table.

These elements are close to the noble gas neon and tend to attain a “neon-like” octet of outer shell electrons when they form covalently bonded molecules.

Covalent bonds are characterized according to several criteria. The first of these is the number of electrons involved. The most common type of covalent bond consists of 2 shared electrons and is a *single bond*. Four shared electrons as shown for the bond joining an O atom to one of the C atoms in the structure of the acetate anion above constitute a *double covalent bond*. And 6 shared electrons as shown for the very stable covalent bond joining the two N atoms in the N_2 molecule illustrated in Chapter 3, Figure 3.6 make up a *triple covalent bond*. These bonds are conventionally shown as lines in the structural formulas of molecules (large numbers of dots in a formula can get a little confusing). So the single covalent bond in H_2 is shown as

$$\mathbf{H{-}H}$$

The double bond consisting of 4 shared electrons holding the two carbon atoms together in C_2H_4 (ethylene, a hydrocarbon used to make polyethylene plastic) are shown by the following:



Ethylene (ethene) C_2H_4

And the very strong triple bond joining the two N atoms in the N_2 molecule are shown by three lines:

$$\mathbf{N{\equiv}N}$$

Figure 3.6 that each N atom has a pair of electrons that are not part of any chemical bonds. These are omitted from the structure above, and are not ordinarily shown when bonds are represented by lines.

Covalent bonds have a characteristic **bond length**. Bond lengths are of the general magnitude of the size of atoms, so they are measured in units of picometers (pm). The H-H bond in H_2 is 75pm long.

A third important characteristic of bonds is **bond energy**. Bond energy is normally expressed in kilojoules (kJ) required to break a mole (6.02×10^{23}) of bonds. (See Section 4.8 for a detailed definition of the mole.) The bond energy of the H-H bond in H_2 is equal to 435 kJ/mole. This means that an amount of energy required to break all the H-H bonds in a mole of H_2 (2.0 grams of H_2, 6.02×10^{23} molecules) is a very substantial 435 kJ.

4.6: Covalent Bonds and Green Chemistry

The nature of covalent bonds is strongly related to green chemistry. Some reasons why this is so include the following:

- High-energy bonds in raw materials require a lot of energy and severe conditions, such as those of temperature and pressure, to take apart in synthesizing
- Especially stable bonds may make substances unduly persistent in the environment.
- Relatively weak bonds may allow molecules to come apart too readily, contributing to reactive species in the atmosphere or in biological systems.
- Unstable bonds or arrangements of bonds may lead to excessive reactivity in chemicals making them prone to explosions and other hazards.
- Some arrangements of bonds contribute to chemical toxicity.

An example of a substance that has a very high bond stability making it an energy-intensive source of raw material is N_2. As mentioned earlier, large amounts of energy and severe conditions are required to take this molecule apart in the synthesis of ammonia, NH_3, the compound that is the basis for most synthetic nitrogen compounds. As discussed with nitrogen in Section 2.5, *Rhizobium* bacteria growing on the roots of leguminous plants such as soybeans convert N_2 to chemically fixed nitrogen. The amount of nitrogen fixed by this totally green route is certainly a welcome addition to the pool of fertilizer nitrogen.

An example of a compound in which especially stable bonds contribute to persistence and ultimate environmental harm is provided by dichlorodifluoromethane, Cl_2CF_2, a chlorofluorocarbon implicated in the destruction of stratospheric ozone (see Chapter 3, Section 3.5, and Chapter 10). The chemical bonds in this compound are so strong that nothing attacks them until the molecule has penetrated many kilometers high into the stratosphere where extremely energetic ultraviolet radiation breaks the C-Cl bond in the molecule. This produces Clatoms that bring about the destruction of protective stratospheric ozone.

A somewhat opposite condition occurs in the case of atmospheric nitrogen dioxide, NO_2, near ground level in the atmosphere. Here the NO bond is relatively weak so that the relatively low-energy ultraviolet radiation ($h\nu$) that is close to the wavelength of visible light and penetrates to the atmosphere at or near ground level can break apart NO_2, molecules:

$$NO_2 + h\nu \rightarrow NO + O \tag{4.6.1}$$

The O atoms released are very reactive and interact with pollutant hydrocarbons, such as those from gasoline, in the atmosphere resulting in the disagreeable condition of photochemical smog.

Some bonding arrangements are notable for instability. These include bonds in which two N atoms are adjacent or very close in a molecule and are bonded with double bonds. Also include dare arrangements in which N and O atoms are adjacent and double bonds are also present.

The presence of some kinds of bonds in molecules can contribute to their biochemical reactivity and, therefore, to their toxicity. An organic compound with one or more C=C double bonds in the molecule is often more toxic than a similar molecule without such bonds.

By avoiding generation, use, or release to the environment of compounds with the kinds of bonds described above as part of a program of green chemistry, the practice of chemistry and the chemical industry can be made much safer. Green chemistry also considers bonds that may have to be protected in chemical synthesis. Often steps must be added to attach protecting groups to bonding groups to prevent their reacting during a step of a synthesis. After the desired step is performed, the protecting groups must be removed to give the final product. Materials are consumed and byproducts are generated by these steps, so the practice of green chemistry attempts to avoid them whenever possible.

4.7: Predicting Formulas of Covalently Bound Compounds

It is often possible to predict the formulas of molecules using the Lewis symbols of the elements in the compound with the octet rule for chemical bonding. This is shown in Figure 4.8 for the hydrogen compounds of several elements in the second period of the periodic table.

The prediction of chemical bonds in compounds in which H is bonded to another atom is very simple because each H atom has to be involved in sharing two electrons and the other kind of atom normally has to have a total of 8 electrons in its valence shell octet; these may be shared in bonds or present as unshared pairs. As an example, consider a well-known compound of carbon, carbon dioxide, chemical formula CO_2. The Lewis symbol of C and those of the two O atoms can be used to deduce the Lewis formula of CO_2 as shown in Figure 4.9.

As another example of the application of the octet rule, consider hydrogen peroxide, H_2O_2. This compound's formula looks a lot like that of water, but it is a lot different from water. Hydrogen peroxide decomposes to release oxygen:

$$2\,H_2O_2(\text{liquid}) \rightarrow O_2(\text{gas}) + 2\,H_2O(\text{liquid}) \tag{4.7.1}$$

As a liquid in the form of a concentrated aqueous solution, hydrogen peroxide provides a source of oxygen so potent that it has been used in rockets. It was the treacherous oxidant used along with hydrazine (N_2H_4) fuel in the German Luftwaffe's Messerschmidt 163 rocket plane at the end of World War II. Trailing an exhaust of lethal NO_2 gas, this minuscule manned missile (on the rare occasions when it worked according to plan) was propelled rapidly into the lower stratosphere, then glided down through waves of Allied bombers, attempting to nick them with machine gunfire as it plummeted back to Earth. Few bombers were damaged but many Me-163 pilots died in the attempt, some as the result of explosions, fires, and spills from the hydrogen peroxide oxidant. Hydrogen peroxide decomposed over a catalyst was also used as a source of oxygen for the diesel engines on several German submarines near the end of World War II. Pre-dating nuclear submarines, these potentially deadly craft were the first true submersibles.

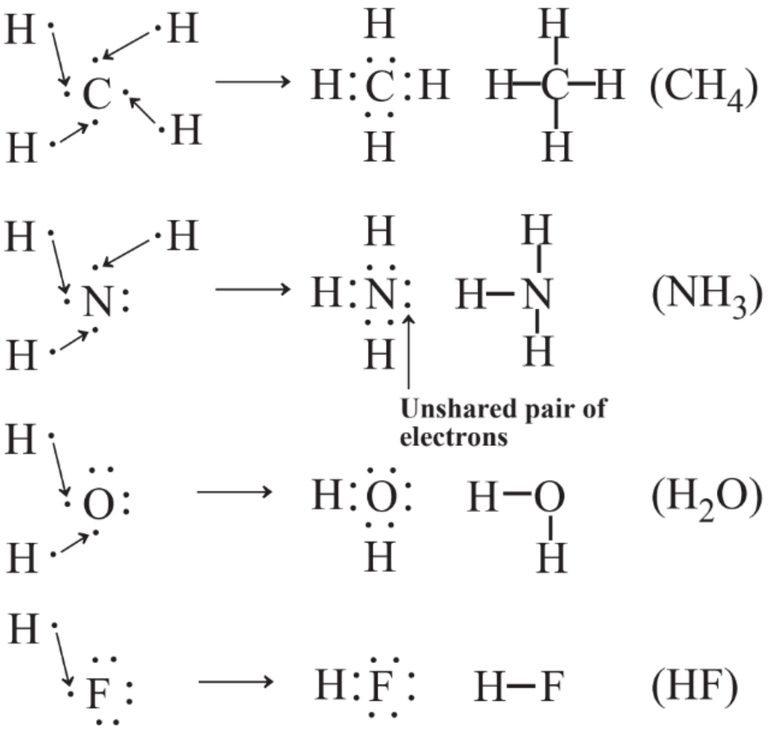


Figure 4.8. Formation of covalent hydrogen compounds with elements in the second row of the periodic table. All of carbon's valence electrons are involved in bonds in CH_4, NH_3 has 1 unshared pair of valence electrons, H_2O has 2 unshared pairs of valence electrons, and HF has 3 unshared pairs of valence electrons. The unshared pairs of electrons are not shown in the structures in which the bonds are represented by straight lines.

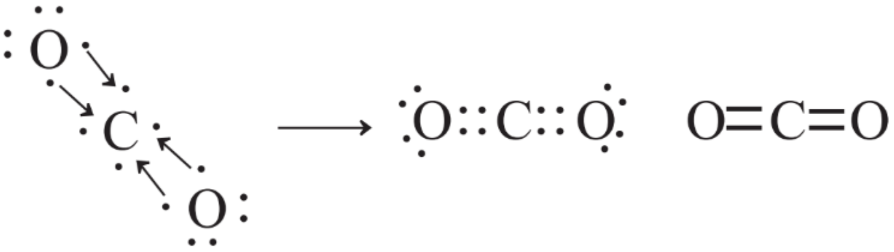


Figure 4.9. Bonding of two oxygen atoms to a central carbon atom to produce carbon dioxide, CO_2. In order to provide an octet of electrons around each of the three atoms with the total of only 16 valence electrons available, it is necessary to have double bonds between C and each of the O atoms.

In assembling the structure of the hydrogen peroxide molecule, one has simply to work with two O atoms each contributing 6 valence electrons and two H atoms each with 1 valence electron. The Lewis formula of the H_2O_2 molecule is

showing that all of the 14 total valence electrons are involved in chemical bonds and both oxygens have octets of outer-shell electrons.

Despite the evil nature of concentrated solutions of hydrogen peroxide, it can be regarded as a green compound in more dilute solutions, such as the 3% hydrogen peroxide commonly used to kill bacteria in treating wounds. Among its green applications, dilute hydrogen peroxide makes an effective and safe bleaching agent that is much safer to handle than elemental chlorine commonly used for bleaching and that does not produce the potentially toxic byproducts that chlorine generates. And even though it kills bacteria, hydrogen peroxide can be pumped underground to serve as an oxidant for acclimated bacteria that attack wastes that have been placed in or seeped into underground locations

Molecules That Do Not Obey the Octet Rule

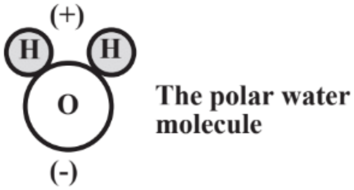
In some cases the octet rule is not obeyed. This occurs when a molecule has an uneven number of electrons so that it is impossible for each atom to have an octet (an even number) of electrons. A simple example of this is nitric oxide, NO, made from an atom of N with 5 valence electrons and one of O with 6 valence electrons. The resulting molecule is shown in Figure 4.10. Since the uneven number of 11 valence electrons cannot provide complete octets of electrons around both the N and O atoms simultaneously, the NO molecule is shown in two forms in which one atom has 8 valence electrons and the other has 7. These are known as **resonance structures.**

Figure 4.10. Formation of NO. The uneven number of electrons cannot accommodate complete octets around both atoms simultaneously, so the structure is a hybrid resonance structure of the two forms shown.

Unequal Sharing of Electrons

The Lewis formula for water,

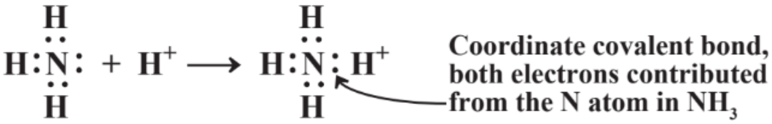
indicates that the molecule is not symmetrical and the two H atoms are located on one side of the molecule and the O atom on the other side. One might think that the electrons shared between Hand O are shared equally. But such is not the case because the relatively larger O atom nucleus with its 8 protons has a stronger attraction for the electrons than do the two H atom nuclei, each with only 1 proton. So the shared electrons spend relatively more time around the O atom and less around the H atoms. This gives each H atom a partial positive charge and the O atom a partial negative charge. An unequal distribution of charge such as that makes a body **polar** and the O-H bonds are **polar covalent bonds**. Because of this phenomenon, the whole water molecule is polar and can be represented as the following, where the small spheres stand for H atoms and the large one for the O atom:



The polar nature of the water molecule has a lot to do with water as a solvent and how it behaves in the environment and in living systems. These aspects are discussed in more detail in Chapter 8.

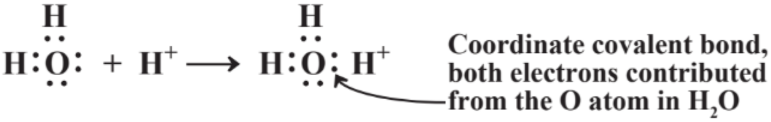
When Only One Atom Contributes to a Covalent Bond

In some cases only one of the two atoms joined by a covalent bond contributes both the electrons in the bond. This occurs with ammonia, NH_3, dissolved in water. Water contains dissolved H^+ cations, and the more acidic water is, the higher the concentration of H^+. The H^+ cation, would be stabilized by two electrons which it can get by binding with dissolved NH_3 as shown in Reaction 4.7.2. Both of the electrons shared between N and the H^+ cation now bound to it as part of a new species, the ammonium ion, NH_4^+, were contributed by the N atom. Such a covalent bond is called a **coordinate covalent bond** or a **dative bond**. In the case of NH_4^+, once the coordinate covalent N-H bond is formed, it is indistinguishable from all the other N-H bonds.



The formation of the coordinate covalent bond in NH_4^+ is very useful when soil is fertilized with nitrogen. The most economical way to apply nitrogen fertilizer is by injecting NH_3 into the soil, but NH_3 is a gas that would be expected to rapidly evaporate from soil. Instead, it becomes attached to H^+ ion from the water in the soil and is bound to the soil as the NH_4^+ ion.

Another important example of a coordinate covalent bond occurs in water. As discussed in Section 4.9, acids, which are very important materials commonly dissolved in water, produce the hydrogen ion, H^+, in water. This ion does not exist simply dispersed in water. Instead, it binds strongly to a water molecule to produce the hydronium ion, H_3O^+:



4.8: Chemical Formulas, the Mole, and Percentage Composition

Chemical formulas represent the composition of chemical compounds. A number of chemical formulas have been shown so far including H_2O for water and NH_3 for ammonia. A chemical formula of a compound contains a lot of significant information as shown in Figure 4.11. Included is the following:

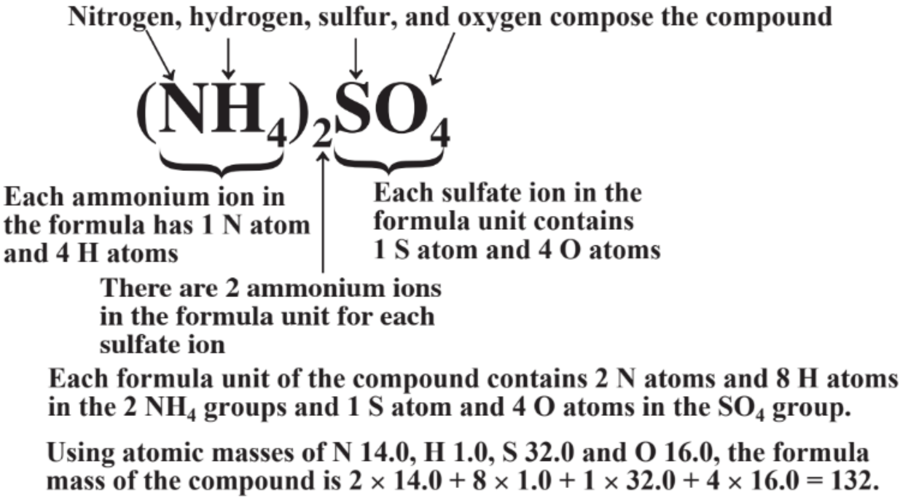


Figure 4.11. Information contained in a chemical formula

- The elements that compose the compound
- The relative numbers of each kind of atom in the compound
- How the atoms are grouped, such as in ions (for example, SO_4^{2-}) present in the compound
- With a knowledge of atomic masses, the molar mass of the compound
- With a knowledge of atomic masses, the percentage composition of the compound

Where the symbols of the elements represent letters in the alphabet of chemical language, the formulas of compounds represent words composed of those letters. As discussed in Chapter 5, formulas are put together in chemical equations that act as sentences in the chemical language to describe what chemical substances do.

The Mole

With a knowledge of atomic masses, the percentage composition of a compound is readily calculated from its formula. Before doing such a calculation for ammonium sulfate, however, it is useful to introduce the concept of the **mole**. Chemists use the mole to express quantities of materials containing a specific number of specified entities, which may be atoms of elements, molecules of elements that exist as diatomic molecules, formula units of ionic compounds, or molecules of covalent compounds. A mole of a substance is simply the atomic mass, molecular mass, or formula mass followed by *grams*. This quantity is called the **molar mass**. The masses of a mole of several typical substances are given below:

Atoms of neon, atomic mass 20.1: 20.1 g/mol

Molecules of H_2, atomic mass 1.0, molecular mass 2.0: 2.0 g/mole

Molecules of CH_4, molecular mass 16.0: 16.0 g/mole

Formula units of ionic CaO, formula mass 56.1: 56.1 g/mol

The number of specified entities in a mole of a substance is always the same regardless of the substance. This number is very large, 6.02×10^{23}, and is called **Avogadro's number**. As examples, a mole of neon contains 6.02×10^{23} neon atoms, a mole of elemental hydrogen contains 6.02×10^{23} H_2 molecules (but $2\times6.02\times10^{23}$ H atoms), and a mole of CaO contains 6.02×1023 formula units (pairs of Ca^{2+} and O^{2-} ions) of CaO.

The calculation of the percentage composition of $(NH_4)_2SO_4$ is given below. Note that the molar mass of the compound is 132 g/mol, each mol of the substance contains 2×1 = 2 mol of N, 2×4 = 8mol of H, 1 mol of S, and 4 mol of O.

$2 \text{ mol N} \times 14.0\text{g N/mol N} = 28.0\text{g N}, \text{ \% N} = \frac{28.0g}{132g} \times 100 = 21.2\% \text{ N}$

$8 \text{ mol H} \times 1.0 \text{ g H/mol H} = 8.0 \text{ g H}, \text{ \% H} = \frac{8.0g}{132g} \times 100 = 6.1 \text{ \% H}$

$1 \text{ mol S} \times 32.0 \text{ g S/mol S} = 32.0 \text{ g S}, \text{ \% S} = \frac{32.0g}{132g} \times 100 = 24.2\% \text{ S}$

$4 \text{ mol O} \times 16.0 \text{ g O/mol O} = 64.0 \text{ g O}, \text{ \% O} = \frac{64.0g}{132g} \times 100 = 48.5\% \text{ O}$

Example: Given the atomic masses Ca 40.0, C 12.0, and O 16.0, what is the percentage composition of calcium oxalate, CaC_2O_4?

Answer: 31.3% Ca, 18.8% C, 50.0% O

4.9: What Are Chemical Compounds Called?

The naming of chemical compounds can get a little complicated. This is particularly true of organic compounds, the names of which are discussed in Chapter 9. Some of the simpler aspects of naming inorganic compounds are discussed here.

In naming compounds, prefixes are used to represent the relative numbers of atoms in the formula unit of the compound. These prefixes through number 10 are given below:

1-mono 3-tri 5-penta 7-hepta 9-nona

2-di 4-tetra 6-hexa 8-octa 10-deca

The first class of inorganic compounds to be addressed here are **binary molecular compounds**. Binary molecular compounds are composed of only 2 kinds of elements and do not contain ions. For these compounds, the first part of the name is simply the name of the first element in the compound formula. The second part of the name is that of the second element in the compound formula modified to have the ending *-ide*. Prefixes are added to indicate how many of each kind of atom are present in the molecule. Consider as an example the name of N_2O_5. The name of the compound is dinitrogen pentoxide where *di* indicates 2 N atoms, *pent* indicates 5 oxygen atoms, and the second element has the *ide* ending. Other examples of this system of naming are $SiCl_4$, silicon tetrachloride; S_2F_6, disilicon hexafluoride; PCl_5, phosphorus pentachloride; and SCl_2, sulfur dichloride.

A number of compounds, including binary molecular compounds, have **common names** that have been used for so long that they are part of the chemical vocabulary. An especially common example is the name of water for H_2O; its official name is dihydrogen monoxide. Another example is dinitrogen monoxide, N_2O, usually called nitrous oxide. Aluminum oxide, Al_2O_3, is commonly called alumina and silicon oxide, SiO_2, is called silica, specific mineral forms of which are sand and quartz.

Recall that *ionic compounds* are those composed of ions that are held together by ionic bonds, rather than covalent bonds. As noted in the discussion of ionic sodium chloride in Section 4.3, ionic compounds do not consist of discrete molecules, but rather of aggregates of ions whose relative numbers make the compound electrically neutral overall. Therefore, it is not correct to refer to molecules of ionic compounds but rather to *formula units* equal to the smallest aggregate of ions that can compose the compound. Consider, for example, the ionic compound composed of Na^+ and SO_4^{2-} ions. Every ionic compound must be electrically neutral with the same number of positive as negative charges. For the compound in question this requires 2 Na^+ ions for each SO_4^{2-} ion. Therefore, the formula of the compound is Na_2SO_4 and a formula unit contains 2 Na^+ ions and 1 SO_4^{2-} ion. Furthermore, a mole of Na_2SO_4 composed of 6.02×10^{23} formula units of Na_2SO_4 contains $2\times6.02\times10^{23}$ Na^+ ions and 6.02×10^{23} SO_4^{2-} ions. Since the ionic charges determine the relative numbers of ions, prefixes need not be used in naming the compound and it is called simply sodium sulfate.

Exercise: Give the formulas and names of compounds formed from each cation on the top row with each anion on the bottom row, below:

1. NH_4^+ 2. Ca^{2+} 3. Al^{3+}

(A) Cl^- (B) SO_4^{2-} (C) PO_4^{3-}

Answers: 1(A) NH_4Cl, ammonium chloride; 1(B) $(NH_4)_2SO_4$, ammonium sulfate; 1(C), $(NH_4)_3PO_4$, ammonium phosphate; 2(A) $CaCl_2$, calcium chloride; 2(B) $CaSO_4$, calcium sulfate; 2(C), $Ca_3(PO_4)_2$, calcium phosphate; 3(A) $AlCl_3$, aluminum chloride; 3(B) $Al_2(SO_4)_3$, aluminum sulfate; 3(C), $AlPO_4$, aluminum phosphate.

Prefixes are used in naming ionic compounds where more than 1 cation or more than 1 anion are present in the formula unit. For example, Na_2HPO_4 in which each formula unit is composed of 2 Na^+ ions, 1 H^+ ion, and 1 PO_4^{3-} ion is called disodium monohydrogen phosphate. And KH_2PO_4 is called monopotassium dihydrogen phosphate.

4.10: Acids, Bases and Salts

Other than binary molecular compounds, most inorganic compounds can be classified as acids, bases, or salts. These three categories of compounds and their names are addressed briefly here.

Acids

Acids are characterized by the H^+ ion, the presence of which in water, makes the water **acidic**. An acid either contains this ion or produces it when it dissolves in water. Sulfuric acid, H_2SO_4, is an example of a compound that contains H^+ ion. Dissolved in water, a molecule of sulfuric acid exists as 2 H^+ ions and 1 SO_4^{2-} ion. An example of a compound that is classified as acidic because it *produces* H^+ ion when it dissolves in water is carbon dioxide, which undergoes the following reaction in water solution:

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^- \tag{4.10.1}$$

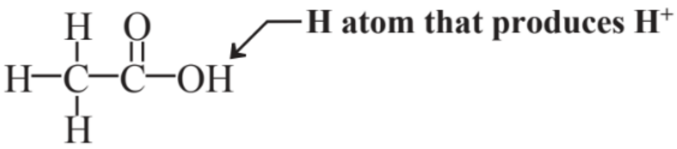
In this case, only a small fraction of the CO_2 molecules dissolved in water undergo the above reaction to produce H^+ so water solutions of CO_2 are **weakly acidic** and carbon dioxide is classified as a **weak acid**. It is the presence of dissolved CO_2 from the carbon dioxide naturally present in air that makes rainfall coming from even nonpolluted atmospheres slightly acidic and, as discussed in Chapter 9, the weakly acidic properties of CO_2 are very important in natural waters in the environment. Other acids, such as hydrochloric acid, HCl, are completely dissociated to H^+ and an anion (in the case of HCl the Cl^- anion) when they are dissolved in water; such acids are **strong acids.**

The naming of acids follows certain rules. In the case of an acid that contains only H and one other element, the acid is a hydro-ic acid. So HCl is called *hydro*chlor*ic* acid. Somewhat different rules apply when an acid contains oxygen. Some elements form acids in which the anion has different amounts of oxygen; examples are H_2SO_4 and H_2SO_3. The acid with more oxygen is an “-ic” acid, so H_2SO_4 is sulfuric acid. The acid with the lesser amount of oxygen is an “-ous” acid, so H_2SO_3 is sulfurous acid. A greater amount of oxygen than even the “-ic” acid is denoted by the prefix “per-”, and a lesser amount of oxygen than even the “-ous” acid is denoted by the prefix “hypo-”. These names are shown very well by the names of the oxyacids of chlorine. So the names of $HClO_4$, $HClO_3$, $HClO_2$, and HClO are, respectively, perchloric acid, chloric acid, chlorous acid and hypochlorous acid.

Acids are extremely important as industrial chemicals, in the environment, and in respect to green chemistry. About 40 million metric tons (40 billion kilograms) of sulfuric acid are produced in the United States each year. It is the number 1 synthetic chemical, largely because of its application to treat phosphate minerals to make phosphate crop fertilizers. Sulfuric acid is also used in large quantities to remove corrosion from steel, a process called steel pickling. Other major uses include detergent synthesis, petroleum refining, lead storage battery manufacture, and alcohol synthesis. About 7-8 million tons of nitric acid, HNO_3, are produced in the U.S. each year giving it a rank of 10th, and hydrochloric acid ranks about 25th with annual production around 3 million metric tons.

Acids are important in the environment. Improperly disposed acid has caused major problems around hazardous waste sites. Sulfuric acid along with smaller quantities of hydrochloric and nitric acid are the major constituents of acid rain (see Chapter 10). Acids figure prominently in the practice of green chemistry. Reclamation and recycling of acids are commonly performed in the practice of industrial ecology. As noted earlier, much of the sulfuric acid now manufactured uses a potential waste and pollutant, hydrogen sulfide, H_2S, removed from sour natural gas sources as a source of sulfur.

In cases where a relatively weak acid can be used, acetic acid made by the fermentation of carbohydrates is an excellent green alternative to stronger acids, such as sulfuric acid. Yeasts can convert the carbohydrates to ethanol (ethyl alcohol, which is present in alcoholic beverages) and other microorganisms in the presence of air convert the ethanol to acetic acid by the same process that vinegar, a dilute solution of acetic acid, is made from cider or wine. The structural formula of acetic acid is



in which only one of the 4 H atoms is ionizable to produce H+ion. The production of acetic acid is a green process that uses biological reactions acting upon renewable biomass raw materials. As a weak acid, acetic acid is relatively safe to use, and contact with humans is not usually very dangerous (we ingest dilute acetic acid as vinegar, but pure acetic acid attacks flesh and is used to remove warts from skin). Another advantage of acetic acid is that it is biodegradable, so any of it released to the environment does not persist.

Bases

A **base** either contains hydroxide ion, OH^-, or reacts with water to produce hydroxide. Most bases that contain hydroxide consist of metal cations and hydroxide; examples are sodium hydroxide, NaOH, and calcium hydroxide, $Ca(OH)_2$. The most common basic substance that produces hydroxide in water is ammonia, NH_3, which reacts with water as follows:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{4.10.2}$$

Only a small fraction of the ammonia molecules undergo this reaction in water, so ammonia does not produce much OH-in water and is known as a **weak base**. The metal hydroxides, such as KOH, that completely dissociate in water are **strong bases**. Metal hydroxides are named by the metal followed by “hydroxide.” Therefore, $Mg(OH)_2$ is magnesium hydroxide.

Salts

Acids and bases react to form a **salt**, an ionic compound that has a cation other than H+and an anion other than OH^-. This kind of reaction always produces water and is known as a **neutralization reaction**. The most well known salt is sodium chloride, NaCl. Although it is commonly what one means in referring to “salt,” there are many other salts as well. These include calcium chloride, $CaCl_2$, used to melt road ice, sodium carbonate, Na_2CO_3, used in cleaning formulations and potassium chloride, KCl, a source of potassium fertilizer for crops. A typical neutralization reaction is the one between NaOH and hydrochloric acid, HCl, to produce sodium chloride:

$$\underbrace{NaOH}_{\text{Base}} + \underbrace{HCl}_{\text{acid}} \rightarrow \underbrace{NaCl}_{\text{a salt, sodium chloride}} + \underbrace{H_2O}_{\text{water}} \tag{4.10.3}$$

Salts are named very simply with just the name of the cation followed by that of the anion. The charges of the ions determine the formulas of the salts, so it is not necessary to add prefixes to denote the relative numbers of each ion. Therefore, $CaCl_2$ is simply calcium chloride, not calcium dichloride. As noted earlier in this chapter, prefixes are added in names of salts that contain more than 1 kind of cation or more than 1 kind of anion to show the relative numbers of ions. As an example, KH_2PO_4 is called potassium dihydrogen phosphate.

Questions and Problems

Access to and use of the internet is assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be "right."

1. What distinguishes the molecules of chemical compounds from those of elements, such as N_2?

2. Several "characteristics of compounds that meet the criteria of being green" were mentioned at the beginning of this chapter. Near the end of the chapter, acetic acid was mentioned as a "green acid." In what respects does it meet the criteria of green compounds?

3. What is sodium stearate? Why is it regarded as being green?

4. Which of the following is **not** usually regarded as a characteristic of green chemical compounds? Why is it not so regarded?

A. Preparation from renewable resources

B. Low tendency to undergo sudden, violent, unpredictable reactions

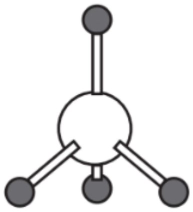
C. Readily biodegradable

D. Extremely high stability

5. What are valence electrons? Why are they particularly important?

6. What is the octet rule? Why is it particularly important in chemistry?

7. What does the structure representing CH_4 below say about bonding and octets of electrons around the central C atom?



8. Considering that the central nitrogen atom in ammonia, NH_3, has an unshared pair of valence electrons and 3 pairs shared between N and H, propose a structure for the ammonia molecule based upon the structure of the methane molecule in the preceding question. Use a pair of dots to represent the unshared pair of electrons.

9. What is an ionic bond? Why is it not regarded as being between one specific cation and a specific anion in an ionic compound?

10. Do ionic compounds such as NaCl obey the octet rule? Explain.

11. Why is NaCl referred to as a formula unit of the ionic compound rather than a molecule of sodium chloride?

12. Energy is involved in several steps of the process by which an elemental metal and an elemental nonmetal are converted to an ionic compound (salt). Of these, which has the largest energy?

13. Place the following ions in decreasing order of size: Na^+, Cl^-, Al^{3+}, K^+

14. What is a major disadvantage of calcium chloride as a road de-icing agent? Why is calcium acetate a good substitute?

15. List some important characteristics of a covalent bond.

16. What is the major characteristic of ions in ionic liquids that enable these materials to be liquid at around room temperature?

17. Can the atoms in NO_2 obey the octet rule? Suggest the structural formula for this molecule inwhich the 2 O atoms are bonded to an N atom.

18. Coordinate covalent bonds are normally regarded as those in which each of two atoms contributes electrons to be shared in the bond. Are there any circumstances in which this is not true? If so, give an example.

19. What are three major ways in which covalent bonds are characterized?

20. What are some of the ways in which the characteristics of covalent bonds are related to green chemistry?

21. Why are elements in the middle of periods of the periodic table less likely to form ionic compounds and more likely to form covalent compounds than those near either end of each period?

22. Predict the formula of the compound formed when H reacts with P and explain.

23. Although hydrogen chloride, HCl, exists as a gas, the contest for the two shared electrons in the bond between H and Cl is unequal, with the Cl nucleus having the greater attraction. Suggest the nature of the H-Cl bond and suggest what may happen when HCl gas dissolves in water to produce hydrochloric acid.

24. Using Lewis formulas, show the bonding in the SO_2 molecule in which two O atoms are bonded to a central O atom. Can another equivalent structure be drawn? Considering the bonding in NO discussed in this chapter, what are these structures called.

25. Summarize the information shown in the formula $Ca_3(PO_4)_2$.

CHAPTER OVERVIEW

5: Chemical Reactions- Making Materials Safely and Sustainable

“The materials that we make and the ways that we make them have an enormous impact on Earth’s environment. Much of green chemistry has to do with making materials safely and sustainably.”

5.1: Describing What Happens with Chemical Equations
5.2: Balancing Chemical Equations
5.3: Just Because You Can Write It Doesn't Mean That It Will Happen
5.4: Yield And Atom Economy in Chemical Reactions
5.5: Catalysts That Make Reactions Go
5.6: Kinds of Chemical Reactions
5.7: Oxidation-Reduction Reactions and Green Chemistry
5.8: Quantitative Information from Chemical Reactions
5.9: Energy in Chemical Reactions
5.10: Stoichiometry by the Mole Ratio Method
5.11: Limiting Reactant and Percent Yield
5.12: Titrations - Measuring Moles by Volume of Solution
5.13: Industrial Chemical Reactions - The Solvay Process
Questions and Problems

5.1: Describing What Happens with Chemical Equations

How far would you have to go to find a diverse chemical factory carrying out hundreds of complex chemical processes? Not far, because your own body is just such a remarkably sophisticated factory that could not be duplicated by the efforts of thousands of chemists and chemical engineers and the expenditure of billions of dollars. As an example of a process that our bodies carry out consider the utilization of glucose sugar, chemical formula $C_6H_{12}O_6$, which is present in our blood and generates energy that the human body uses by the following metabolic biochemical reaction:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \tag{5.1.1}$$

This is a **chemical equation** that represents a chemical reaction, something that actually occurs with chemicals. It states that glucose reacts with molecular oxygen to produce carbon dioxide and water. The chemical reaction also produces energy and that is why the body carries it out to obtain the energy needed to move, work, and grow. The production of energy is sometimes denoted in the equation by adding "+ energy" to the right side.

Just as a chemical formula contains a lot of information about a chemical compound, a chemical equation contains much information about a chemical process. A chemical equation is divided into two parts by the arrow, which is read "yields." On the left of the arrow are the **reactants** and on the right are the **products**. A key aspect of a correctly written chemical equation is that it is **balanced**, with the same number of atoms of each element on the left as on the right. Consider the chemical equation above. The single molecule of $C_6H_{12}O_6$ contains 6 C atoms, 12 H atoms, and 6 O atoms. The 6 O_2 molecules contain 12 O atoms, giving a total of 18 O atoms among the reactants. Adding up all the atoms on the left gives 6 C atoms, 12 H atoms, and 18 O atoms among the reactants. On the right, the products contain 6 C atoms in the 6 CO_2 molecules, 12H atoms in the 6 H_2O molecules, and 12 O atoms in the 6 CO_2 molecules, as well as 6 O atoms in the 6 H_2O molecules, a total of 18 O atoms. So there are 6 C atoms, 12 H atoms, and 18 O atoms among the products, the same as in the reactants. Therefore, the equation is balanced.

An important exercise is the process of balancing a chemical equation. This consists of putting the correct numbers before each of the reactants and products so that equal numbers of each kind of atom are on both the left and right sides of the equation. The procedure for balancing a chemical equation is addressed in section 5.2.

Learning chemistry is largely an exercise in learning chemical language. In the chemical language the symbols of the elements are the alphabet. The formulas of the compounds are the words. And chemical equations are the sentences that tell what actually happens.

It is often important to know the physical states of reactants and products in chemical reactions. Suppose, for example, that a geologist tested a sample of rock to see if it were limestone by adding some liquid hydrochloric acid to the rock and observing the CO_2 gas coming off. The equation for the chemical reaction that occurred is

$$\mathrm{CaCO_3}(s) + \mathrm{2HCl}(aq) \rightarrow \mathrm{CO_2}(g) + \mathrm{CaCl_2}(aq) + \mathrm{H_2O}(l)$$

$$\mathrm{CaCO_3(s) + 2\,HCl(aq) \rightarrow CO_2(g) + CaCl_2(aq) + H_2O(l)} \tag{5.1.2}$$

Here abbreviations in parentheses are used to represent the physical state of each reaction participant — (*s*) for solid, (*aq*) for a substance in solution, (*g*) for gas, and (*l*) for liquid. The equation above states that solid calcium carbonate reacts with an aqueous solution of hydrochloric acid to produce carbon dioxide gas, a solution of calcium chloride, and liquid water.

Chemical reactions often are **reversible**, that is, they may go either forward or backward. A reversible reaction is shown with a doublearrow, ← →. Asan example, consider the reaction of dissolved ammonia, NH_3, with water to produce ammonium ion, $NH4^+$, and hydroxide ion, OH^-.

$$\mathrm{NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)} \tag{5.1.3}$$

Actually, only a small fraction of NH_3 molecules undergo this reaction at any given time, and those that are converted to NH_4^+ are rapidly converted back to NH_3. The double arrow in the chemical equation shows that both the forward and reverse processes occur. Another symbol that is sometimes used in chemical equations is Δ. This symbol denotes that heat is applied to make the chemical reaction occur at a more rapid pace. It is normally placed over the arrow in the chemical reaction. Chemical equations are used to calculate the quantities of chemicals involved in a chemical reaction, either as reactants or as products. This is an important area of chemistry that is addressed by the topic of stoichiometry discussed later in this chapter in Section 5.8.

5.2: Balancing Chemical Equations

As noted earlier, a *balanced* chemical equation shows the same number of each kind of atom on both sides of the equation. The process of balancing chemical equations is an important exercise in chemistry and is addressed here.

Consider a simple example of balancing a chemical equation, the reaction of methane, CH_4, with elemental chlorine, Cl_2, to produce dichloromethane, CH_2Cl_2, an important laboratory solvent, and byproduct hydrogen chloride, HCl. The unbalanced chemical equation is

$$\mathrm{CH_4 + Cl_2 \rightarrow CH_2Cl_2 + HCl} \tag{5.2.1}$$

Inspection of this equation as it is written shows that it is not balanced because it has 4 H on the left, but just 3 on the right and 2 Cl on the left, but 3 Cl on the right. In order to balance such an equation, consider one element at a time. Carbon is already balanced, so it is best to avoid changing any of the numbers in front of the C-containing compounds. The equation can be balanced for H by putting a 2 in front of HCl:

$$\mathrm{CH_4 + Cl_2 \rightarrow CH_2Cl_2 + 2\,HCl} \tag{5.2.2}$$

Now everything is balanced except for Cl, of which there are 4 on the right, but just 2 on the left.Placing a 2 in front of Cl, gives the required 4 Cls on the left:

$$\mathrm{CH_4 + 2\,Cl_2 \rightarrow CH_2Cl_2 + 2\,HCl} \tag{5.2.3}$$

This equation is now balanced with 1 C, 4 Hs, and 4 Cls on both the left and the right.

A crucial thing to remember in balancing a chemical equation is that *the chemical formulas must not be altered. Only the relative numbers of reactant and product species may be changed.*

Next consider the reaction of methane, CH_4, with iron oxide, Fe_2O_3, to give iron metal, Fe, carbon dioxide, CO_2, and water, H_2O. The unbalanced equation is

$$\mathrm{CH_4 + Fe_2O_3 \rightarrow Fe + CO_2 + H_2O} \tag{5.2.4}$$

In this case it is helpful to note that CH_4 is the only source of both C and H and that 4 times as many H atoms as C atoms must appear in the products. That means that for each CO_2 there must be 2 H_2Os. Both C and H are balanced in the following:

$$\mathrm{CH_4 + Fe_2O_3 \rightarrow Fe + CO_2 + 2\,H_2O} \tag{5.2.5}$$

But now O is not balanced. Furthermore, the 3 Os in Fe_2O_3 means that the number of O atoms must be divisible by 3, so try multiplying the three species balanced so far — CH_4, CO_2, and $2H_2O$ — by 3:

$$\mathrm{3\,CH_4 + Fe_2O_3 \rightarrow Fe + 3\,CO_2 + 6\,H_2O} \tag{5.2.6}$$

That gives a total of 12 O atoms on the right, 6 each in 3 CO_2 and 6 H_2O. Taking 4 times Fe_2O_3 gives 12 Os on the left:

$$\mathrm{3\,CH_4 + 4\,Fe_2O_3 \rightarrow Fe + 3\,CO_2 + 6\,H_2O} \tag{5.2.7}$$

The only species remaining to be balanced is Fe, which can be balanced by putting 8 in front of Fe on the right. The balanced equation is

$$\mathrm{3\,CH_4 + 4\,Fe_2O_3 \rightarrow 8\,Fe + 3\,CO_2 + 6\,H_2O} \tag{5.2.8}$$

Checking the answer shows on both left and right 3 C, 8 Fe, 12 H, and 12 O demonstrating that the equation is in fact balanced.

Exercise: Balance the following:

1. $\mathrm{Fe_2O_3 + CO \rightarrow Fe + CO_2}$
2. $\mathrm{FeSO_4 + O_2 + H_2O \rightarrow Fe(OH)_3 + H_2SO_4}$
3. $\mathrm{C_2H_2 + O_2 \rightarrow CO_2 + H_2O}$
4. $\mathrm{Mg_3N_2 + M_2O \rightarrow Mg(OH)_2 + NH_3}$
5. $\mathrm{NaAlH_4 + H_2O \rightarrow H_2 + NaOH + Al(OH)_3}$

6. $Zn(C_2H_5)_2 + O_2 \rightarrow ZnO + CO_2 + H_2O$

Answers: (1) $Fe_2O_3 + 3\,CO \rightarrow 2\,Fe + 3\,CO_2$, (2) $4\,FeSO_4 + O_2 + 10\,H_2O \rightarrow 4\,Fe(OH)_3 + 4\,H_2SO_4$, (3) $2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O$, (4) $Mg_3N_2 + 6\,H_2O \rightarrow 3\,Mg(OH)_2 + 2\,NH_3$ (5) $NaAlH_4 + 4\,H_2O \rightarrow 4\,H_2 + NaOH + Al(OH)_3$, (6) $Zn(C_2H_5)_2 + 7\,O_2 \rightarrow ZnO + 4\,CO_2 + 5\,H_2O$

5.3: Just Because You Can Write It Doesn't Mean That It Will Happen

The fact that a balanced chemical equation can be written does not necessarily mean that the chemical reaction that it represents will occur. As an example, it is known that a number of metals will react with acid to release elemental hydrogen gas and produce a metal salt. For example, if iron wire, Fe, is placed into a solution of sulfuric acid, H_2SO_4, H_2 gas is evolved,

$$\mathrm{Fe(s) + H_2SO_4(aq) \rightarrow H_2(g) + FeSO_4(aq)} \tag{5.3.1}$$

leaving $FeSO_4$ salt in solution. The copper salt, $CuSO_4$, is also known to exist. So one might believe that it could be prepared by reacting copper metal with H_2SO_4:

$$\mathrm{Cu(s) + H_2SO_4(aq) \rightarrow H_2(g) + CuSO_4(aq)} \tag{5.3.2}$$

This equation is balanced and it looks like it could occur. But, placing copper metal into a solution of H_2SO_4 in the laboratory results in — nothing. The reaction simply does not occur. The lesson here is that a balanced chemical equation is not sufficient reason to conclude that a reaction will take place.

Since $CuSO_4$ is known to exist, there has to be a way to prepare it. There are, in fact several ways. One pathway to the preparation of this salt starting with copper metal is to first react the copper with oxygen at a relatively high temperature to produce copper oxide:

$$\mathrm{2\,Cu(s) + O_2(g) \rightarrow 2\,CuO(s)} \tag{5.3.3}$$

The CuO product reacts with sulfuric acid to give $CuSO_4$ salt:

$$\mathrm{CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)} \tag{5.3.4}$$

Alternate Reaction Pathways in Green Chemistry

Much of the science of green chemistry involves making decisions about alternative chemical reactions to choose a reaction or reaction sequence that provides maximum safety, produces minimum byproduct, and utilizes readily available materials. Consider two ways of preparing iron sulfate, $FeSO_4$. This chemical is commonly used to treat (clarify) water because when it is added to water and air is bubbled through the water, it produces $Fe(OH)_3$, a gelatinous solid that settles in the water and carries suspended mud and other particles with it. Consider two possible ways of making $FeSO_4$. The first of these was shown earlier and consists of the reaction of iron metal with sulfuric acid:

$$\mathrm{Fe(s) + H_2SO_4(aq) \rightarrow H_2(g) + FeSO_4(aq)} \tag{5.3.5}$$

leaving $FeSO_4$ salt in solution. The copper salt, $CuSO_4$, is also known to exist. So one might believe that it could be prepared by reacting copper metal with H_2SO_4:

$$\mathrm{Cu(s) + H_2SO_4(aq) \rightarrow H_2(g) + CuSO_4(aq)} \tag{5.3.6}$$

This equation is balanced and it looks like it could occur. But, placing copper metal into a solution of H_2SO_4 in the laboratory results in — nothing. The reaction simply does not occur. The lesson here is that a balanced chemical equation is not sufficient reason to conclude that a reaction will take place.

Since $CuSO_4$ is known to exist, there has to be a way to prepare it. There are, in fact several ways. One pathway to the preparation of this salt starting with copper metal is to first react the copper with oxygen at a relatively high temperature to produce copper oxide:

$$\mathrm{2\,Cu(s) + O_2(g) \rightarrow 2\,CuO(s)} \tag{5.3.7}$$

The CuO product reacts with sulfuric acid to give $CuSO_4$ salt:

$$\mathrm{CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)} \tag{5.3.8}$$

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Much of the science of green chemistry involves making decisions about alternative chemical reactions to choose a reaction or reaction sequence that provides maximum safety, produces minimum byproduct, and utilizes readily available materials. Consider two ways of preparing iron sulfate, $FeSO_4$. This chemical is commonly used to treat (clarify) water because when it is added to water and air is bubbled through the water, it produces $Fe(OH)_3$, a gelatinous solid that settles in the water and carries suspended mud and other particles with it. Consider two possible ways of making $FeSO_4$. The first of these was shown earlier and consists of the reaction of iron metal with sulfuric acid:

$$\mathrm{Fe(s)} + \mathrm{H_2SO_4(aq)} \rightarrow \mathrm{H_2(g)} + \mathrm{FeSO_4(aq)} \tag{5.3.9}$$

A second pathway would be to react iron oxide, FeO, with sulfuric acid:

$$\mathrm{FeO(s)} + \mathrm{H_2SO_4(aq)} \rightarrow \mathrm{FeSO_4(aq)} + \mathrm{H_2O(aq)} \tag{5.3.10}$$

Which of these reactions would be the better choice? Both would work. The first reaction generates elemental H_2 gas as a byproduct. That has a potential downside because elemental hydrogen is highly explosive and flammable and could cause an explosion or fire hazard. But, in a contained reaction vessel that allowed for capture of H_2, the elemental hydrogen could be put to use as a fuel or reacted directly in a fuel cell to produce electricity (Section 3.2 and Figure 3.2). Furthermore, scrap iron metal and waste sulfuric acid are common materials that should be recycled and the synthesis of $FeSO_4$ by the direct reaction of the two can prepare a useful material from the two recyclable substances.

The second reaction (5.3.6) also gives the desired product. Its only byproduct is innocuous water. And there is no hazard from elemental hydrogen. In principle, the FeO required could be made by reacting scrap iron metal with oxygen from the air.

$$2\,\mathrm{Fe} + \mathrm{O_2} \rightarrow 2\,\mathrm{FeO} \tag{5.3.11}$$

but in practice the reaction tends to produce other oxides of iron, particularly Fe_2O_3 and Fe_3O_4.

5.4: Yield And Atom Economy in Chemical Reactions

A fundamental concept basic to green chemistry that can be illustrated by chemical reactions is the distinction between yield and atom economy. In Chapter 2 *yield* was defined as a percentage of the degree to which a chemical reaction or synthesis goes to completion and *atom economy* was defined as the fraction of reactants that go into final products. Those two ideas are illustrated here for the preparation of HCl gas which, dissolved in water, produces hydrochloric acid. There are several ways in which HCl can be prepared. One of these commonly used in the laboratory is the reaction of concentrated sulfuric acid, H_2SO_4, with common table salt, NaCl, accompanied by heating to drive off the volatile HCl vapor:

$$2\,\mathrm{NaCl(s)} + \mathrm{H_2SO_4(l)} \rightarrow 2\,\mathrm{HCl(g)} + \mathrm{Na_2SO_4(s)} \tag{5.4.1}$$

This reaction can be performed so that all of the NaCl and H_2SO_4 react, which gives a 100% yield. But it produces Na_2SO_4 byproduct, so the atom economy is less than 100%. The percent atom economy is calculated very simply by the relationship

$$\text{Percent atom economy} = \frac{\text{Mass of desired product}}{\text{Total mass of product}} \times 100 \tag{5.4.2}$$

(We could just as well divide by the total mass of reactants since in a chemical reaction it is equal to the total mass of products.) In this case, the mass of the desired product is that of 2 HCl and the total mass of product is that of 2HCl + Na_2SO_4. Given the atomic masses H 1.0, Cl 35.5, Na 23.0, and O 16.0 gives the following:

$$\text{Mass of desired product} = 2 \times (1.0 + 35.5) = 73.0 \tag{5.4.3}$$

$$\text{Total mass product} = 2 \times (1.0 + 35.5) + (2 \times 23.0 + 32.0 + 4 \times 16.0) = 215 \tag{5.4.4}$$

$$\text{Percent atom economy} = \frac{73.0}{215} \times 100 = 34.0\% \tag{5.4.5}$$

This result shows that even with 100% yield, the reaction is only 34.0% atom economical and if it were used as a means to prepare HCl large quantities of Na_2SO_4, a material with only limited value, would be produced. In contrast, the direct reaction of hydrogen gas with chlorine gas to give HCl gas,

$$\mathrm{H_2(g)} + \mathrm{Cl_2(g)} \rightarrow 2\,\mathrm{HCl(g)} \tag{5.4.6}$$

can be carried out with 100% atom economy if all of the H_2 reacts with Cl_2. There is no waste byproduct.

5.5: Catalysts That Make Reactions Go

Carbon monoxide will certainly burn in the presence of oxygen from air as shown by the reaction

$$2\,\mathrm{CO} + \mathrm{O_2} \rightarrow 2\,\mathrm{CO_2} \tag{5.5.1}$$

Carbon monoxide is a product of automobile exhausts and an undesirable, toxic air pollutant. One way of ridding automobile exhaust gases of this pollutant is to pump air into the exhaust and convert the carbon monoxide to carbon dioxide as shown by the reaction above. However, even in the presence of oxygen, this reaction does not proceed to completion in an ordinary automobile exhaust system. It is enabled to occur, however, by passing the exhaust mixed with air over a solid honeycomb-like surface of ceramic coated with a metal that enables the reaction to occur, but is not itself consumed in the reaction. Such a substance is called a **catalyst**. Most people who have an automobile are vaguely aware that they have an automotive exhaust catalyst. They become much more acutely aware of this fact if the automobile's exhaust system fails an emissions test and the catalytic converter in it has to be replaced at a cost of several hundred dollars!

We do not have to go any farther than our own bodies to find catalysts. That is because all living organisms have biological catalysts that enable reactions to occur. Such living catalysts consist of specialized proteins called **enzymes**. Enzymes are discussed in Chapter 7.

A common enzyme-catalyzed process is the reaction of glucose (blood sugar, $C_6H_{12}O_6$) with molecular oxygen to produce energy mentioned at the beginning of this chapter:

This is the important process of **oxic respiration** carried out by all organisms that live in contact with air and utilize oxygen from air to react with food materials. Although the overall reaction for oxic respiration can be written very simply, the actual process requires many steps and several catalytic enzymes are used. Other enzymes are used for various life processes, such as protein synthesis. There are enzymes that detoxify toxic substances, and in some cases they inadvertantly make toxic substances out of nontoxic ones. Some of the more common cancer-causing substances are actually synthesized from other molecules by enzyme action. Obviously enzymes are very important in life processes.

Catalysts speed up reactions. Depending upon the conditions the **rate of reaction** can vary significantly. Rates of chemical reactions are addressed by the area of **chemical kinetics**.

Catalysts are very important in green chemistry. One reason that this is so is because catalysts enable reactions to be carried out very specifically. Also, the right catalyst can enable reactions to occur with relatively less energy consumption and at relatively lower temperatures.

5.6: Kinds of Chemical Reactions

It is useful to place chemical reactions in various categories. The important categories of chemical reactions are addressed here.

The simplest kind of chemical reaction to visualize is a **combination reaction** in which two substances come together to form a new substance. The substances may be two elements, two compounds, or an element and a compound. An example of a combination reaction occurs when elemental carbon burns,

$$\mathrm{C + O_2 \rightarrow CO_2} \tag{5.6.1}$$

to produce carbon dioxide. Since this reaction generates only one product, it occurs with 100% atom economy. Another combination reaction occurs when calcium oxide, CaO, present in a bed of solid material in a fluidized bed furnace used to burn coal reacts with sulfur dioxide:

$$\mathrm{CaO + SO_2 \rightarrow CaSO_3} \tag{5.6.2}$$

The sulfur dioxide is a potential air pollutant produced from the burning of sulfur present in the coal. By injecting pulverized coal into a bed of CaO and other minerals kept in a fluid-like state by the injection of air, the sulfur dioxide produced has the opportunity to react with CaO and is not emitted as a pollutant with the stack gas.

In addition to being a combination reaction, the reaction above could also be called an **addition reaction** because the SO_2 adds to the CaO. Addition reactions are very desirable in the practice of green chemistry because they are 100% atom economical.

The opposite of a combination reaction is a **decomposition reaction**. An example of such a reaction occurs when a direct electrical current is passed between two electrodes through water to which a salt such as Na_2SO_4 has been added to make a solution in the water that is electrically conducting:

$$\mathrm{2\,H_2O(l) \xrightarrow{Electrolysis} 2\,H_2(g) + O_2(g)} \tag{5.6.3}$$

Reactions such as this that occur by the action of electricity passed through a solution are called **electrolysis** reactions. As written, the reaction is 100% atom economical. However, some side reactions may occur that reduce the efficiency. For example, impurity chloride ion, Cl^-, must be avoided in solution because it can produce some Cl_2 gas, a toxic, undesirable byproduct. Another inefficiency occurs because not all of the electricity passed through the solution is utilized to decompose water.

An example of a useful decomposition reaction is the high-temperature decomposition of methane,

$$\mathrm{CH_4(g) \xrightarrow{\Delta} C(s) + 2\,H_2(g)} \tag{5.6.4}$$

to produce elemental C and H_2 gas (where the triangle over the arrow shows that heat is applied —in this case to a temperature of 1260–1425°C — to make the reaction occur). The elemental carbon from this reaction is generated as a fine powder called **carbon black**. Carbon black is an ingredient of the paste in dry cells (such as those used in portable electronic devices); it is used as a filler in tires and to make electrodes for electrolysis processes such as the one by which aluminum metal is prepared.

Decomposition reactions do not always produce elements. For example, sodium bicarbonate mineral, $NaHCO_3$ may be heated,

$$\mathrm{2\,NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + CO_2(g) + H_2O(g)} \tag{5.6.5}$$

to produce sodium carbonate, Na_2CO_3, commonly used as an industrial chemical to treat water, in cleaning solutions, and as an ingredient of glass.

> **Example:** Using atomic masses Na 23.0, H 1.0, C 12.0, and O 16.0, calculate the percent atom economy of the above reaction for the production of Na_2CO_3.
>
> *Answer:* When 2 formula units of $NaHCO_3$ react, 1 formula unit of Na_2CO_3 is produced. The masses involved in atomic mass units, u, are the following:
>
> $\text{Mass 2NaHCO}_3 = 2 \times (23.0 + 1.0 + 12.0 + 3 \times 16.0) = 168\ \mathrm{u}$
>
> $Na_2CO_3 = 2 \times 23.0 + 12.0 + 3 \times 16.0 = 106\ \mathrm{u}$
>
> $\text{Percent atom economy} = \frac{160\ \mathrm{u}}{168\ \mathrm{u}} \times 100 = 63.1\%$

A **substitution** or **replacement** reaction is one such as the reaction of iron and sulfuric acid,

$$\mathrm{Fe(s)} + \mathrm{H_2SO_4(aq)} \rightarrow \mathrm{H_2(g)} + \mathrm{FeSO_4(aq)} \tag{5.6.6}$$

in which Fe replaces H in H_2SO_4, a reaction shown earlier for the preparation of $FeSO_4$. This reaction also falls under the classification of reactions involving **evolution of a gas**, in this case evolution of hydrogen gas. A **double replacement** reaction, also called a **metathesis** reaction, is one in which two compounds trade ions or other groups. When dissolved calcium chloride reacts with dissolved sodium carbonate,

$$\mathrm{CaCl_2(aq)} + \mathrm{Na_2CO_3(aq)} \rightarrow \mathrm{CaCO_3(s)} + 2\,\mathrm{NaCl(aq)} \tag{5.6.7}$$

the Ca^{2+} ion in calcium chloride simply switches places with the Na^{+} ions in the sodium carbonate to produce solid calcium carbonate and NaCl in solution. This is also a **precipitation** reaction in which a solid material forms from two substances dissolved in water; the solid formed is a **precipitate**. The removal of calcium from water as shown by this reaction is a common water treatment process called **water softening**. It is done because excessive levels of calcium cause formation of scale that can clog water pipes and damage plumbing apparatus. Whenever an acid and a base react, as shown here for the reaction of hydrochloric acid with sodium hydroxide,

$$\mathrm{HCl(aq)} + \mathrm{NaOH(aq)} \rightarrow \mathrm{H_2O(l)} + \mathrm{NaCl(aq)} \tag{5.6.8}$$

water and a salt are formed. Such a reaction is a **neutralization reaction** or simply an **acid-base** reaction.

> **Exercise:** Classify each of the following reactions as combination, decomposition, substitution, metathesis, neutralization, precipitation, or evolution of a gas. In some cases, a reaction will fit into more than one category.
>
> (a) $ce2Ca(s) + O2(g) \rightarrow 2CaO(s)$
>
> (b) $2\,\mathrm{KClO_3(s)} \underset{\rightarrow}{\Delta} 2\,\mathrm{KCl(s)} + 3\,\mathrm{O_2(g)}$
>
> (c) $\mathrm{SO_3(g)} + \mathrm{H_2O(l)} \rightarrow \mathrm{H_2SO_4(aq)}$
>
> (d) $\mathrm{MgCO_3(s)} + 2\,\mathrm{HCl(aq)} \rightarrow \mathrm{MgCl_2(aq)} + \mathrm{H_2O(l)} + \mathrm{CO_2(g)}$
>
> (e) $\mathrm{Zn(s)} + \mathrm{CuCl_2(aq)} \rightarrow \mathrm{Cu(s)} + \mathrm{ZnCl_2(aq)}$
>
> (f) $\mathrm{KOH(aq)} + \mathrm{Hcl(aq)} \rightarrow \mathrm{KCl(aq)} + \mathrm{H_2O(l)}$
>
> (g) $\mathrm{MgSO_4(aq)} + 2\,\mathrm{KOH(aq)} \rightarrow \mathrm{Mg(OH)_2(s)} + \mathrm{K_2SO_4(aq)}$
>
> *Answers:* (a) Combination, (b) decomposition, evolution of a gas, (c) combination, (d)metathesis, evolution of a gas, (e) substitution, (f) neutralization, metathesis, (g) precipitation, metathesis

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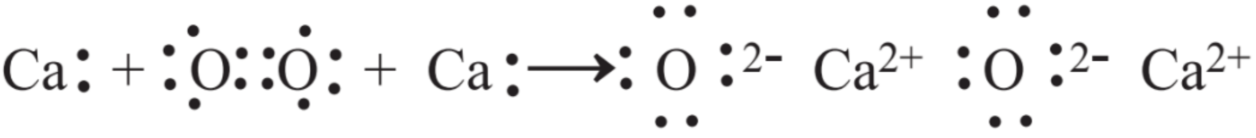
5.7: Oxidation-Reduction Reactions and Green Chemistry

Many reactions, including some of those given in the preceding section, are **oxidation-reduction** reactions, frequently called **redox** reactions. This name derives from the long standing use of *oxidation* to describe the reaction of a substance with oxygen. Consider the following reaction of elemental calcium with elemental oxygen:

$$2\,\mathrm{Ca} + \mathrm{O_2} \rightarrow 2\,\mathrm{CaO} \tag{5.7.1}$$



Combining with oxygen, Ca is *oxidized*. Whenever something is oxidized, something else has to be *reduced*. In this case, elemental oxygen is reduced to produce the oxide ion, O2-in CaO. It is seen from this reaction that the calcium atoms lose electrons when they are oxidized and the oxygen atoms gain electrons. This leads to another definition of oxidation-reduction reactions, which is that *when a chemical species loses electrons in a chemical reaction it is oxidized and when a species gains electrons it is reduced.*

Elemental hydrogen is commonly involved in oxidation-reduction. *Whenever a chemical species reacts with elemental hydrogen, it is reduced*. As an example, iron(II) oxide, FeO, can be reacted with elemental hydrogen,

$$\mathrm{FeO} + \mathrm{H_2} \rightarrow \mathrm{Fe} + \mathrm{H_2O} \tag{5.7.2}$$

In this case the Fe in FeO is reduced to iron metal and the hydrogen in elemental H_2 is oxidized to H_2O.

When elemental oxygen reacts to produce chemically combined oxygen, it is acting as an **oxidizing agent** and is reduced. And when elemental hydrogen reacts to produce chemically combined hydrogen, it acts as a **reducing agent** and is oxidized. Consider what happens when the opposite reactions occur. When chemically combined oxygen is released as elemental oxygen from a chemical reaction, the oxygen is *oxidized*. And when elemental hydrogen is released as the result of a chemical reaction, hydrogen is *reduced*. A good illustration of these definitions may be seen when a direct electrical current is passed between two metal electrodes through water made electrically conducting by dissolving in it a salt, such as Na_2SO_4 as shown in Figure 5.1. At the left electrode, electrons are pumped into the system *reducing* the chemically bound H in H_2O to elemental H_2. An electrode at which *reduction* occurs is called the **cathode**. At the other electrode, electrons are removed from the system, elemental O_2 is released, and the oxygen in H_2O is *oxidized*. An electrode at which oxidation occurs is called the **anode.**

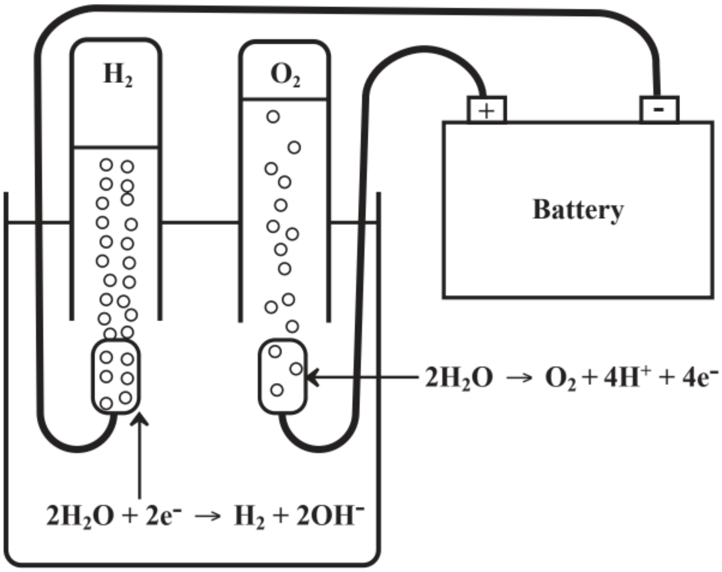


Figure 5.1. Electrolysis of water containing some dissolved salt to make it electrically conducting. At the left electrode(cathode) H in H_2O is reduced by adding electrons releasing H_2 gas. At the right electrode (anode) electrons are removed from chemically

bound O in H_2O releasing elemental O_2 and the oxygen is oxidized.

The reaction shown above is an **electrolysis** reaction. It is very significant in the practice of green chemistry because it is a means of getting pure hydrogen and pure oxygen from water without the use of any other chemical reagents. For example, using a nonpolluting source of energy, such as wind power, elemental hydrogen can be generated for use in nonpolluting fuel cells (see Figure 3.2 and Chapter 16)

Oxidation-reduction reactions are very significant in energy conversion processes. An important example is photosynthesis,

$$6\,CO_2 + 6\,H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{5.7.3}$$

in which solar energy ($h\nu$) from sunlight is used by plants to produce glucose sugar, $C_6H_{12}O_6$, a high-energy compound that is used by organisms to provide energy for their metabolic needs. Since elemental oxygen is produced, oxygen is oxidized. Although it is not obvious based upon the discussion of oxidation-reduction so far, carbon is reduced; the carbon in the $C_6H_{12}O_6$ product is reduced compared to the carbon in the CO_2 reactant. The reverse of this reaction shown at the beginning of this chapter is

$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O + \text{energy} \tag{5.7.4}$$

which occurs when organisms—including humans—utilize glucose sugar to produce energy. In this case, oxygen reacts, an obvious oxidation process. The oxygen is reduced and carbon is oxidized by the action of the elemental oxygen.

A very common oxidation-reduction reaction occurs when fossil fuels are burned to produce energy. One such reaction occurs when natural gas (methane, CH_4) burns,

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O + \text{energy} \tag{5.7.5}$$

to produce carbon dioxide and water, releasing energy. The burning of gasoline, diesel fuel, coal,wood, and even hydrogen gas are oxidation-reduction reactions in which carbon or hydrogen are oxidized by the action of oxygen yielding usable energy.

Oxidation-reduction reactions are the most important kinds of reactions considered in green chemistry. That is true in part because of the central role currently played by the oxidation of fossil fuels and other materials in producing energy needed for chemical processes. Furthermore, the most common raw material currently used for making plastics, synthetic fabrics, and other manufactured materials is petroleum hydrocarbon. There are many hydrocarbon compounds all containing chemically bound carbon and hydrogen. A typical such compound is ethane, C_2H_6. The hydrogen and carbon in a hydrocarbon are in the most chemically reduced form, but required raw materials often are partially oxidized hydrocarbons in which O atoms are bonded to the hydrocarbon (complete oxidation of a hydrocarbon yields CO_2 and H_2O). Ethanol, C_2H_6O, used in chemical synthesis and as an oxygenated additive to make gasoline burn more smoothly with emission of fewer air pollutants is a partially oxidized hydrocarbon.

Large quantities of materials and energy are expended in converting petroleum hydrocarbons to partially oxidized compounds used as raw materials. For example, ethanol can be made from ethane taken from petroleum and natural gas by a series of chemical reactions for which the net process is the following:

$$2\,C_2H_6 + O_2 \rightarrow 2\,C_2H_6O \tag{5.7.6}$$

This transformation requires relatively severe conditions and a net loss of energy. A greener alternative is to use glucose sugar produced by photosynthesis (Reaction 5.7.3) to grow yeasts that produce an ethanol product

$$C_6H_{12}O_6 \rightarrow 2\,C_2H_6O + 2\,CO_2 \tag{5.7.7}$$

a process that occurs under room temperature conditions. In addition to making ethanol, this fermentation process yields carbon dioxide in a concentrated form that can be used for carbonated beverages, supercritical carbon dioxide solvent, or pumped underground for tertiary petroleum recovery. The protein-rich yeast biomass produced in fermentation makes a good animal feed additive.

5.8: Quantitative Information from Chemical Reactions

Much of green chemistry is involved with calculations of quantities of materials involved in chemical reactions. It is essential to do such calculations in order to deal with the important concepts of percent yield and atom economy. Fortunately, it is easy to calculate quantities of materials if a balanced chemical reaction is known along with the pertinent atomic and formula masses. Both energy (Section 5.9) and mass (Section 5.10) in chemical reactions can be calculated.

To this point, we have been viewing chemical reactions in terms of individual atoms and molecules and have been thinking of masses in atomic mass units, u, used to express the masses of individual atoms and molecules. But that is much too small a scale to use in the laboratory. The chemist conveniently deals with grams and moles where a mole of a substance (see Section 4.8) typically has a mass of several to several hundred grams. Much of the remainder of this chapter deals with quantitative information from chemical reactions. Energy changes in chemical reactions are addressed first followed by consideration of masses of reactants and products.

5.9: Energy in Chemical Reactions

In addition to changes in the distribution of mass among various chemical species that occur with chemical reactions, another important participant in chemical reactions is **energy**. Chapter 15 defines and discusses energy in more detail. Here energy is considered in the form of **heat** manifested by the movement of atoms and molecules and as **chemical energy**, which is energy stored in chemical bonds in matter. The standard unit of energy is the **joule**, abbreviated **J**. A total of 4.184 J of heat energy will raise the temperature of 1 g of liquid water by 1°C.

As an example of energy involved with chemical reactions, Consider what happens in a burner on a kitchen range fueled by natural gas. The flame is obviously hot; something is going on that is releasing heat energy. The flame is also giving off light energy, probably as a light blue glow. A chemical reaction is taking place as the methane in the natural gas combines with oxygen in the air,

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \tag{5.9.1}$$

to produce carbon dioxide and water. Most of the energy released during this chemical reaction is released as heat, and a little bit as light. It is reasonable to assume that the methane and oxygen contain stored energy as **chemical potential energy** and that it is released in producing carbon dioxide and water. Common sense tells us that it would be hard to get heat energy out of either of the products. They certainly won't burn! Water is used to put out fires, and carbon dioxide is even used in fire extinguishers.

The potential energy contained in chemical species is contained in the chemical bonds of the molecules that are involved in the chemical reaction. Figure 5.2 shows the kinds of bonds involved in methane, elemental oxygen, carbon dioxide, and water and the energy contained in each. The bond energies are in units of the number of kilojoules (thousands of joules, kJ) required to break a mole (6.02×1023, see Section 4.8) of the bonds (kJ/mol). The same amount of energy is released when a mole of a bond is formed. By convention, energy put into a system is given a positive sign and energy released is denoted by a negative sign.

To calculate the energy change when a mole of methane reacts with oxygen as shown in Reaction 5.9.1, the difference is taken between the sum of the energies of the bonds in the products and the sum of the energies of the bonds in the reactants. Examination of Reaction 5.9.1 and Figure 5.2 shows the following total bond energies in the products:

$$1\text{ mol }CO_2 \times \frac{2\text{ mol C=O}}{\text{mol }CO_2} \times \frac{799\text{ kJ}}{\text{mol C=O}} = 1598\text{ kJ}$$

$$2\text{ mol }H_2O \times \frac{2\text{ mol O-H}}{\text{mol }H_2O} \times \frac{459\text{ kJ}}{\text{mol O-H}} = 1836\text{ kJ}$$

A similar calculation gives the total bond energies in the reactants

$$1\text{ mol }CH_4 \times \frac{4\text{ mol C-H}}{1\text{ mol }CH_4} \times \frac{411\text{ kJ}}{\text{mol C-H}} = 1644\text{ kJ}$$

$$2\text{ mol }O_2 \times \frac{1\text{ mol O=O}}{\text{mol }O_2} \times \frac{494\text{ kJ}}{\text{mol O=O}} = 988\text{ kJ}$$

Total bond energy in reactants = 1644 kJ + 988 kJ = 2632 kJ

The difference in bond energies between products and reactants is 3434 kJ - 2632 kJ = 802 kJ

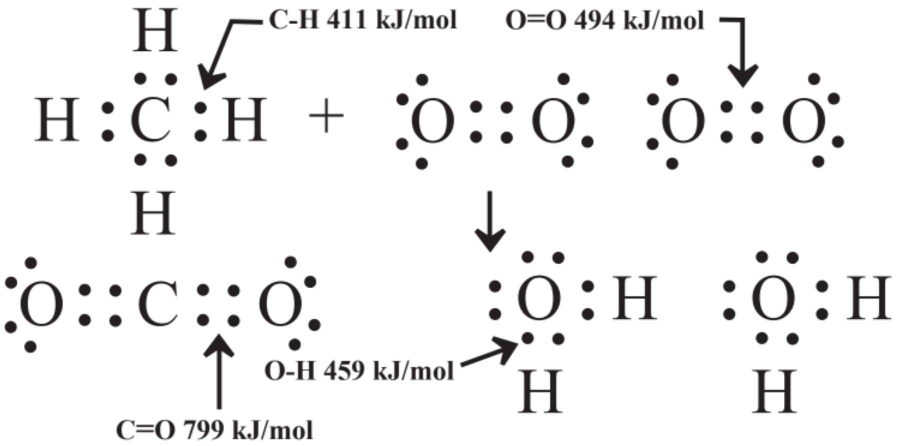


Figure 5.2. Bonds and their energies in the chemical species involved when methane burns in oxygen to produce carbon dioxide and water.

This calculation states that, based upon considerations of bond energy, alone, the energy released when 1 mole of CH_4 reacts with 2 moles of O_2 to produce 1 mole of CO_2 and 2 moles of H_2O, is 802 kJ. This is an **exothermic** reaction in which heat energy is *released*, so it is denoted as-802 kJ. This value is close to the value that would be obtained by experimentally measuring the heat energy released by the reaction, assuming all the reactants and products were in the gas phase. (A significant amount of heat energy is released when vapor-phase water condenses to liquid. Highly efficient condensing gas furnaces capture this heat in a heat exchanger where the water vapor in the furnace exhaust condenses to the liquid phase.) For the most part, therefore, the amount of heat energy released in a chemical reaction, and the amount of potential chemical energy contained in the reactants is equal to the difference between the total bond energies of the products and those of the reactants.

5.10: Stoichiometry by the Mole Ratio Method

The calculation of quantities of materials involved in chemical reactions is called **stoichiometry.** To illustrate stoichiometric calculations consider a typical chemical reaction, in this case the heat-producing combustion of ethane, a hydrocarbon fuel with a chemical formula of C_2H_6:

$$2\,C_2H_6 + 7\,O_2 \rightarrow 4\,CO_2 + 6\,H_2O \tag{5.10.1}$$

Rather than viewing this reaction in terms of individual molecules, it is possible to scale up to moles. Recall from Section 4.8 that the mole is a fundamental unit for quantity of material and that each mole contains Avogadro's number (6.022×10^{23}) of formula units (molecules of covalently bound compounds). This equation simply says that 2 moles of C_2H_6 react with 7 moles of O_2 to yield 4 moles of CO_2 and 6 moles of H_2O. Now we can examine the equation in more detail to do some quantitative calculations. Before doing that, however, review the following two terms

Formula mass: The sum of the atomic masses of all the atoms in a formula unit of a compound. Although the average masses of atoms and molecules may be expressed in atomic mass units (amu or u), formula mass is generally viewed as being relative and without units.

Molar mass: Where X is the formula mass, the molar mass is X grams of an element or compound, that is, the mass in grams of 1 mole of the element or compound

Given the atomic masses H 1.0, C 12.0, and O 16.0 the molar mass of C_2H_6 is 2×12.0 + 6×1.0 = 30.0 g/mol, that of O_2 is 2×16.0 = 32.0 g/mol, that of CO_2 is 12.0 + 2×16.0 = 44.0 g/mol, and that of H_2O is 2×1.0 + 16.0 = 18.0 g/mol. Now consider the chemical equation

$$2\,C_2H_6 + 7\,O_2 \rightarrow 4\,CO_2 + 6\,H_2O \tag{5.10.2}$$

in terms of the minimum whole number of moles reacting and produced and the masses in grams of these quantities. The equation states that 2 moles of C_2H_6 with a mass of 2×30.0 g = 60.0 g of C_2H_6 react with 7 moles of O_2 with a mass of 7×32.0 g = 224 g of O_2 to produce 4 moles of CO_2 with a mass of 4×44.0 g = 176 g of CO_2 and 6 moles of H_2O with a mass of 6×18.0 g = 108 g of H_2O. The total mass of reactants is

$$60.0 \text{ g of } C_2H_6 + \text{ 224 g of } O_2 = 284.0\text{g of reactants} \tag{5.10.3}$$

and the total mass of products is

$$176 \text{ g of } CO_2 + 108\text{g of } H_2O = 284 \text{ g of products} \tag{5.10.4}$$

Note that, as in all chemical reactions, the total mass of products equals the total mass of reactants. Stoichiometry, the calculation of quantities of materials involved in chemical reactions, is based upon the *law of conservation of mass* which states that *the total mass of reactants in a chemical reaction equals the total mass of products*, because matter is neither created nor destroyed in chemical reactions. The basic premise of the **mole ratio method** of stoichiometric calculations is that the relative numbers of moles of reactants and products remain the same regardless of the total quantity of reaction. To illustrate stoichiometric calculations, consider again the following reaction:

$$2\,C_2H_6 + 7\,O_2 \rightarrow 4\,CO_2 + 6\,H_2O \tag{5.10.5}$$

As noted above, this equation states that 2 moles C_2H_6 react with 7 moles of O_2 to produce 4 moles of CO_2 and 6 moles of H_2O. The same ratios hold true regardless of how much material reacts. So for 10 times as much material, 20 moles C_2H_6 react with 70 moles of O_2 to produce 40 moles of CO_2 and 60 moles of H_2O

Suppose that it is given that 18.0 g of C_2H_6 react. What is the mass of O_2 that will react with this amount of C_2H_6? What mass of CO_2 is produced? What mass of H_2O is produced? This problem can be solved by the **mole ratio method**. Mole ratios are, as the name implies, simply the ratios of various moles of reactants and products to each other as shown by a chemical equation. Mole ratios are obtained by simply examining the chemical equation in question; the three that will be used in solving the problem posed are the following:

Suppose that it is given that 18.0 g of C_2H_6 react. What is the mass of O_2 that will react with this amount of C_2H_6? What mass of CO_2 is produced? What mass of H_2O is produced? This problem can be solved by the **mole ratio method**. Mole ratios are, as the name implies, simply the ratios of various moles of reactants and products to each other as shown by a chemical equation. Mole

ratios are obtained by simply examining the chemical equation in question; the three that will be used in solving the problem posed are the following:

$$\frac{7\text{mol } O_2}{2 \text{ mol } C_2H_6} \quad \frac{4 \text{ mol } CO_2}{2 \text{ mol } C_2H_6} \quad \frac{6 \text{ mol } H_2O}{2 \text{ mol } C_2H_6}$$

To solve for the mass of O_2 reacting the following steps are involved:

A. Mass of C_2H_6 reacting B. Convert to moles of C_2H_6 C. Convert to moles of O_2 D. Convert to mass of O_2

In order to perform the calculation, it will be necessary to have the molar mass of C_2H_6, stated earlier as 30.0 g/mol, the molar mass of O_2(18.0 g/mol) and the mole ratio relating moles of O_2 reactant to moles of C_2H_6, 7 mol O_2/2 mol C_2H_6. The calculation becomes the following

$$\text{Mass of } O_2 = 18.0 \text{ g } C_2H_6 \times \frac{1 \text{ mol } C_2H_6}{30.0 \text{ g } C_2H_6} \times \frac{7 \text{ mol } O_2}{2 \text{ mol } C_2H_6} \times \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} = 67.2 \text{ g } O_2$$

Note that in this calculation units cancel above and below the line, starting with units of g C_2H_6. Now that the mass of O_2 reacting has been calculated, it is possible using the appropriate mole ratios and molar masses to calculate the masses of CO_2 and of H_2O produced as follows:

$$\text{Mass of } CO_2 = 18.0 \text{ g } C_2H_6 \times \frac{1 \text{ mol } C_2H_6}{30.0 \text{ g } C_2H_6} \times \frac{6 \text{ mol } H_2O}{2 \text{ mol } C_2H_6} \times \frac{18.0 \text{ g } H_2O}{1 \text{ mol } H_2O} = 32.4 \text{ g } H_2O$$

$$\text{Mass of } H_2O = 18.0 \text{ g } C_2H_6 \times \frac{1 \text{ mol } C_2H_6}{30.0 \text{g} C_2H_6} \times \frac{6 \text{ mol } H_2O}{2 \text{ mol } C_2H_6} \times \frac{18.0 \text{ g } H_2O}{1 \text{ mol } H_2O} = 32.4 \text{ g } H_2O$$

Are the masses calculated above correct? A good check is to compare the total mass of reactants, 18.0 g C_2H_6 + 67.2 g O_2= 85.2 g of reactants, with the total mass of products, 52.8 g CO_2 + 32.4 g H_2O = 85.2 g of products. The fact that the total mass of reactants is equal to the total mass of products gives confidence that the calculations are correct.

As one more example consider the reaction of 15.0 g of Al with Cl_2 to give $AlCl_3$:

$$2 \text{ Al} + 3 \text{ Cl}_2 \rightarrow 2 \text{ AlCl}_3 \tag{5.10.6}$$

What mass of Cl_2 reacts and what is the mass of $AlCl_3$ produced? The atomic mass of Al is 27.0 and that of Cl is 35.5. Therefore, the molar mass of Cl_2 is 71.0 g/mol and the molar mass of $AlCl_3$ is 133.5 g/mole. The mass of Cl_2 reacting is

$$\text{Mass of } Cl_2 = 15.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \times \frac{3 \text{ mol } Cl_2}{2 \text{ mol Al}} \times \frac{71.0 \text{ g } Cl_2}{1 \text{ mol } Cl_2} = 59.2 \text{ g } Cl_2$$

$$\text{Mass of } AlCl_3 = 15.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \times \frac{2 \text{ mol } AlCl_3}{2 \text{ mol Al}} \times \frac{133.5 \text{ g } AlCl_3}{1 \text{ mol } AlCl_3} = 74.2 \text{ g } AlCl_3$$

As a check, 15.0 g Al + 59.2 g Cl_2 reactant gives a total of 74.2 g of reactants equal to the mass of the $AlCl_3$ product.

Exercise

Calculate the mass of CH_4 that reacts and the masses of the products when 25.0 g of Fe_2O_3 undergo the reaction below. The atomic masses involved are H 1.0, C12.0, O 16.0, Fe 55.8

$$4 \text{ Fe}_2\text{O}_3 + 3 \text{ CH}_4 \rightarrow 8 \text{ Fe} + 3 \text{ CO}_2 + 6 \text{ H}_2\text{O}$$

Answer

Answer: 1.88 g CH4, 17.5 g Fe, 5.2 g CO2, 4.2 g H2O

Exercise

Calculate the mass of O_2 that reacts and the masses of the products when 100 g of benzoic acid, $C_7H_6O_2$ undergo the reaction below. The atomic masses involved are H 1.0, C 12.0, and O 16.0.

$$2 \text{ C}_7\text{H}_6\text{O}_2 + 15 \text{ O}_2 \rightarrow 14 \text{ CO}_2 + 6 \text{ H}_2\text{O}$$

Answer

197 g O_2, 252 g CO_2, 44.3 g H_2O

5.11: Limiting Reactant and Percent Yield

Mixing of exact amounts of reactants such that all are consumed and none left over in a chemical reaction almost never occurs. Instead, one of the reactants is usually a **limiting reactant**. Suppose, for example that 100 g of elemental zinc (atomic mass 65.4) and 80 g of elemental sulfur (atomic mass 32.0) are mixed and heated undergoing the following reaction:

$$\mathrm{Zn + S \rightarrow ZnS} \tag{5.11.1}$$

What mass of ZnS, formula mass 97.4 g/mol, is produced? If 100 g of zinc react completely, the mass of S reacting and the mass of ZnS produced would be given by the following calculations:

$$\text{Mass s} = 100.0 \text{ G Zn} \times \frac{1 \text{ mol Zn}}{65.4 \text{ g Zn}} \times \frac{1 \text{ mol S}}{1 \text{ mol Zn}} \times \frac{32.0 \text{ g S}}{1 \text{ mol S}} = 48.9 \text{ g S}$$

$$\text{Mass ZnS} = 100.0\text{g Zn} \times \frac{1 \text{ mol Zn}}{65.4 \text{ g Zn}} \times \frac{1 \text{ mol S}}{1 \text{ mol Zn}} \times \frac{97.4 \text{ g ZnS}}{1 \text{ mol ZnS}} = 149 \text{ g S}$$

Only 48.9 g of the available S react, so sulfur is in excess and zinc is the limiting reactant. A similar calculation for the amount of Zn required to react with 80 g of sulfur would show that 164g of Zn would be required, but only 100 g is available.

Exercise

A solution containing 10.0 g of HCl dissolved in water (a solution of hydrochloric acid) was mixed with 8.0 g of Al metal undergoing the reaction

$$\mathrm{2\,Al + 6\,HCl \rightarrow 2\,AlCl_3 + 3\,H_2}$$

Given atomic masses H 1.0, Al 27.0, and Cl 35.5, which reactant was left over? How much? What mass of $AlCl_3$ was produced?

Answer

HCl was the limiting reactant. Only 2.47 g of Al were consumed leaving 5.53 g of Al unreacted. The mass of $AlCl_3$ produced was 12.2 g

Percent Yield

The mass of product calculated from the mass of limiting reactant in a chemical reaction is called the **stoichiometric yield** of a chemical reaction. By measuring the actual mass of a product produced in a chemical reaction and comparing it to the mass predicted from the stoichiometric yield it is possible to calculate the *percent yield*. This concept is illustrated by the following example.

Suppose that a water solution containing 25.0 g of $CaCl_2$ was mixed with a solution of excess sodium sulfate,

$$\mathrm{CaCl_2(aq) + Na_2SO_4(aq) \rightarrow CaSO_4(s) + 2\,NaCl(aq)} \tag{5.11.2}$$

to produce a solid precipitate of $CaSO_4$, the desired product of the reaction. (Recall that a *precipitate* is a solid formed by the reaction of species in solution; such a solid is said to *precipitate* from the solution.) Removed by filtration and dried, the precipitate was found to have a mass of 28.3 g, the **measured yield**. What was the percent yield?

Using atomic masses Ca 40.0, Cl 35.5, Na 23.0, and O, 16.0 gives molar masses of 111 g/mol for $CaCl_2$ and 136 g/mol for $CaSO_4$. Furthermore, 1 mole of $CaCl_2$ yields 1 mol of $CaSO_4$. The stoichiometric yield of $CaSO_4$ is given by the following calculation

$$\text{Mass CaSO}_4 = 25.0 \text{ g CaCl}_2 \times \frac{1 \text{ mol CaCl}_2}{111 \text{ g CaCl}_2} \times \frac{1 \text{ mol CaSO}_4}{1 \text{ mol CaCl}_2} \times \frac{136 \text{ g CaSO}_4}{1 \text{ mol CaSO}_4} = 30.6 \text{ g CaSO}_4 \tag{5.11.3}$$

The percent yield is calculated by the following:

$$\text{Percent yield} = \frac{\text{Measured yield}}{\text{Stoichiometric yield}} \times 100 \tag{5.11.4}$$

$$\text{Percent yield} = \frac{28.3 \text{ g}}{30.6 \text{ g}} \times 100 = 92.5\% \tag{5.11.5}$$

5.12: Titrations - Measuring Moles by Volume of Solution

Masses are commonly measured with a laboratory balance that registers in grams. Masses of industrial chemicals are measured with much larger industrial scales that commonly give masses in kilograms or tons. In doing laboratory stoichiometric measurements with species in solution, it is often convenient to measure volumes of solution rather than masses of reactants. Solutions can be prepared that contain known numbers of moles per unit volume of solution. The volume of the reagent that must be added to another reagent to undergo a particular reaction can be measured with a device called a **buret**. A buret is shown in Figure 5.3. By measuring the volume of a solution of known concentration of solute required to react with another reactant, the number of moles of solute reacting can be calculated and stoichiometric calculations can be performed based upon the reaction. This procedure is commonly used in chemical analysis and is called **titration**.

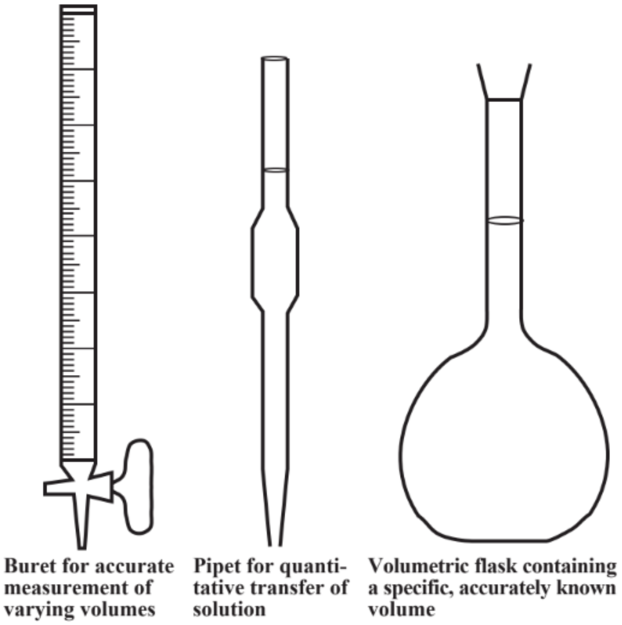


Figure 5.3. A buret consists of a narrow glass tube marked off in divisions of milliliters (mL) further subdivided into tenths of mL, usually with a total capacity of 50 mL. It enables accurate measurements of volumes of solution delivered through a stopcock estimated to the nearest 0.01 mL. A pipet delivers a fixed volume of solution. A volumetric flask contains a fixed volume of solution.

It is especially easy to relate volumes of solutions stoichiometrically when the solution concentrations are expressed as *molar concentration*, *M*. This concentration unit is defined as

$$\mathrm{M}=\frac{\text{moles of solute}}{\text{number of liters of solution}} \tag{5.12.1}$$

The number of moles of a substance, in this case the moles of solute, is related to the mass of the substance by

$$\text{Moles of solute}=\frac{\text{moles of solute}}{\text{molar mass of solute, g/mol}} \tag{5.12.2}$$

These two relationships can be combined to give the following useful equation:

$$\mathrm{M}=\frac{\text{mass of solute}}{(\text{molar mass of solute})\times(\text{number of liters of solution})} \tag{5.12.3}$$

A solution of known concentration that is added to a reaction mixture during the procedure of titration is a **standard solution**. One of the most common of these is a standard base solution of sodium hydroxide, NaOH. Typically, the concentration of sodium hydroxide in such a standard solution is 0.100 mol/L. Suppose that it is desired to make exactly 2 liters of a solution of 0.100mol/L sodium hydroxide. What mass of NaOH, molar mass 40.0 g/mol, is dissolved in this solution? To do this calculation, use Equation 5.12.3 rearranged to solve for mass of solute:

$$\text{Mass NaOH}=\mathrm{M}\times(\text{molar mass NaOH})\times(\text{liters NaOH}) \tag{5.12.4}$$

$$\text{Mass NaOH} = 0.100\ \text{mol/L} \times 40.0\ \text{g/mol} \times 2.00\ \text{L} = 8.00\ \text{g NaOH} \tag{5.12.5}$$

A common titration procedure is to use a standard solution of base to titrate an unknown solution of acid or to use standard acid to determine base. As an example consider an analysis for acid of a sample of water used to scrub exhaust gas from a hospital incinerator. The water is acidic because of the presence of hydrochloric acid produced by the scrubbing of HCl gas from the incinerator stack gas where the HCl was produced in the burning of polyvinyl chloride in the incinerator. Suppose that a sample of 100 mL of the scrubber water was taken for titration with a 0.125 mol/L standard NaOH and that the volume of standard NaOH consumed was 11.7 mL. What was the molar concentration of HCl in the stack gas scrubber water? To solve this problem it is necessary to know that the reaction between NaOH and HCl is,

$$\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} \tag{5.12.6}$$

a neutralization reaction in which water and a salt, NaCl are produced. Examination of the reaction shows that 1 mole of HCl reacts for each mole of NaOH. Equation 5.12.1 applies to both the standard NaOH solution and the HCl solution being titrated leading to the following equations:

$$M_{HCl} = \frac{moles_{HCl}}{liters_{HCl}} = \text{and } \text{M}_{NaOH} = \frac{moles_{NaOH}}{liters_{NaOH}} \tag{5.12.7}$$

When exactly enough NaOH has been added to react with all the HCl present, the reaction is complete with no excess of either HCl or NaOH. In a titration this **end point** is normally shown by the change of color of a dye called an **indicator** dissolved in the solution being titrated. At the endpoint moles HCl= moles NaOH and the two equations above can be solved to give,

$$\text{M}_{\text{HCl}} \times \text{liters}_{\text{HCl}} = \text{M}_{\text{NaOH}} \times \text{liters}_{\text{NaOH}} \tag{5.12.8}$$

which can be used to give the molar concentration of HCl:

$$\text{M}_{\text{HCl}} = \frac{\text{M}_{\text{NaOH}} \times \text{liters}_{\text{NaOH}}}{\text{liters}_{\text{HCl}}} \tag{5.12.9}$$

Converting the volumes given from mL to liters and substituting into this equation gives the molar concentration of HCl in the incinerator scrubber water:

$$\text{M}_{\text{HCl}} = \frac{0.125\text{mol/L} \times 0.0117\text{L}}{0.100\ \text{L}} = 0.0146\text{mol/L} \tag{5.12.10}$$

Determining Percentage Composition by Titration

A useful application of titration, or **titrimetric analysis** as it is called, is to determine the percentage of a substance in a solid sample that will react with the titrant. To see how this is done, consider a sample consisting of basic lime, $Ca(OH)_2$, and dirt with a mass of 1.26 g. Using titration with a standard acid solution it is possible to determine the mass of basic $Ca(OH)_2$ in the sample and from that calculate the percentage of $Ca(OH)_2$ in the sample. Assume that the solid sample is placed in water and titrated with 0.112 mol/L standard HCl, a volume of 42.2 mL(0.0422 L) of the acid being required to reach the end point. The $Ca(OH)_2$ reacts with the HCl

$$\text{Ca(OH)}_2 + 2\,\text{HCl} \rightarrow \text{CaCl}_2 + 2\,\text{H}_2\text{O} \tag{5.12.11}$$

whereas the dirt does not react. Examination of this reaction shows that at the end point the mole ratio

$$\frac{1\ \text{mol Ca(OH)}_2}{2\ \text{mol HCl}} \tag{5.12.12}$$

applies. At the end point, the number of moles of HCl can be calculated from

$$\text{Mol}_{\text{HCl}} = \text{liters}_{\text{HCl}} \times \text{M}_{\text{HCl}} \tag{5.12.13}$$

and, since the molar mass of $Ca(OH)_2$ is 74.1 (given atomic masses 40.1, 16.0, and 1.0 for Ca, O, and H, respectively), the mass of $Ca(OH)_2$ is given by

$$\text{Mass}_{\text{Ca(OH)}_2} = \text{moles}_{\text{Ca(OH)}_2} \times \text{molar mass}_{\text{Ca(OH)}_2} \tag{5.12.14}$$

With this information it is now possible to calculate the mass of $Ca(OH)_2$:

$$\text{Mass}_{\text{Ca(OH)}_2} = \text{mol}_{\text{Ca(OH)}_2} \times \frac{74.1 \text{ g Ca(OH)}_2}{1 \text{ mol Ca(OH)}_2} \tag{5.12.15}$$

$$\text{Mass}_{\text{Ca(OH)}_2} = \underbrace{\text{Liters}_{\text{HCl}} \times \text{M}_{\text{HCl}}}_{\text{Moles HCl reacting}} \times \underbrace{\frac{1 \text{ mol Ca(OH)}_2}{2 \text{ mol HCl}}}_{\text{Converts from moles HCl to moles Ca(OH)}_2} \times \underbrace{\frac{74.1 \text{ g Ca(OH)}_2}{1 \text{ mol Ca(OH)}_2}}_{\text{Gives mass Ca(OH)}_2 \text{ from moles Ca(OH)}_2} \tag{5.12.16}$$

$$\text{Mass}_{\text{Ca(OH)}_2} = 0.0422 \text{L HCl} \times \frac{0.112 \text{ mol HCl}}{1 \text{ L HCl}} \times \frac{1 \text{ mol Ca(OH)}_2}{2 \text{ mol HCl}} \times \frac{74.1 \text{ g Ca(OH)}_2}{1 \text{ mol Ca(OH)}_2} \tag{5.12.17}$$

$$\text{Mass Ca(OH)}_2 = 0.175 \ g \tag{5.12.18}$$

$$\text{Percent}_{\text{Ca(OH)}_2} = \frac{\text{mass Ca(OH)}_2}{\text{mass sample}} \times \frac{0.175g}{1.26g} \times 100 = 13.9\% \tag{5.12.19}$$

Exercise

Exercise: A 0.638 g sample consisting of oxalic acid, H_2C_2O4, and sodium oxalate, $Na_2C_2O_4$ was dissolved and titrated with 0.116 mol/L sodium hydroxide, of which 47.6mL (0.0476 L) was required. Each molecule of $H_2C_2O_4$ releases 2 H^+ ions. Calculate the percentage of oxalic acid in the sample.

Answer

38.9%

5.13: Industrial Chemical Reactions - The Solvay Process

Literally thousands of chemical reactions are used to make important industrial products. Most of these involve organic chemicals, which are addressed in Chapter 9 and later chapters of this book. Some are used to make inorganic chemicals in large quantities. One such synthesis operation is the **Solvay process**, long used to make sodium bicarbonate and sodium carbonate, industrial chemicals required for glass making, cleaning formulations, and many other applications. The Solvay process is examined in some detail in this section because it illustrates some important inorganic chemical reactions and can be used for the discussion of green chemistry in industry.

The key reaction in Solvay synthesis is,

$$\mathrm{NaCl + NH_3 + Co_2 + H_2O \rightarrow NaHCO_3(s) + NH_4Cl} \tag{5.13.1}$$

in which a sodium chloride solution (brine) is saturated with ammonia gas (NH_3), then with carbon dioxide, and finally cooled. This is a precipitation reaction in which solid sodium bicarbonate, $NaHCO_3$, comes out of solution. When heated, the solid $NaHCO_3$ yields solid sodium carbonate, Na_2CO_3, water vapor, and carbon dioxide gas:

$$\mathrm{2\,NaHCO_3 + heat \rightarrow Na_2CO_3 + H_2O(g) + CO_2(g)} \tag{5.13.2}$$

In keeping with the practice of green chemistry (although Solvay developed the process long before anyone ever thought of green chemistry), the CO_2 from Reaction 5.13.2 is recycled back into Reaction 5.13.1

The raw materials for the Solvay process are cheap. The NaCl solution can be pumped from the ground from brine deposits in some locations, or fresh water can be pumped into a salt formation to dissolve NaCl and the resulting brine pumped to the surface. The most expensive raw material is ammonia, which is made by the reaction of elemental hydrogen and nitrogen over an iron-based catalyst,

$$\mathrm{3\,H_2 + N_2 \rightarrow 2\,NH_3} \tag{5.13.3}$$

a means of making ammonia developed by Haber and Bosch in Germany in 1913. However, as shown below, the ammonia is recycled, so only relatively small quantities of additional makeup NH_3 are required.

In addition to NaCl, the major consumable raw material in the Solvay process is calcium carbonate, $CaCO_3$, which is abundantly available from deposits of limestone. It is heated (calcined)

$$\mathrm{CaCO_3 + heat \rightarrow CaO + CO_2} \tag{5.13.4}$$

to produce calcium oxide and carbon dioxide gas. The carbon dioxide gas is used in Reaction 5.13.1, another green chemical aspect of the process. The calcium oxide is reacted with water (it is said to be slaked),

$$\mathrm{CaO + H_2O \rightarrow Ca(OH)_2} \tag{5.13.5}$$

to produce basic calcium hydroxide. This base is then reacted with the solution from which solid $NaHCO_3$ has been precipitated (Reaction 5.13.1) and that contains dissolved ammonium chloride,

$$\mathrm{Ca(OH)_2(s) + 2\,NH_4Cl(aq) \rightarrow 2\,NH_3(g) + CaCl_2(aq) + 2\,H_2O(l)} \tag{5.13.6}$$

releasing ammonia gas that is recycled back into Reaction 5.13.1 for $NaHCO_3$ synthesis. This has the advantage of recycling ammonia, which is essential for the process to be economical. It has the disadvantage of generating a solution of calcium chloride, $CaCl_2$. The commercial demand for this salt is limited, although concentrated solutions of it are used for de-icing ice-covered roads. It has such a voracious appetite for water that it cannot be dried economically for storage in a dry form.

Does the Solvay process meet the criteria for a green chemical synthesis? There is not a simple answer to that question. There are two respects in which it does meet green chemical criteria:

1. It uses inexpensive, abundantly available raw materials in the form of NaCl brine and limestone ($CaCO_3$). A significant amount of NH_3 is required to initiate the process with relatively small quantities to keep it going.

2. It maximizes recycle of two major reactants, ammonia and carbon dioxide. The calcination of limestone (Reaction 5.13.4) provides ample carbon dioxide to make up for inevitable losses from the process, but some additional ammonia has to be added to compensate for any leakage.

What about the percent yield and atom economy of the Solvay process? The percent yield of reaction generating the product, Reaction 5.13.1, can be expected to be significantly less than 100% in large part because the stoichiometric amount of $NaHCO_3$ cannot be expected to precipitate from the reaction mixture. To calculate the maximum atom economy for Na_2CO_3 production, it must be assumed that all reactions go to completion without any losses. In such an ideal case, the overall reaction for the process is

$$\mathrm{CaCO_3 + 2\,NaCl \rightarrow Na_2CO_3 + CaCl_2} \tag{5.13.7}$$

Using the atomic masses Ca 40.0, C 12.0, O 16.0, and Cl 35.5 gives the molar masses of $CaCO_3$, 100 g/mol; NaCl, 58.5 g/mol; Na_2CO_3, 106 g/mol; and $CaCl_2$, 111 g/mol. If the minimum whole number of moles of reactants were to react, 100 g of $CaCO_3$ would react with 2×58.5 = 117 g of NaCl to produce 106 g of Na_2CO_3 and 111 g of $CaCl_2$. Note that the mass of NaCl reacting is 2 times the molar mass because 2 moles of NaCl are reacting. So, for these amounts of materials inthe reaction, a total mass of 100 + 117 = 217 g of reactants produces 106 g of the Na_2CO_3 product. Therefore, the percent atom economy is

$$\text{Percent atom economy} = \frac{\text{Mass of desired product}}{\text{Total mass of reactants}} \times 100 = \frac{106g}{217g} \times 100 = 48.8\% \tag{5.13.8}$$

This is the maximum possible value assuming complete reactions and no losses. If the CaCl2byproduct is considered to be a useful product, the atom economy can be regarded as being higher.

Is the Solvay process green with respect to environmental impact? Again, the answer to this question is mixed. Extraction of the two major raw materials, limestone and NaCl, normally can be accomplished with minimal adverse effects on the environment. Quarrying of limestone in open pits results in dust production and blasting of the rock, which is usually carried out with an explosive mixture of fuel oil mixed with ammonium nitrate, NH_4NO_3, causes some disturbance. Open-pit lime stone quarries can be unsightly, but can also serve as artificial lakes. In some places the underground spaces left from the underground quarrying of limestone have found excellent commercial use as low-cost warehouses that largely provide their own climate control. Truck transport of quarried lime definitely has negative environmental impacts. Extraction of liquid NaCl brine usually has minimal environmental impact. The Solvay process, itself, releases significant quantities of greenhouse gas CO_2 and some gaseous ammonia to the atmosphere. Solvay production of sodium carbonate requires significant amounts of energy.

There are numerous natural deposits of sodium bicarbonate and sodium carbonate. The most common source of these salts is a mineral called **trona**, for which the chemical formula is Na_2CO_3•$NaHCO_3$•$2H_2O$. (This formula shows that a formula unit of trona mineral consists of 1 formula unit of ionic Na_2CO_3, 1 formula unit of ionic $NaHCO_3$ and 2 molecules of H_2O). The development of huge deposits of trona in the state of Wyoming and elsewhere in the world has lowered dependence on the Solvay process for sources of sodium bicarbonate and sodium carbonate and the process is no longer used in the United States.

Questions and Problems

1. How do chemical equations relate to chemical reactions?

2. Summarize the information contained in the chemical equation below. How would this reaction be classified? $CaCl_2(aq)$ + $Na_2CO_3(aq) \rightarrow CaCO_3(s)$ + 2NaCl(*aq*)

3. What are the meanings of (*s*), (*l*), (*g*), and (*aq*) after formulas in a chemical equation? What are the meanings of Δ and $\leftarrow \rightarrow$?

4. What is wrong with balancing the chemical equation $S + O_2 \rightarrow SO_3$ as $S + O_2 \rightarrow SO_2$?

5. From your knowledge of chemistry and chemical formulas write the balanced equation for heating magnesium carbonate to give magnesium oxide and carbon dioxide, indicating the physical states of the reactants and products.

6. Balance the equation $FeSO_4+ H_2SO_4+ O_2 \rightarrow Fe_2(SO_4)_3+ H_2O$, which is for a reaction involved in the formation of pollutant acid mine water.

7. Balance each of the following: (a) $C_2H_4+ O_2 \rightarrow CO_2+ H_2O$, (b) $KClO_4 \rightarrow KClO + O_2$, (c)$FeS_2+ O_2+ H_2O \rightarrow FeSO_4+ H_2SO_4$ (d) $Fe_2O_3+ CO \rightarrow Fe + CO_2$, (e) $H_3PO_4+ H2 \rightarrow PH_3 + H_2O$, (f) $P + Cl_2 \rightarrow PCl_5$

8. Explain how chemical equations fit in with the general scheme of chemistry as a language.

9. A chemical equation that describes the action of hydrogen sulfide, H2S, dissolved in water is$H2S \leftarrow \rightarrow H++ HS-$. What does this equation say and how is it consistent with the fact that dissolved hydrogen sulfide is a weak acid?.

10. From the discussion of reactions of metals with sulfuric acid in Section 5.3 and your knowledge of the properties of silver jewelry, explain what is likely to happen when silver metal is placed in sulfuric acid.

11. Zinc is a very reactive metal. Explain with chemical equations what you would expect to happen if zinc metal were placed in sulfuric acid and what would happen if zinc oxide, ZnO, were placed in sulfuric acid.

12. Finely divided steel wool heated red hot and quickly placed into a bottle of oxygen burns vigorously undergoing the reaction $4Fe + 3O_2 \rightarrow 2Fe_2O_3$. Why is there no concern that a steel beam used in construction will burn in air? However, such a beam can be cut with an oxyacetylene torch by first heating a small portion of it with the torch, then turning off the acetylene and slowly running the torch across the beam. What is happening in this case?

13. A water solution of hydrogen peroxide, H_2O_2, is relatively stable. But, if a small quantity of solid manganese oxide is placed in the solution of hydrogen peroxide, bubbles are given off near the surface of the manganese oxide, although the solid appears to remain intact. Explain what happens and the role of the manganese oxide.

14. The following reactions were given in connection with the Solvay process used to makesodium bicarbonate and sodium carbonate: (A) $NaCl + NH3+ CO_2+ H_2O \rightarrow NaHCO_3(s) + NH_4Cl$, (B) $2NaHCO_3+$ heat$\rightarrow$ $Na_2CO_3+ H_2O(g) + CO2(g)$ (C) $3H_2+ N_2 \rightarrow 2NH_3$, (D) $CaCO_3+$ heat$\rightarrow CaO + CO_2$, (E) $CaO + H_2O \rightarrow Ca(OH)_2$. Classify each of these reactions in the categories given in Section 5.6.

15. Given the chemical reaction $4CH_4+ 6NO_2 \rightarrow 4CO + 3N_2+ 8H_2O$, write all the possible mole ratios relating N_2 to each of the other reaction participants.

16. Given the atomic masses N 14.0, H 1.0, and Cl 35.5 and the reaction below, calculate the mass of HCl produced when 12.7 g of NH_3 react.

$$2NH_3+ 3Cl_2 \rightarrow N_2+ 6HCl$$

17. Given the atomic masses C 12.0, H 1.0, and O 16.0 and the reaction below, calculate the mass of H_2O produced when 15.6 g of O_2react.

$$C_2H_4+ 3O_2 \rightarrow 2CO_2+ 2H_2O$$

18. Match the reaction type from the list on the left with the example reaction from the right, below. $PbSO_4$ is insoluble in water.

A. Decomposition 1. $HCl + NaOH \rightarrow H2O + NaCl$

B. Neutralization 2. $Pb(NO_3)_2+ Na_2SO_4 \rightarrow PbSO_4+ 2NaCl$

C. Substitution 3. $2H_2O_2 \rightarrow 2H_2O + O_2$

D. Double displacement 4. $CuSO_4(aq) + Fe(s) \rightarrow FeSO_4(aq) + Cu(s)$

19. Of the following, the **untrue** statement is

A. The symbol ← → is used to show that a reaction goes both ways.

B. The notation (l) is used to show that a reactant or product is dissolved in water.

C. A catalyst changes the rate of a reaction but is not itself consumed.

D. The symbol, Δ, is used to show application of heat to a reaction.

E. Simply because a chemical equation may be written and balanced does **not** indicate for certain that the chemical reaction it indicates will occur.

20. Given the reaction $2S + 3O_2 \rightarrow 2SO_2$ and atomic masses of 32.0 and 16.0 for S and O, respectively, calculate the mass of O_2 reacting with 15.0 g of S.

21. Given the reaction $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$ and atomic masses of C, 12.0, H, 1.0; and O16.0, calculate the total mass of products formed when 24.0 g of CH_4 reacts.

22. Given the reaction $3CH_4 + 4Fe_2O_3 \rightarrow 3CO_2 + 6H_2O + 8Fe$ and atomic masses of C, 12.0; H,1.0; Fe, 55.8; and O, 16.0, what is the mass of CO_2 produced by the reaction of 36.0 g of Fe_2O_3?

23. What is the basis of stoichiometry in respect to relative amounts of materials in reactions?

23. What are the major steps in doing a stoichiometric calculation?

24. What is a limiting reactant?

25. A solution of $FeSO_4$ was prepared by mixing 100 g of pure H_2SO_4 with water and putting it in contact with 50.0 g of iron metal. What reaction occurred? What masses of reaction products were generated and what were the masses of reactants, if any, left over? The atomic masses needed are H 1.0, Fe 55.8, S 32.0, and O 16.0.

26. What is the difference between the stoichiometric yield and the measured yield in a chemical reaction? How are they used to calculated percent yield?

27. How are titrations and stoichometry related?

28. A solid mineral sample consisting of calcium carbonate, $CaCO_3$, and nonreactive mineral matter weighing 0.485 g was stirred in some water to which 0.115 mol/L standard hydrochloric acid, HCl, was added from a buret. The reaction was $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$. If 48.6 milliliters (0.0486 L) of HCl was required to react with all the $CaCO_3$ in the sample, what was the percentage of $CaCO_3$ in the sample given that the molar mass of $CaCO_3$ is 100 g/mol?

29. A 250 mL sample of incinerator exhaust gas scrubber water contaminated with HCl was titrated with 0.104 mol/L standard NaOH, of which 11.3 mL were required to reach the endpoint. What was the molar concentration of HCl in the water sample?

30. What is made by the Solvay process? What is the overall chemical reaction that describes the Solvay process? What are the two major raw materials consumed and what are two major species that are recycled through the process?

31. What are major green aspects of the Solvay process? What are some aspects that are less green?

32. What is a major alternative to use of the Solvay process?

33. Calculate the number of moles of total of $AlCl_3$ in 38.6 g of the compound and the number of moles of CH_4, in 217 g of methane. Use 27.0, 35.5, 12.0, and 1.0 for the atomic masses of Al, Cl, C, and H, respectively.

34. Why might you expect stoichiometric ratios of reactants to be used in industrial chemical reactions? If one of two reactants used in an industrial process is much more expensive than another, suggest why and in which way a stoichiometric ratio might not be used? Also, suppose that one of two reactants is quite toxic whereas the other reactant is not. Why might the practice of green chemistry suggest using a nonstoichometric ratio of reactants in such a case?

35. Given the reaction $2H_2 + O_2 \rightarrow 2H_2O$, identify which species is oxidized, which is reduced, which is the oxidizing agent, and which is the reducing agent.

36. Given the reaction that occurs when a direct electrical current is passed through liquid ionic NaCl, $2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2$, identify which species is oxidized and which is reduced. Justify the answer.

37. Identify which reactions given in Section 5.6 are oxidation-reduction reactions

CHAPTER OVERVIEW

6: The Wonderful World of Carbon - Organic Chemistry and Biochemicals

“The first few of what are now known to be organic chemicals to be discovered were produced by living organisms and were therefore called ‘organic.’ One such compound is urea, which occurs in urine. In 1828 Friedrich Wöhler disproved the idea that all organic compounds must come from living organisms when he accidentally discovered that urea could be made by the reaction of cyanic acid (HOCN) and ammonia, both simple organic compounds. This discovery established the science of organic chemistry based upon the unique bonding capabilities of the carbon atom leading to the synthesis and discovery of tens of millions of unique organic compounds. In 2009 the American Chemical Society Chemical Abstract Service registered the 60 millionth compound(most of which are organic compounds) only 9 months after the registration of the 40 millionth, apace of discovery of more than one new compound per minute.”

6.1: Rings and Chains of Carbon Atoms
6.2: Compounds of Carbon and Hydrogen - Hydrocarbons
6.3: Using Lines To Show Organic Structural Formulas
6.4: Functional Groups
6.5: Giant Molecules from Small Organic Molecules
Questions and Problems
Supplementary References

6.1: Rings and Chains of Carbon Atoms

Most of the molecules of chemical compounds studied so far have been clusters of only a few atoms. Therefore, molecules of water, H_2O, exist as individual clusters of 2 H atoms bonded to 1O atom and molecules of ammonia, NH_3, each consist of an atom of N to which are bonded 3 H atoms. In cases where atoms of a particular element in chemical compounds have a tendency to bond with atoms of the same element, the number of possible compounds is increased tremendously. This is the case with carbon, C. Groups of carbon atoms can bond together to form straight chains, branched chains, and rings, leading to a virtually limitless number of chemical compounds. Such carbon-containing compounds are **organic chemicals**, the study of which is **organic chemistry**. Adding to the enormous diversity of organic chemistry is the fact that two carbon atoms may be connected by **single bonds** consisting of 2 shared electrons, **double bonds** composed of 4 shared electrons, and even **triple bonds** that contain 6 shared electrons.

Organic chemicals comprise most of the substances with which chemists are involved. Petroleum, which serves as the raw material for vast polymer, plastics, rubber, and other industries consists of hundreds of compounds composed of hydrogen and carbon called **hydrocarbons**.Among organic chemicals are included the majority of important industrial compounds, synthetic polymers, agricultural chemicals, and most substances that are of concern because of their toxicities and other hazards. The carbohydrates, proteins, lipids (fats and oils), and nucleic acids(DNA) that make up the biomass of living organisms are organic chemicals made by biological processes. The feedstock chemicals needed to manufacture a wide range of chemical products are mostly organic chemicals, and their acquisition and processing are of great concern in the practice of green chemistry. The largest fraction of organic chemicals acquired from petroleum and natural gas sources are burned to fuel vehicles, airplanes, home furnaces, and power plants. Prior to burning, these substances may be processed to give them desired properties. This is particularly true of the constituents of gasoline, the molecules of which are processed and modified to give gasoline desired properties of smooth burning (good antiknock properties) and low air pollution potential. Pollution of the water, air, and soil environments by organic chemicals is an area of significant concern. Much of the effort put into green chemistry has involved the safe manufacture, recycling, and disposal of organic compounds.

A number of organic compounds are made by very sophisticated techniques to possess precisely tailored properties. This is especially true of pharmaceuticals, which must be customized to deliver the desired effects with minimum undesirable side effects. A single organic compound that is effective against one of the major health problems — usually one out of hundreds or even thousands tested — has the potential for hundreds of millions of dollars per year in profits.

Organic chemicals differ widely in their toxicities. Some compounds are made and used because of their toxicities to undesirable organisms. These are the **pesticides**, including, especially, **insecticides** used to kill unwanted insects and **herbicides** used to eradicate weeds that compete with desired crops. Green chemistry is very much involved with these kinds of applications. One of the more widely applied uses of genetically modified crops has been the development of crops that produce their own insecticides in the form of insecticidal proteins normally made by certain kinds of bacteria whose genes have been spliced into field crops. Another application of green chemistry through genetic engineering is the development of crops that resist the effects of specific organic molecules commonly used as herbicides. These herbicides may be applied directly to target crops, leaving them unscathed while competing weeds are killed.

It should be obvious from this brief discussion that organic chemistry is a vast, diverse, highly useful discipline based upon the unique bonding properties of the carbon atom. The remainder of this chapter discusses major aspects of organic chemistry. Many of the most interesting and important organic chemicals are made by biological processes. Indeed, until 1828, it was generally believed that only organisms could synthesize organic chemicals. In that year, Friedrich Wöhlers succeeded in making urea, an organic chemical that is found in urine, from ammonium cyanate, an inorganic material. Because of the important role of organisms in making organic chemicals, several of the most significant kinds of these chemicals made biologically are also discussed in this chapter. Additional details regarding the ways in which living organisms make and process chemicals are given in Chapters 9 and 13.

6.2: Compounds of Carbon and Hydrogen - Hydrocarbons

The tremendous variety and diversity of organic chemistry is due to the ability of carbon atoms to bond with each other in a variety of straight chains, branched chains, and rings and of adjacent carbon atoms to be joined by single, double, or triple bonds. This bonding ability can be illustrated with the simplest class of organic chemicals, the **hydrocarbons** consisting only of hydrogen and carbon. Figure 6.1 shows some hydrocarbons in various configurations. Hydrocarbons are the major ingredients of petroleum and are pumped from the ground as crude oil or extracted as natural gas. They have two major uses. The first of these is combustion as a source of fuel. The most abundant hydrocarbon in natural gas, methane, CH_4, is burned in home furnaces, electrical power plants, and even in vehicle engines,

$$\mathrm{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O + heat energy} \tag{6.2.1}$$

to provide energy. The second major use of hydrocarbons is as a raw material for making rubber, plastics, polymers, and many other kinds of materials. Given the value of hydrocarbons as a material, it is unfortunate that so much of hydrocarbon production is simply burned to provide energy, which could be generated by other means.

There are several major class of hydrocarbons, all consisting of only hydrogen and carbon. **Alkanes** have only single bonds between carbon atoms. Cyclohexane, *n*-heptane, and 3-ethyl-2,5-dimethylhexane in Figure 6.1 are alkanes; the cyclohexane is a cyclic hydrocarbon. **Alkenes**, such as propene shown in Figure 6.1, have at least one double bond consisting of 4 shared electrons between two of the carbon atoms in the molecule. **Alkynes** have at least one triple bond between carbon atoms in the molecule as shown for acetylene in Figure 6.1. Acetylene is an important fuel for welding and cutting torches; otherwise, the alkynes are of relatively little importance and will not be addressed farther. A fourth class of hydrocarbon consists of **aromatic** compounds which have rings of carbon atoms with special bonding properties as discussed later in this chapter

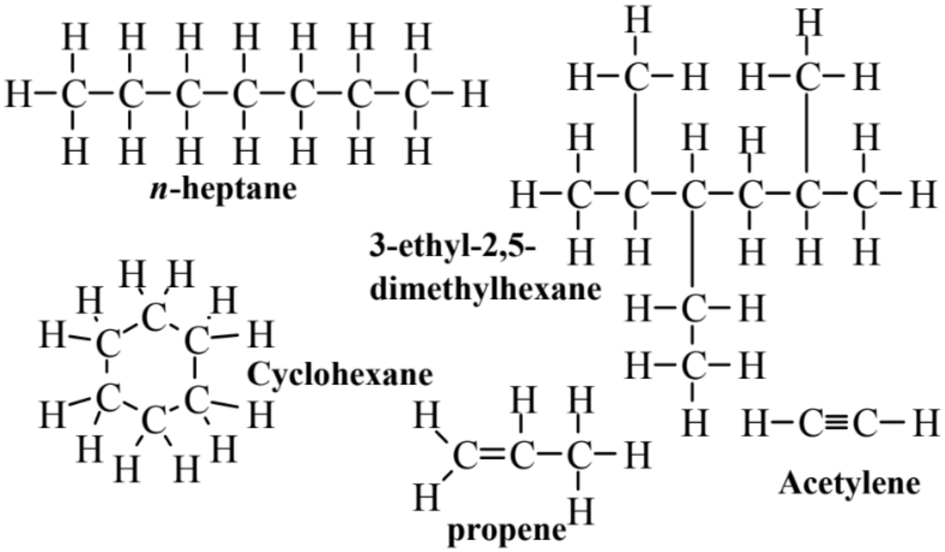


Figure 6.1. Some typical hydrocarbons. These formulas illustrate the bonding diversity of carbon which gives rise to an enormous variety of hydrocarbons and other organic compounds.

Alkanes

The molecular formulas of non-cyclic alkanes are CnH2n+2. By counting the numbers of carbon and hydrogen atoms in the molecules of alkanes shown in Figure 6.1, it is seen that the molecular formula of *n*-heptane is C_7H_6 and that of 3-ethyl-2,5-dimethylhexane is $C_{10}H_{22}$, both of which fit the general formula given above. The general formula of cyclic alkanes is C_nH_{2n}; that of cyclohexane, the most common cyclic alkane, is C_6H_{12}. These formulas are **molecular formulas**, which give the number of carbon and hydrogen atoms in each molecule, but do not tell anything about the structure of the molecule. The formulas given in Figure 6.1 are **structural formulas** which show how the molecule is assembled. The structure of *n*-heptane is that of a straight chain of carbon atoms; each carbon atom in the middle of the chain is bound to 2 H atoms and the 2 carbon atoms at the ends of the chain are each bound to 3 H atoms. The prefix *hep* in the name denotes 7 carbon atoms and the*n*-indicates that the compound consists of a single straight chain. This compound can be represented by a **condensed structural formula** as $CH_3(CH_2)_5CH_3$

representing 7 carbon atoms in a straight chain. In addition to methane mentioned previously, the lower alkanes include the following:

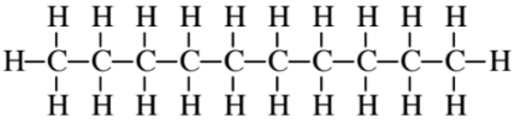
Ethane: CH_3CH_3 Propane: $CH_3CH_2CH_3$ Butane: $CH_3(CH_2)_2CH_3$ *n*-Pentane: $CH_3(CH_2)3CH_3$

For alkanes with 5 or more carbon atoms, the prefix (*pen* for 5,*hex* for 6,*hept* for 7,*oct* for 8,*non* for 9) shows the total number of carbon atoms in the compound and *n*-may be used to denote a straight-chain alkane. Condensed structural formulas may be used to represent branched chain alkanes as well. The condensed structural formula of 3-ethyl-2,5-dimethylhexane is

$$CH_3CH(CH_3)CH(C_2H_5)CH_2CH(CH_3)CH_3$$

In this formula, the C atoms and their attached H atoms that are not in parentheses show carbons that are part of the main hydrocarbon chain. The (CH_3) after the second C in the chain shows a methyl group attached to it, the (C_2H_5) after the third carbon atom in the chain shows an ethyl group attached to it, and the (CH_3) after the fifth carbon atom in the chain shows a methyl group attached to it.

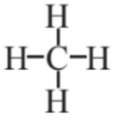
Compounds that have the same molecular formulas but different structural formulas are **structural isomers**. For example, the straight-chain alkane with the molecular formula $C_{10}H_{22}$ is *n*-decane



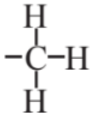
***n*-decane**

which is a structural isomer of 3-ethyl-2,5-dimethylhexane.

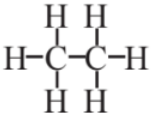
The names of organic compounds are commonly based upon the structure of the hydrocarbon from which they are derived using the longest continuous chain of carbon atoms in the compound as the basis for the name. For example, the longest continuous chain of carbon atoms in 3-ethyl-2,5-dimethylhexane shown in Figure 6.1 is 6 carbon atoms, so the name is based upon *hex*ane. The names of the chain branches are also based upon the alkanes from which they are derived. As shown below,



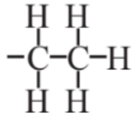
Methane (CH_4)



Methyl group (CH_3)



Ethane (C_2H_6)



Ethyl group (C_2H_5)

the two shortest-chain alkanes are methane with 1 carbon atom and ethane with 2 carbon atoms. Removal of 1 of the H atoms from methane gives the **methyl** group and removal of 1 of the H atoms from ethane gives the **ethyl** group. These terms are used in the name 3-ethyl-2,5-dimethylhexane to show groups attached to the basic hexane chain. The carbon atoms in this chain are numbered sequentially from left to right. An ethyl group is attached to the 3rd carbon atom, yielding the “3-ethyl” part of the name, and methyl groups are attached to the 2nd and 5th carbon atoms, which gives the “2,5-dimethyl” part of the name.

The names discussed above are **systematic names**, which are based upon the actual structural formulas of the molecules. In addition, there are **common names** of organic compounds that do not indicate the structural formulas. Naming organic compounds is a complex topic, and no attempt is made here to teach it to the reader. However, from the names of compounds given in this and later chapters, some appreciation of the rationale for organic compound names should be obtained.

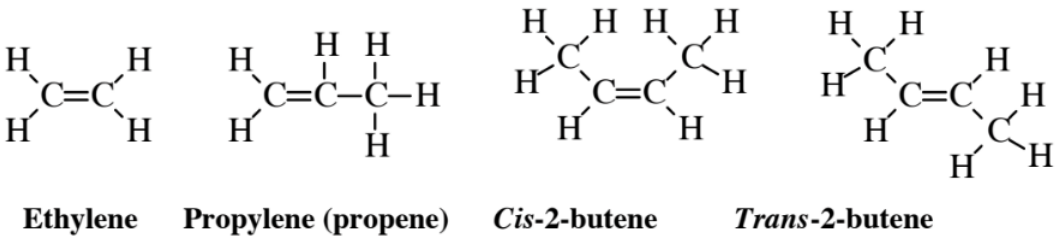
Other than burning them for energy, the major kind of reaction with alkanes consists of **substitution reactions** such as,

$$C_2H_6 + 2\,Cl_2 \rightarrow C_2H_4Cl_2 + 2\,HCl \tag{6.2.2}$$

in which one or more H atoms are displaced by another kind of atom. This is normally the first step in converting alkanes to compounds containing elements other than carbon or hydrogen for use in synthesizing a wide variety of organic compounds.

Alkenes

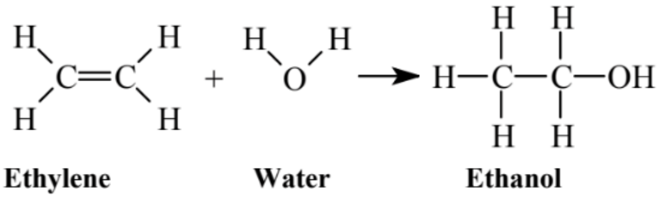
Four common alkenes are shown in Figure 6.2. Alkenes have at least one C=C double bond per molecule and may have more. The first of the alkenes in Figure 6.2, ethylene, is a very widely produced hydrocarbon used to synthesize polyethylene plastic and other organic compounds. About 25 billion kilograms (kg) of ethylene are processed in the U.S. each year. About 14.5 billion kg of propylene are used in the U.S. each year to produce polypropylene plastic and other chemicals. The two 2-butene compounds illustrate an important aspect of alkenes, the possibility of ***cis*-*trans*** isomerism. Whereas carbon atoms and the groups substituted onto them joined by single bonds can freely rotate relative to each other as though they were joined by a single shaft, carbon atoms connected by a double bond behave as though they were attached by two parallel shafts and are not free to rotate. So, *cis*-2-butene in which the two end methyl (-CH3) groups are on the same side of the molecule is a different compound from *trans*-2-butene in which they are on opposite sides. These two compounds are *cis*-*trans* isomers



Ethylene **Propylene (propene)** ***Cis*-2-butene** ***Trans*-2-butene**

Figure 6.2. Examples of alkene hydrocarbons

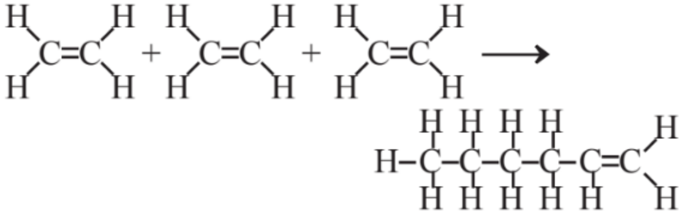
Alkenes are chemically much more active than alkanes. This is because the double bond is **unsaturated** and has electrons available to form additional bonds with other atoms. This leads to **addition reactions** in which a molecule is added across a double bond. For example, the addition of H_2O to ethylene



(6.2.3)

yields ethanol, the same kind of alcohol that is in alcoholic beverages. In addition to adding immensely to the chemical versatility of alkenes, addition reactions make them quite reactive in the atmosphere during the formation of photochemical smog. The presence of double bonds also adds to the biochemical and toxicological activity of compounds in organisms

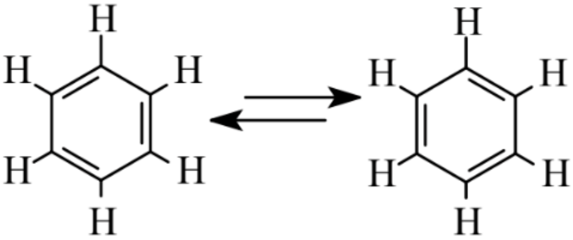
Because of their double bonds, alkenes can undergo **polymerization** reactions in which large numbers of individual molecules add to each other to produce big molecules called **polymers** (see Section 6.5). For example, 3 ethylene molecules can add together as follows:



a process that can continue, forming longer and longer chains and resulting in the formation of huge molecules molecules of polyethylene

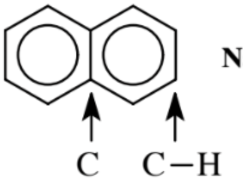
Aromatic Hydrocarbons

A special class of hydrocarbons consists of rings of carbon atoms, almost always containing 6C atoms, which can be viewed as having alternating single and double bonds as shown below:



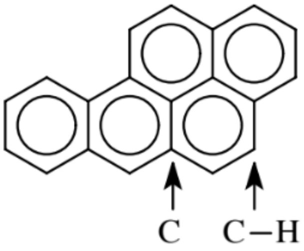
These structures show the simplest aromatic hydrocarbon, benzene, C6H6. Although the benzene molecule is represented with 3 double bonds, chemically it differs greatly from alkenes, for example undergoing substitution reactions rather than addition reactions. The properties of aromatic compounds are special properties called **aromaticity**. The two structures shown above are equivalent **resonance** structures, which can be viewed as having atoms that stay in the same places, but in which the bonds joining the atoms can shift positions with the movement of electrons composing the bonds. Since benzene has different chemical properties from those implied by either of the above structures, it is commonly represented as a hexagon with a circle in the middle:

Many aromatic hydrocarbons have two or more rings. The simplest of these is naphthalene,



Naphthalene, $C_{10}H_8$

a two-ringed compound in which two benzene rings share the carbon atoms at which they are joined; these two carbon atoms do not have any H attached, each of the other 8 C atoms in the compound has 1 H attached. Aromatic hydrocarbons with multiple rings, called **polycyclic aromatic hydrocarbons**, PAH, are common and are often produced as byproducts of combustion. One of the most studied of these is benzo(a)pyrene,



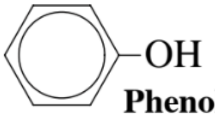
Benzo(a)pyrene, $C_{20}H_{12}$

found in tobacco smoke, diesel exhaust, and charbroiled meat. This compound is toxicologically significant because it is partially oxidized by enzymes in the body to produce a cancer-causing metabolite.

The presence of hydrocarbon groups and of elements other than carbon and hydrogen bonded to an aromatic hydrocarbon ring gives a variety of **aromatic compounds**. Three examples of common aromatic compounds are given below. Toluene is widely used for chemical synthesis and as a solvent. The practice of green chemistry now calls for substituting toluene for benzene wherever possible because benzene is suspected of causing leukemia, whereas the body is capableof metabolizing toluene to harmless metabolites (see Chapter 7). About 850 million kg of aniline are made in the U.S. each year as an intermediate in the synthesis of dyes and other organic chemicals. Phenol is a relatively toxic oxygen-containing aromatic compound which, despite its toxicity to humans, was the first antiseptic used in the 1800s.

Toluene

Aniline



Phenol

6.3: Using Lines To Show Organic Structural Formulas

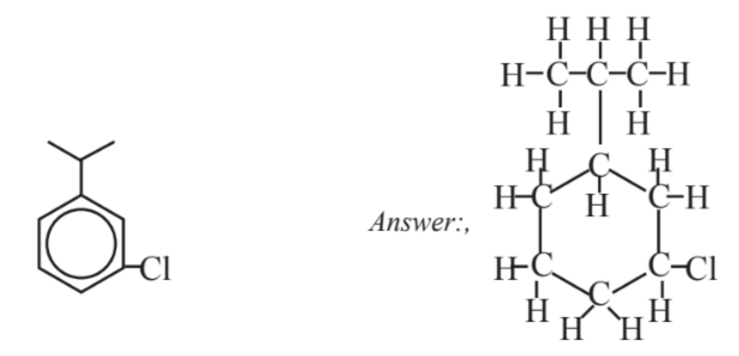
The aromatic structures shown above use a hexagon with a circle in it to denote an aromatic benzene ring. Organic chemistry uses lines to show other kinds of structural formulas as well. The reader who may have occasion to look up organic formulas will probably run into this kind of notation, so it is important to be able to interpret these kinds of formulas. Some line formulas are shown in Figure 6.3.

In using lines to represent organic structural formulas, the corners where lines intersect and the ends of lines represent C atoms, and each line stands for a covalent bond (2 shared electrons). It is understood that each C atom at the end of a single line has 3 H atoms attached, each C atom at the intersection of 2 lines has 2 C atoms attached, each C at the intersection of 3 lines has 1 H attached, and the intersection of 4 lines denotes a C atom with no H atoms attached. Multiple lines represent multiple bonds as shown for the double bonds in 1,3-butadiene. Substituent groups are shown by their symbols (for individual atoms), or formulas of functional groups consisting of groups of atoms; it is understood that each such group substitutes for a hydrogen atom as shown in the formula of 2,3-dichlorobutane in Figure 6.3. The 6-carbon-atom aromatic ring is denoted by a hexagon with a circle in it.

Exercise

What is the structural formula of the compound represented on the left, below?

Answer



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6.4: Functional Groups

Numerous elements in addition to carbon and hydrogen occur in organic compounds. These are contained in **functional groups**, which define various classes of organic compounds. The $-NH_2$ group in aniline and the -OH groups in phenol mentioned above are examples of functional groups. The same organic compound may contain two or more functional groups. Among the elements common in functional groups are O, N, Cl, S, and P. There is not space here to discuss all the possible functional groups and the classes of organic compounds that they define. Some important examples are given to provide an idea of the variety of organic compounds with various functional groups. Other examples are encountered later in the text

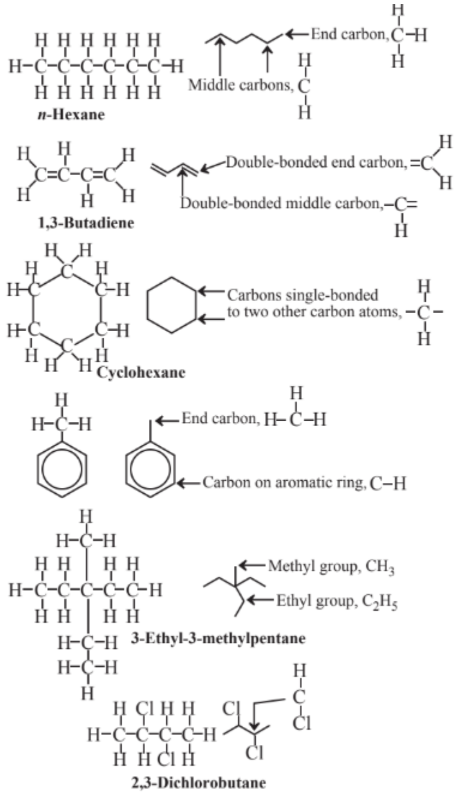
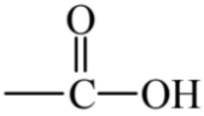


Figure 6.3. Representation of organic structural formulas with lines. The structural formulas showing the atoms are on the left and the corresponding line formulas on the right. Each line corner and end represents a carbon atom unless otherwise specified. Each C atom has four covalent bonds or equivalent attached and the presence of H atoms is implied to provide the required bonds.

In using lines to represent organic structural formulas, the corners where lines intersect and the ends of lines represent C atoms, and each line stands for a covalent bond (2 shared electrons). It is understood that each C atom at the end of a single line has 3 H atoms attached, each C atom a the intersection of 2 lines has 2 C atoms attached, each C at the intersection of 3 lines has 1 H attached, and the intersection of 4 lines denotes a C atom with no H atoms attached. Multiple lines

Organooxygen Compounds

Figure 6.4 shows several important classes of organic compounds that contain oxygen. **Ethylene oxide** is a sweet-smelling, colorless, flammable, explosive gas. It is an **epoxide** characterized by an oxygen atom bridging two carbon atoms that are also bonded with each other. Ethylene oxide is toxic and is used as a sterilant and fumigant as well as a chemical intermediate. Because of the toxicity and flammability of this compound, the practice of green chemistry tries to avoid its generation and use. **Ethanol**, which occurs in alcoholic beverages, is an **alcohol**, a class of compound in which the -OH group is bonded to an alkane or alkene (attachment of the -OH group to an aromatic hydrocarbon molecule gives a **phenolic** compound). **Acetone** is a ketone, a class of compounds that has the C=O functional group in the middle of a hydrocarbon chain. Acetone is an excellent organic solvent and relatively safe. **Butyric** acid, which occurs in butter, is an organic carboxylic acid, all of which contain the functional group,



$$-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

which can release the H+ion characteristic of acids. **Methyltertiarybutyl ether**, MTBE, is an example of an ether in which an O atom connects 2 C atoms. When highly toxic tetraethyllead was phased out of gasoline as an octane booster, MTBE was chosen as a substitute. It was subsequently found to be a particularly noxious water pollutant, and its use has been largely banned

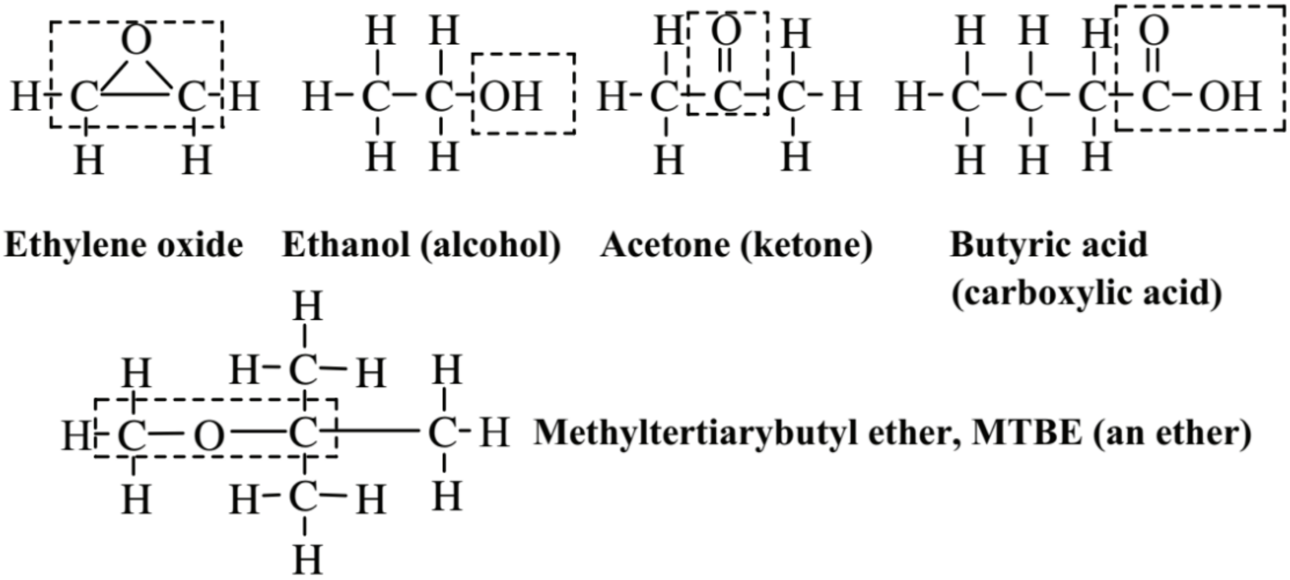
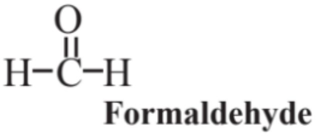
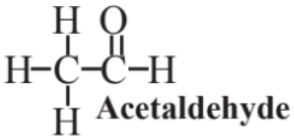


Figure 6.4. Examples of important classes of organic compound with oxygen-containing functional groups. The functional groups characteristic of various classes of compounds are outlined by dashed lines.

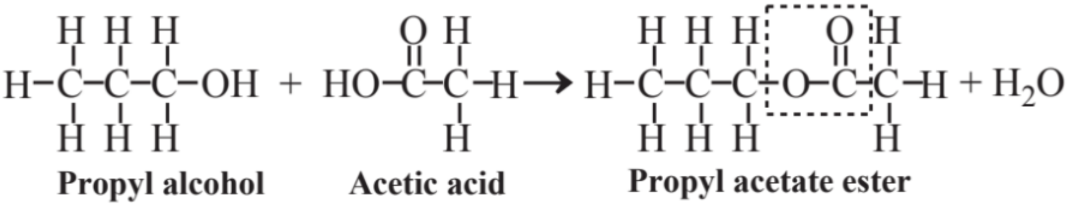
The C=O group in the middle of an organic molecule is characteristic of ketones. When this group is located at the end of a molecule and the carbon is also bonded to H, the compound is an **aldehyde**. The two lowest aldehydes are formaldehyde and acetaldehyde,





of which formaldehyde is the most widely produced. Despite its many uses, formaldehyde lacks characteristics of green chemicals because it is a volatile, toxic, noxious substance. Formaldehyde tends to induce hypersensitivity (allergies) in people who inhale the vapor or whose skin is exposed to it.

The reaction of an alcohol and an organic acid,

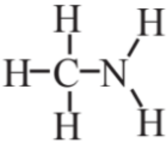


(6.4.1)

produces an important kind of organic compound called **esters**. The linkage characteristic of esters is outlined by the dashed box in the structure of propyl acetate above. A large number of the naturally-occurring esters made by plants are noted for their pleasant odors. Propyl acetate, for example gives pears their pleasant odor. Other fruit odors due to esters include methyl butyrate, apple; ethyl butyrate, pineapple; and methyl benzoate, ripe kiwi fruit.

Organonitrogen Compounds

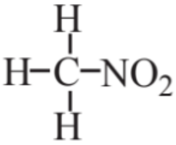
Methylamine,



Methylamine

is the simplest of the amines, compounds in which an N atom is bonded to a hydrocarbon group. In an amine, the N atom may be bonded to 2 H atoms, or one or both of these H atoms may be substituted by hydrocarbon groups as well. Although it is widely used in chemical synthesis because no suitable substitutes are available, methylamine is definitely not compatible with the practice of green chemistry. That is because it is highly flammable and toxic. It is a severe irritant to skin, eyes, and mucous membranes of the respiratory tract. It has a noxious odor and is a significant contributor to the odor of rotten fish. In keeping with the reputation of amines as generally unpleasant compounds, another amine, putrescine, gives decayed flesh its characteristic odor.

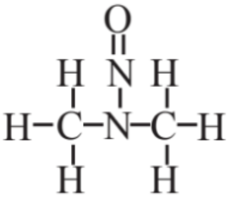
Many organonitrogen compounds contain oxygen as well. One such compound is nitromethane



$$H-\overset{H}{\underset{H}{C}}-NO_2$$

Nitromethane

used in chemical synthesis and as a fuel in some race cars. As seen in the structural formula above, the nitro group, -NO_2, is the functional group in this compound and related nitro compounds. Another class of organonitrogen compounds also containing oxygen consists of the **nitrosamines**, or N-nitroso compounds, which have figured prominently in the history of green chemistry before it was defined as such. These are compounds that have the N-N=O functional group, which are of concern because several are known carcinogens (cancer-causing agents). The most well known of these is **dimethylnitrosamine** shown below:



$$H-\overset{H}{\underset{H}{C}}-\overset{\overset{O}{\|}}{N}-\overset{H}{\underset{H}{C}}-H$$

Dimethylnitrosamine

This compound used to be employed as an industrial solvent and was used in cutting oils. However, workers exposed to it suffered liver damage and developed jaundice, and the compound as well as other nitrosamines was found to be a carcinogen. A number of other nitrosamines were later found in industrial materials and as byproducts of food processing and preservation. Because of their potential as carcinogens, nitrosamines are avoided in the practice of green chemistry.

Organohalide Compounds

Organohalides exemplified by those shown in Figure 6.5 are organic compounds that contain halogens — F, Cl, Br, or I — but usually chlorine, on alkane, alkene, or aromatic molecules. Organohalides have been widely produced and distributed for a variety of applications, including industrial solvents, chemical intermediates, coolant fluids, pesticides, and other applications. They are for the most part environmentally persistent and, because of their tendency to accumulate in adipose (fat) tissue, they tend to undergo bioaccumulation and biomagnification in organisms

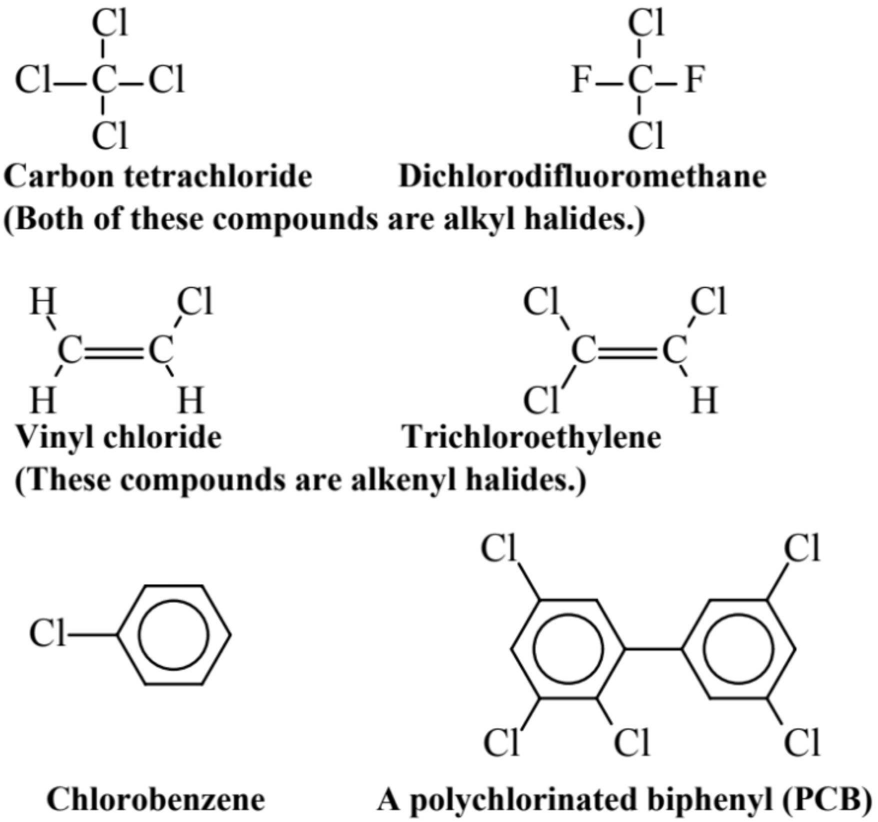


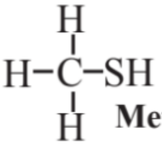
Figure 6.5. Examples of important organohalide compounds including alkyl halides based upon alkanes, alkenyl halides based upon alkenes, and aromatic halides

Carbon tetrachloride is produced when all four H atoms on methane, CH_4, are substituted by Cl. This compound was once widely used and was even sold to the public as a solvent to remove stains and in fire extinguishers, where the heavy CCl_4 vapor smothers fires. It was subsequently found to be very toxic, causing severe liver damage, and its uses are severely restricted. **Dichlorodifluoromethane**is a prominent member of the **chlorofluorocarbon** class of compounds, popularly known as Freons. Developed as refrigerant fluids, these compounds are notably unreactive and nontoxic. However, as discussed in Chapter 10, they were found to be indestructible in the lower atmosphere, persisting to very high altitudes in the stratosphere where chlorine split from them by ultraviolet radiation destroys stratospheric ozone. So the manufacture of chlorofluorocarbons is now prohibited. **Vinyl chloride**, an alkene-based organohalide compound, is widely used to make polyvinylchloride polymers and pipe. Unfortunately, it is a known human carcinogen, so human exposure to it is severely limited. **Trichloroethylene** is an excellent organic solvent that is nonflammable. It is used as a dry cleaning solvent and for degreasing manufactured parts, and was formerly used for food extraction, particularly to decaffeinate coffee. **Chlorobenzene** is the simplest aromatic organochloride. In addition to its uses in making other chemicals, it serves as a solvent and as a fluid for heat transfer. It is extremely stable, and its destruction is a common test for the effectiveness of hazardous waste incinerators. The **polychlorinated biphenyl**(**PCB**) compound shown is one of 209 PCB compounds that can be formed by substituting from 1 to 10 Cl atoms onto the basic biphenyl (two-benzene-ring) carbon skeleton. These compounds are notably stable and persistent, leading to their uses in electrical equipment, particularly as coolants in transformers and in industrial capacitors, as hydraulic fluids, and other applications. Their extreme environmental persistence has led to their being banned. Sediments in New York's Hudson River are badly contaminated with PCBs that were (at the time, legally) dumped or leaked into the river from electrical equipment manufacture from the 1950s into the 1970s.

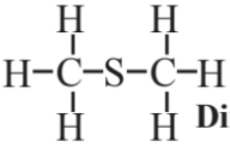
From the discussion above, it is obvious that many organohalide compounds are definitely not green because of their persistence and biological effects. A lot of the effort in the development of green chemistry has been devoted to finding substitutes for organohalide compounds. A 2001 United Nations treaty formulated by approximately 90 nations in Stockholm, Sweden, designated a "dirty dozen" of 12 organohalide compounds of special concern as persistent organic pollutants(POP); other compounds have subsequently been added to this list.

Organosulfur and Organophosphorus Compounds

A number of organosulfur and organophosphorus compounds have been synthesized for various purposes including pesticidal applications. A common class of organosulfur compounds consists of the thiols, the simplest of which is methanethiol:



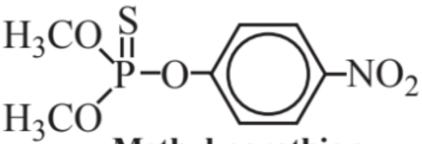
Methanethiol



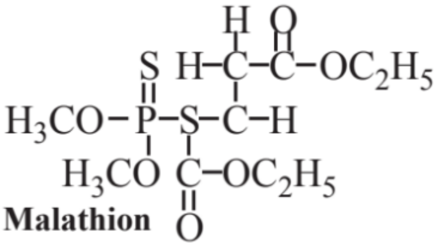
Dimethylsulfide

As with other thiols, which contain the -SH group, this compound is noted for its foul odor. Thiols are added to natural gas so that their odor can warn of gas leaks. Dimethylsulfide, also shown above, is a volatile compound released by ocean-dwelling microorganisms to the atmosphere in such quantities that it constitutes the largest flux of sulfur-containing vapors from Earth to the atmosphere.

Among the most prominent organophosphorus compounds are the organophosphates as shown by methyl parathion and malathion (below). These compounds are both insecticides and contain sulfur as well as phosphorus. Parathion was developed during the 1940s and was once widely used as an insecticide in place of DDT because parathion is very biodegradable, whereas DDT is not and undergoes bioaccumulation and biomagnification in ecosystems. Unfortunately, parathion has a high toxicity to humans and other animals and some human fatalities have resulted from exposure to it. Like other organophosphates, it inhibits acetylcholinesterase, an enzyme essential for nerve function (the same mode of action as its deadly cousins, the “nerve gas” military poisons, such as Sarin). Because of its toxicity, parathion is now banned from general use. Malathion is used in its place and is only about 1/100 as toxic as parathion to mammals because they — though not insects — have enzyme systems that can break it down.



Methyl parathion



Malathion

6.5: Giant Molecules from Small Organic Molecules

Reaction 6.2.4 showed the bonding together of molecules of ethylene to form larger molecules. This process, widely practiced in the chemical and petrochemical industries, is called *polymerization* and the products are *polymers*. Many other unsaturated molecules, usually based upon alkenes, undergo polymerization to produce synthetic polymers used as plastics, rubber, and fabrics. As an example, tetrafluoroethylene polymerizes as shown in Figure 6.6 to produce a polymer (Teflon) that is exceptionally heat- and chemical-resistant and that can be used to form coatings to which other materials will not stick (for example, frying pan surfaces).

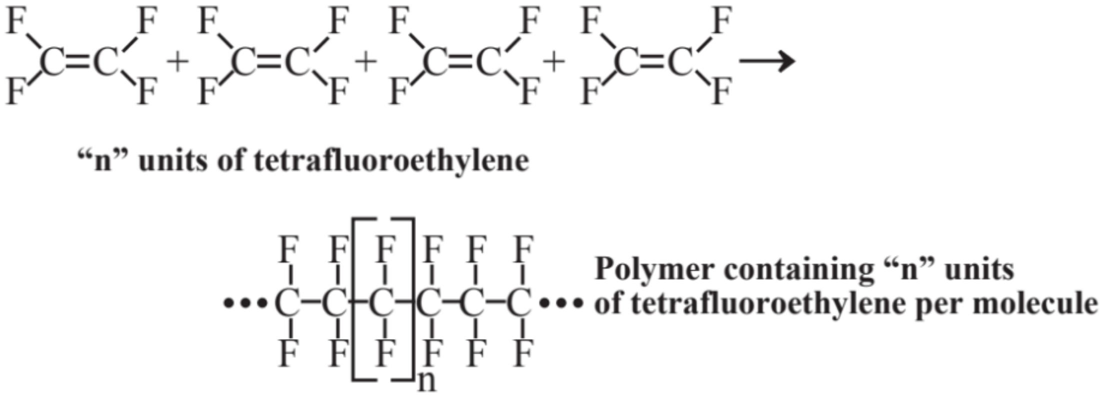
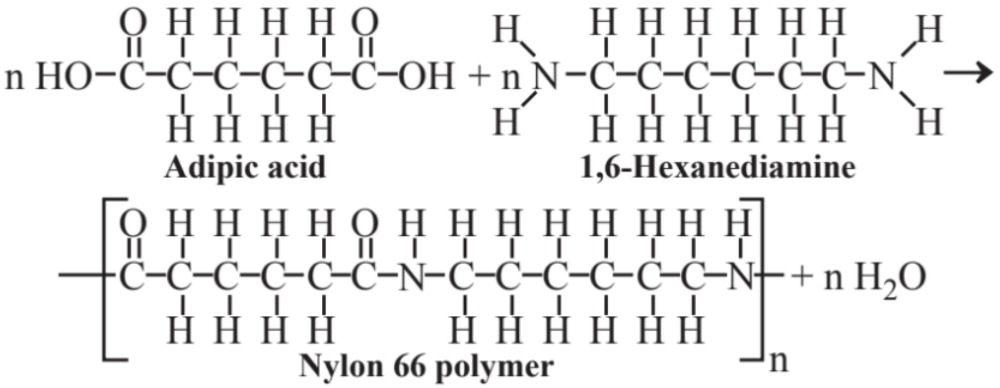


Figure 6.6. Polymerization of tetrafluoroethylene to produce large molecules of a polymer commonly known as Teflon

Polyethylene and polytetrafluoroethylene are both **addition polymers** in that they are formed by the chemical addition together of the monomers making up the large polymer molecules. Other polymers are **condensation polymers** that join together with the elimination of a molecule of water for each monomer unit joined. A common condensation polymer is **nylon**, which is formed by the bonding together of two different kinds of molecules. There are several forms of nylon, the original form of which is nylon 66 discovered by Wallace Carothers, a DuPont chemist, in 1937 and made by the polymerization of adipic acid and 1,6-hexanediamine:

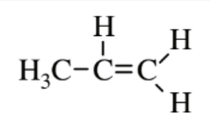
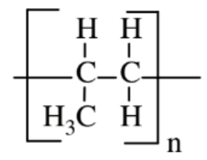
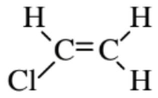
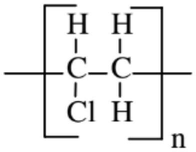
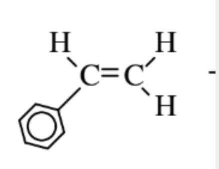
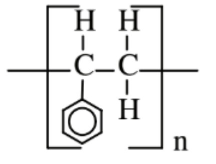
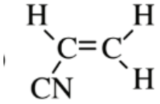
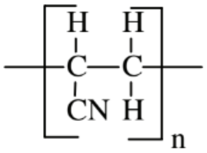
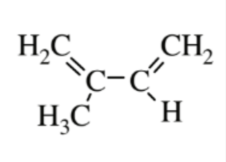
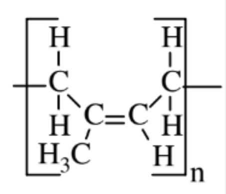


(6.5.1)

There are many different kinds of synthetic polymers that are used for a variety of purposes. Some examples in addition to the ones already discussed in this chapter are given in Table 6.1.

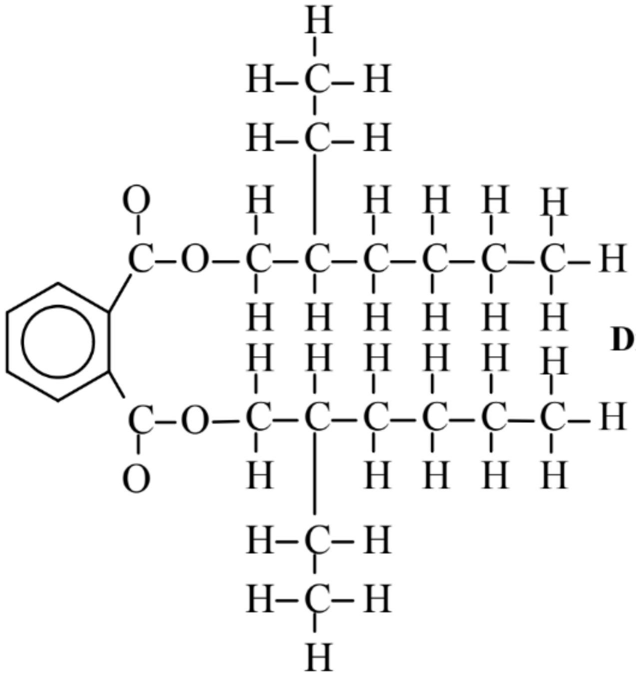
Polymers and the industries upon which they are based are of particular concern in the practice of green chemistry for a number of reasons. The foremost of these is because of the huge quantities of materials consumed in the manufacture of polymers. In addition to the enormous quantities of ethylene and propylene previously cited in this chapter, the U.S. processes about 1.5 billion kg of acrylonitrile, 5.4 billion kg of styrene, 2.0 billion kg of butadiene, and 1.9 kg of adipic acid (for nylon 66) each year to make polymers containing these monomers. These and similarly large quantities of monomers used to make other polymers place significant demands upon petroleum resources and the energy, materials, and facilities required to make the monomers.

Table 6.1. Some Typical Polymers and the Monomers from Which they Are Formed

Monomer	Monomer Formula	Polymer	Applications
Propylene (polypropylene)			Applications requiring harder plastic, luggage, bottles, outdoor carpet
Vinyl chloride (polyvinyl chloride)			Thin plastic wrap, hose, flooring, PVC pipe
Styrene (polystyrene)			Plastic furniture, plastic cups and dishes, blown to produce styrofoam plastic products
Acrylonitrile (polyacrylonitrile)			Synthetic fabrics (Orlon, Acrilan, Creslan), acrylic paints
Isoprene (polyisoprene)			Natural rubber

There is a significant potential for the production of pollutants and wastes from monomer processing and polymer manufacture. Some of the materials contained in documented hazardous waste sites are byproducts of polymer manufacture. Monomers are generally volatile organic compounds with a tendency to evaporate into the atmosphere, and this characteristic combined with the presence of reactive C=C bonds tends to make monomer emissions active in the formation of photochemical smog (see Chapter 10). Polymers, including plastics and rubber, pose problems for waste disposal, as well as opportunities and challenges for recycling. On the positive side, improved polymers can provide long-lasting materials that reduce material use and have special applications, such as liners in waste disposal sites that prevent waste leachate migration and liners in lagoons and ditches that prevent water loss. Strong, lightweight polymers are key components of the blades and other structural components of huge wind generators that are making an increased contribution to renewable energy supplies around the world (see Chapter 16).

Some of the environmental and toxicological problems with polymers have arisen from the use of additives to improve polymer performance and durability. The most notable of these are **plasticizers**, normally blended with plastics to improve flexibility, such as to give polyvinylchloride the flexible characteristics of leather. The plasticizers are not chemically bound as part of the polymer and they leak from the polymer over a period of time, which can result in human exposure and environmental contamination. The most widely used plasticizers are phthalates, esters of phthalic acid as shown by the example of di(2-ethylhexyl) phthalate below. Though not particularly toxic, these compounds are environmentally persistent, resistant to treatment processes, and prone to undergo bioaccumulation. They are found throughout the environment and have been implicated by some toxicologists as possible estrogenic agents that mimic the action of female sex hormone and cause premature sexual development in young female children.



Di(2-ethylhexyl) phthalate

Questions and Problems

Access to and use of the internet is assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several “right” answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be “right.”

1. What are two major reactions of alkanes?

2. What is the difference between molecular formulas and structural formulas of organic compounds?

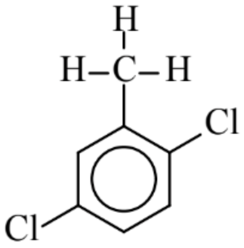
3. What is the difference between ethane and the ethyl group?

4. What is the structural formula of 3-ethyl-2,3-dimethylpentane?

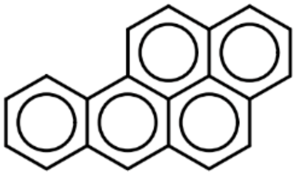
5. What is a type of reaction that is possible with alkenes, but not with alkanes?

6. What is represented by the structure below?

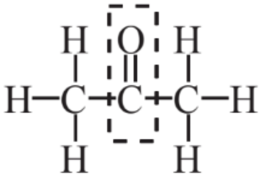
7. Suggest a name for the compound below, which is derived from the hydrocarbon toluene



8. What is a health concern with the aromatic compound below:



9. What do the groups of atoms outlined by dashed lines represent in the structure below?



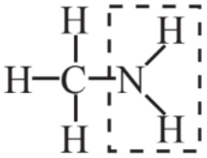


Figure 6.4, what are the similarities and differences between organic oxides and ethers.

11. What are 3 separate kinds of groups characteristic of organonitrogen compounds?

12. What is a class of organochlorine compounds consisting of many different kinds of molecules that is noted for environmental persistence?

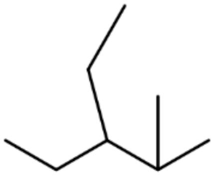
13. What is a notable characteristic of organosulfur thiols?

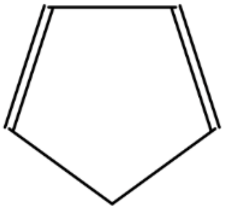
14. What is a particularly toxic organophosphorus compound? What is a biochemical molecule containing phosphorus?

15. What are polymers and why are they important?

16. Examination of the formulas of many of the monomers used to make polymers reveals a common characteristic. What is this characteristic and how does it enable polymer formation? Does nylon illustrate a different pathway to monomer formation? Explain.

17. Write the complete structural formulas corresponding to each of the line structures below:


(A)


(B)

18. Some of the most troublesome organic pollutant compounds are organochlorine compounds including the “dirty dozen” persistent organic pollutants mentioned in this chapter. Organohalides involving a halogen other than chlorine are emerging as significant pollutants. Doing some research on the internet, find which class of compounds these are and why they are significant pollutants.

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CHAPTER OVERVIEW

7: Chemistry of Life and Green Chemistry

“A microscopic cell of photosynthetic cyanobacteria constitutes a complex of chemical factories that carry out a multitude of biochemical processes. Powered by solar energy and operating under ambient conditions, these organisms take carbon dioxide and nitrogen from air and simple inorganic ions dissolved in water and make all the life molecules they need for their metabolism and reproduction. In eons past these kinds of organisms generated all of the oxygen that is in Earth’s atmosphere. For all their knowledge of chemistry it would be impossible for humans to reproduce the chemical processes of these remarkable bacteria”

7.1: Green Biochemistry
7.2: Biochemistry and the Cells
7.3: Carbohydrates
7.4: Proteins
7.5: Lipids - Fats, Oils, and Hormones
7.6: Nucleic Acids
7.7: Enzymes
7.8: Biochemical Processes in Metabolism
7.9: Biochemistry of Toxic Substances and Toxicological Chemistry
Literature Cited
Questions and Problems
Supplementary References

7.1: Green Biochemistry

Biochemistry is the science of chemical processes that occur in living organisms.[1] By its nature biochemistry is a green chemical and biological science. This is because over eons of evolution organisms have evolved that carry out biochemical processes sustainably. Because the enzymes that carry out biochemical processes can only function under mild conditions, particularly of temperature, biochemical processes take place under safe conditions, avoiding the high temperatures, high pressures, and corrosive and reactive chemicals that often characterize synthetic chemical operations. Therefore, it is appropriate to refer to **green biochemistry**.

The ability of organisms to carry out chemical processes is truly amazing, even more so when one considers that many of them occur in single-celled organisms. Photosynthetic cyanobacteria consisting of individual cells less than a micrometer (μm) in size can make all the complex biochemicals they need to exist and reproduce using sunlight for energy and simple inorganic substances such as CO_2, K^+ ion, NO_3^- ion and HPO_4^{2-} ion for raw materials. Beginning soon after conditions on Earth became hospitable to life, these photosynthetic bacteria produced the oxygen that now composes about 20% of Earth's atmosphere. Fossilized stromatolites (bodies of sedimentary materials bound together by films produced by microorganisms) produced by cyanobacteria have been demonstrated dating back 2.8 billion years, and this remarkable microorganism that converts atmospheric carbon dioxide to biomass and atmospheric N_2 to chemically fixed N may have been on Earth as long as 3.5 billion years ago.

It is fascinating to view single live cells of animal-like protozoa through an optical microscope. An ameba appears as a body of cellular protoplasm and moves by oozing about like a living blob of jelly. Examination of *Euglena* protozoa may show a cell several μm in size with many features including a cell nucleus that serves to direct metabolism and reproduction, green chloroplasts for photosynthetic production of biomass, a red eye-spot sensitive to light, a mouth-like contractile vacuole by which the cell expels excess water, and a thin tail-like structure(flagella) that moves rapidly and propels the cell. More detailed examination by electron microscope of such cells and those that make up more complex organisms reveals many more cell parts that are involved with biochemical function.

At least a rudimentary knowledge of biochemistry is needed to understand green chemistry, environmental chemistry, and sustainability science and technology. One reason is the ability of organisms to synthesize a vast variety of substances. The most obvious of these is biomass made by the photosynthetic fixation of carbon dioxide and that forms the basis of nature's food webs.Organisms make many of the materials upon which humans rely. In addition to food, one such material is the lignocellulose that composes most of plant biomass such as wood used for construction, paper-making, and fuel. Very complex molecules are made by organisms, for example, human insulin produced by genetically engineered organisms. Organisms make materials under very mild conditions compared to those used in the anthrosphere. An important example is chemically fixed nitrogen from the atmosphere which is produced synthetically in the anthrosphere as ammonia (NH_3) at high temperatures and pressures whereas *Rhizobium* bacteria attached to the roots of soybeans and other legume plants fix nitrogen in the mild conditions of the soil environment. Increasingly as supplies of petroleum and other non-renewable raw materials become more scarce, humans are turning to microorganisms and plants to make essential materials.

Another major reason for considering biochemistry as part of green chemistry and sustainability is the protection of organisms from products and processes in the anthrosphere. It is essential to know the potential toxic effects of various materials, a subject addressed by **toxicological chemistry**.[2] One of the fundamental goals of green chemistry is to minimize the production and use of products that may have adverse environmental effects. Sustainability of the entire planet requires that humans not disperse into the environment substances that may undergo bioaccumulation and be toxic to humans and other organisms.

Biochemical processes not only are profoundly influenced by chemical species in the environment, they largely determine the nature of these species, their degradation, and even their syntheses, particularly in the aquatic and soil environments. The study of such phenomena forms the basis of **environmental biochemistry.**

This chapter is designed to give an overview of biochemistry and how it relates to green chemistry and sustainability science and technology. A glance at the structural formulas of some of the biochemicals shown in this chapter gives a hint of the complexity of biochemistry. This chapter is designed to provide a basic understanding of this complex science with enough detail for it to be meaningful but to avoid overwhelming the reader. It begins with an overview of the four major classes of biochemicals— proteins, carbohydrates, lipids, and nucleic acids. Many of the compounds in these classes are polymers with molecular masses of the order of a million or even larger. Proteins and nucleic acids consist of macromolecules, lipids are usually relatively small molecules, carbohydrates range from small sugar molecules to high-molar-mass macromolecules such as those in cellulose.

The behavior of a substance in a biological system depends to a large extent upon whether the substance is hydrophilic ("water-loving") or hydrophobic ("water-hating"). Some important toxic substances are hydrophobic, a characteristic that enables them to traverse cell membranes readily and to bioaccumulate in lipid (fat) tissue. Many hydrocarbons and organohalide compounds synthesized from hydrocarbons are hydrophobic. Part of the detoxification process carried on by living organisms is to render such molecules hydrophilic, therefore water-soluble and readily eliminated from the body.

7.2: Biochemistry and the Cells

For the most part, biochemical processes occur within cells, the very small units of which living organism are composed.[3] Cells are discussed in more detail as basic units of life in Chapter 12, Section 12.3; here they are regarded as what chemical engineers would call “unit operations” for carrying out biochemical processes. Many organisms consist of single cells or individual cells growing together in colonies. Bacteria, yeasts, protozoa, and some algae consist of single cells. Other than these microorganisms, organisms are composed of many cells that have different functions. Liver cells, muscle cells, brain cells, and skin cells in the human body are quite different from each other and do different things. Two major kinds of cells are **eukaryotic** cells which have a nucleus and **prokaryotic** cells which do not. Prokaryotic cells are found predominately in single-celled bacteria. Eukaryotic cells occur in multicellular plants and animals — higher life forms.

Cell structure has an important influence on determining the nature of biomaterials. Muscle cells consist largely of strong structural proteins capable of contracting and movement. Bone cells secrete a protein mixture that then mineralizes with calcium and phosphate to produce solid bone.The walls of cells in plants are largely composed of strong cellulose, which makes up the sturdy structure of wood.

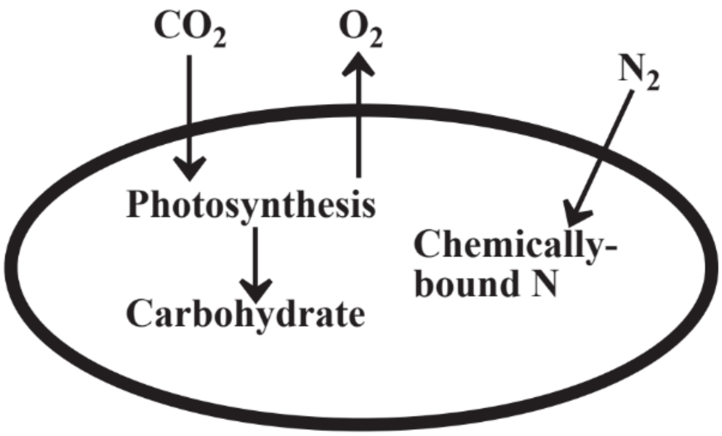


Figure 7.1. Cyanobacteria are remarkable organisms that within a single “simple” prokaryotic cell carry out all the biochemical processes needed to convert atmospheric carbon dioxide to carbohydrate and biomass and that can split the chemically very stable atmospheric nitrogen molecule and convert the nitrogen to chemically and biochemically bound nitrogen

7.3: Carbohydrates

Carbohydrates are biomolecules consisting of carbon, hydrogen, and oxygen having the approximate simple formula CH_2O. One of the most common carbohydrates is the simple sugar glucose shown in Figure 7.2. Units of glucose and other simple sugars called **monosaccharides** join together in chains with the loss of a water molecule for each linkage to produce macromolecular **polysaccharides**. These include **starch** and **cellulose** in plants and starch-like glycogen in animals.

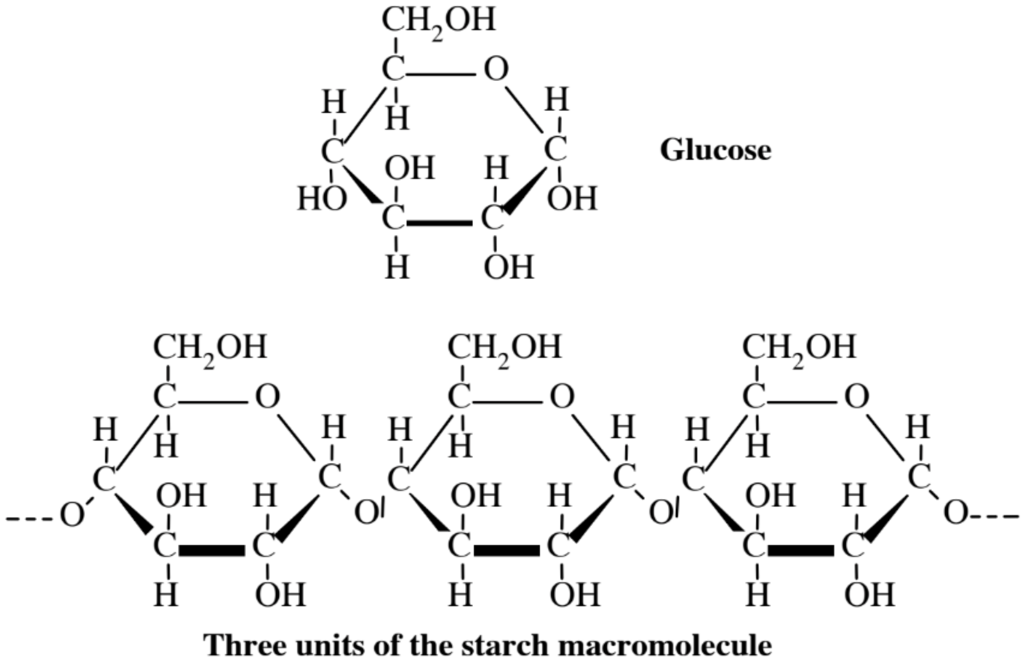


Figure 7.2. Glucose, a monosaccharide, or simple sugar, and a segment of the starch molecule, which is formed when glucose molecules polymerize with the elimination of one H_2O molecule per glucose monomer.

Glucose carbohydrate is the biological material generated from water and carbon dioxide when solar energy in sunlight is utilized in photosynthesis. The overall reaction is

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{7.3.1}$$

This is obviously an extremely important reaction because it is the one by which inorganic molecules are used to synthesize high-energy carbohydrate molecules that are in turn converted to the vast number of biomolecules that comprise living systems. There are other simple sugars, including fructose, mannose, and galactose, that have the same simple formula as glucose, $C_6H_{12}O_6$, but which must be converted to glucose before being utilized by organisms for energy. Common table sugar, sucrose, $C_{12}H_{22}O_{11}$, consists of a molecule of glucose and one of fructose linked together (with the loss of a water molecule); because it is composed of two simple sugars sucrose is called a **disaccharide**.

Starch molecules, which may consist of several hundred glucose units joined together, are readily broken down by organisms to produce simple sugars used for energy and to produce biomass. For example, humans readily digest starch in potatoes or bread to produce glucose used for energy (or to make fat tissue).

The chemical formula of starch is $(C_6H_{10}O_5)_n$, where n may represent a number as high as several hundreds. What this means is that the very large starch molecule consists of as many as several hundred units of $C_6H_{10}O_5$ from glucose joined together. For example, if n is 100, there are 6 times 100 carbon atoms, 10 times 100 hydrogen atoms, and 5 times 100 oxygen atoms in the molecule. Its chemical formula is $C_{600}H_{1000}O_{500}$. The atoms in a starch molecule are actually present as linked rings represented by the structure shown in Figure 7.2. Starch occurs in many foods, such as bread, potatoes, and cereals. It is readily digested by animals, including humans.

Cellulose is a polysaccharide which is also made up of $C_6H_{10}O_5$ units. Molecules of cellulose are huge, with molecular masses of around 400,000. The cellulose structure (Figure 7.3) is similar to that of starch. Cellulose is produced by plants and forms the structural material of plant cell walls. Wood is about 60% cellulose, and cotton contains over 90% of this material. Fibers of cellulose are extracted from wood and pressed together to make paper.

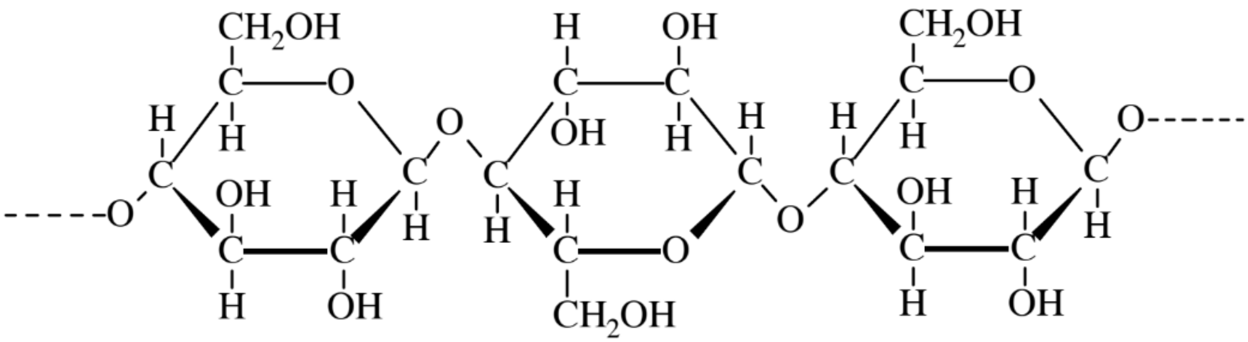


Figure 7.3. A segment of a cellulose molecule. These molecules are biosynthesized from glucose with the loss of one H_2O for each linkage formed

Humans and most other animals cannot digest cellulose because they lack the enzyme needed to hydrolyze the oxygen linkages between the glucose molecules. Ruminant animals (cattle, sheep, goats, moose) have bacteria in their stomachs that break down cellulose into products which can be used by the animal. Fungi and termites existing synergistically with cellulose-degrading bacteria biodegrade huge quantities of cellulose. Chemical processes are available to convert cellulose to simple sugars by the reaction

$$\underbrace{(\mathrm{C_6H_{10}O_5})_n}_{\textbf{cellulose}} + \mathrm{nH_2O} \rightarrow \underbrace{\mathrm{nC_6H_{12}O_6}}_{\textbf{glucose}} \tag{7.3.2}$$

where *n* may be 2000-3000. This involves breaking the linkages between units of $C_6H_{10}O_5$ by adding a molecule of H_2O at each linkage, a hydrolysis reaction. Large amounts of cellulose from wood, sugar cane, and agricultural products go to waste each year. The hydrolysis of cellulose enables these products to be converted to sugars, which can be fed to animals. The potential for producing very large quantities of glucose from cellulose have led to intense efforts to hydrolyze cellulose to glucose with enzymes (biological catalysts) and is an important effort in green chemistry.

Carbohydrates are potentially very important in green chemistry. For one thing, they are a concentrated form of organic energy synthesized and stored by plants as part of the process by which plants capture solar energy through photosynthesis. Carbohydrates can be utilized directly for energy or fermented to produce ethanol, C_2H_6O, a combustible alcohol that is added to gasoline or can even be used in place of gasoline. Secondly, carbohydrates are a source of organic raw material that can be converted to other organic molecules to make plastics and other useful materials.

7.4: Proteins

Proteins are macromolecules that are composed of nitrogen, carbon, hydrogen, and oxygen along with smaller quantities of sulfur. The small molecules of which proteins are made are composed of 20 naturally occurring **amino acids**. The simplest of these, glycine, is shown in the first structure in Figure 7.4, along with two other amino acids. As shown in Figure 7.4, amino acids join together with the loss of a molecule of H_2O for each linkage formed. The three amino acids in Figure 7.4 are shown linked together as they would be in a protein in the bottom structure in the figure. Many hundreds of amino acid units may be present in a protein molecule.

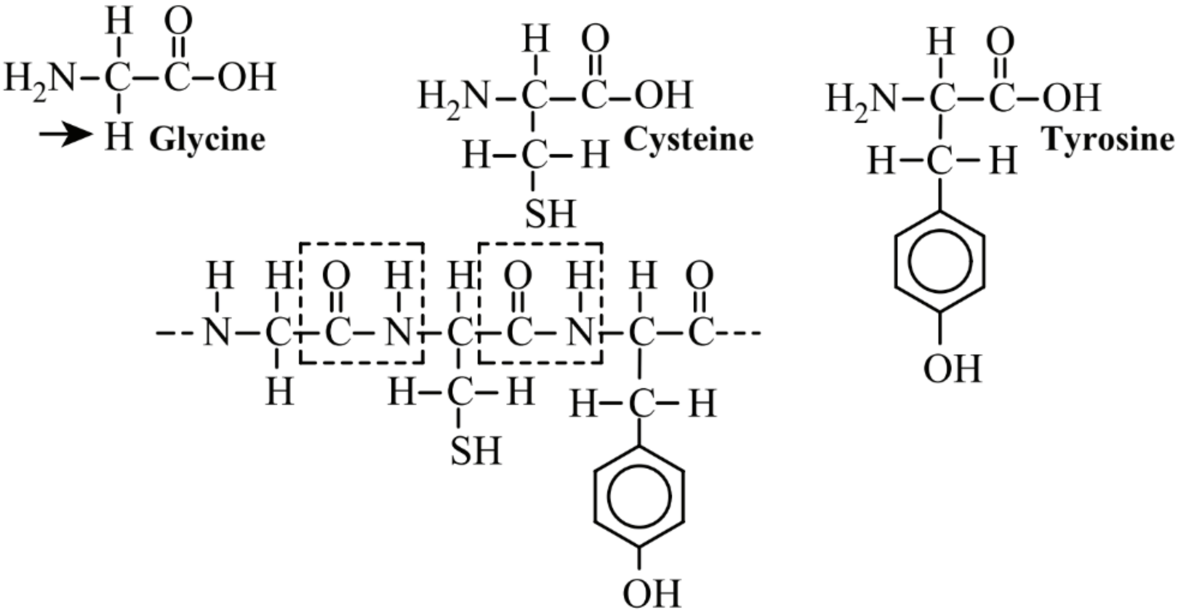


Figure 7.4. Three amino acids. Glycine is the simplest amino acid. All others have the basic glycine structure except that different groups are substituted for the H designated in glycine by an arrow. The lower structure shows these three amino acids linked together in a macromolecule chain composing a protein. For each linkage, one molecule of H_2O is lost. The peptide linkages holding amino acids together in proteins is outlined by a dashed rectangle.

The three-dimensional structures of protein molecules are of the utmost importance and largely determine what the proteins do in living systems and how they are recognized by other biomolecules. Enzymes, special proteins that act as catalysts to enable biochemical reactions to occur, recognize the substrates upon which they act by the complementary shapes of the enzyme molecules and substrate molecule. There are several levels of protein structure. The first of these is determined by the order of amino acids in the protein macromolecule. Folding of protein molecules and pairing of two different protein molecules further determine structure. The loss of protein structure, called **denaturation**, can be very damaging to proteins and to the organism in which they are contained.

Two major kinds of proteins are tough **fibrous proteins** that compose hair, tendons, muscles, feathers, and silk, and spherical or oblong-shaped **globular proteins**, such as hemoglobin in blood or the proteins that comprise enzymes. Proteins serve many functions. These include **nutrient proteins**, such as casein in milk, **structural proteins**, such as collagen in tendons, **contractile proteins**, such as those in muscle, and **regulatory proteins**, such as insulin, that regulate biochemical processes.

Proteins with carbohydrate groups attached constitute an important kind of biomolecule called **glycoproteins**. Collagen is a crucial glycoprotein that provides structural integrity to body parts. It is a major constituent of skin, bones, tendons, and cartilage.

Some proteins are very valuable biomaterials for pharmaceutical, nutritional, and other applications and their synthesis is an important aspect of green chemistry. The production of specific proteins has been greatly facilitated in recent years by the application of genetic engineering to transfer to bacteria the genes that direct the synthesis of specific proteins. The best example is insulin, a protein injected into diabetics to control blood sugar. Insulin injected for blood glucose control used to be isolated from the pancreas's of slaughtered cattle and hogs. Although this enabled many diabetics to live normal lives, the process of getting the insulin was cumbersome, supply was limited, and the insulin from this source was not exactly the same as that made in the human body, which often caused the body to have an allergic response to it as a foreign protein. The transfer through recombinant DNA technology of the human gene for insulin production into prolific *Escherichia coli* bacteria has enabled large-scale production of human insulin by the bacteria.

7.5: Lipids - Fats, Oils, and Hormones

Lipids differ from most other kinds of biomolecules in that they are repelled by water. Lipids can be extracted from biological matter by organic solvents, such as diethyl ether or toluene. Recall that proteins and carbohydrates are distinguished largely by chemically similar characteristics and structures. However, lipids have a variety of chemical structures that share the common physical characteristic of solubility in organic solvents. Many of the commonly encountered lipid fats and oils are esters of glycerol alcohol, $CH_2(OH)CH(OH)CH_2(OH)$, and long-chain carboxylic acids (fatty acids), such as stearic acid, $CH_3(CH_2)_{16}CO_2H$. The glycerol molecule has three -OH groups to each of which a fatty acid molecule may be joined through the carboxylic acid group with the loss of a water molecule for each linkage that is formed. Figure 7.5shows a fat molecule formed from three stearic acid molecules and a glycerol molecule. Such a molecule is one of many possible **triglycerides**. Also shown in this figure is cetyl palmitate, the major ingredient of spermaceti wax extracted from sperm whale blubber and used in some cosmetics and pharmaceutical preparations. Cholesterol shown in Figure 7.5 is one of several important lipid **steroids**, which share the ring structure composed of rings of 5 and 6 carbon atoms shown in the figure for cholesterol.

Although the structures shown in Figure 7.5 are diverse, they all share a common characteristic. This similarity is the preponderance of hydrocarbon chains and rings so that lipid molecules largely resemble hydrocarbons. Their hydrocarbon-like molecules make lipids soluble in organic solvents.

Some of the steroid lipids are particularly important because they act as **hormones**, chemical messengers that convey information from one part of an organism to another. Major examples of steroid hormones are cholesterol, testosterone (male sex hormone), and estrogens (female sex hormones). Steroid lipids readily penetrate the membranes that enclose cells, which are especially permeable to more hydrophobic lipid materials. Hormones, start and stop a number of body functions and regulate the expression of many genes. In addition to steroid lipids, many hormones including insulin and human growth hormone are proteins. Hormones are given off by ductless glands in the body called **endocrine glands**. The locations of important endocrine glands are shown in Figure 7.6.

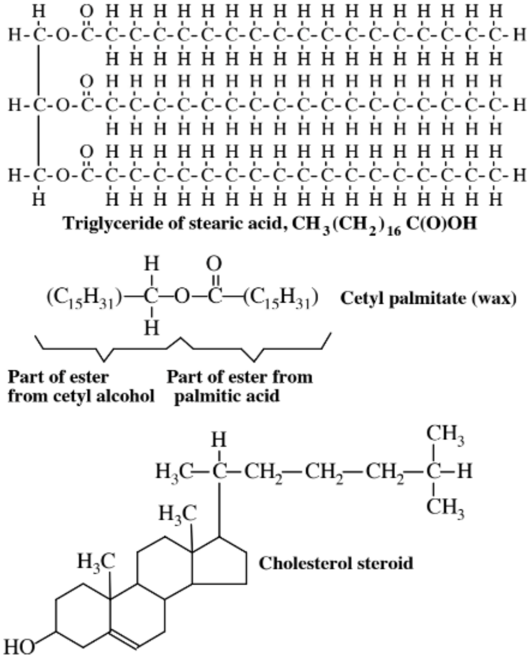


Figure 7.5. Three examples of lipids formed in biological systems. Note that a line structure is used to show the ring structure of cholesterol. The hydrocarbon-like nature of these compounds which makes them soluble in organic compounds is obvious.

Lipids are important in green chemistry for several reasons. Lipids are very much involved with toxic substances, the generation and use of which are always important in green chemistry. Poorly biodegradable substances, particularly organochlorine compounds, that are always an essential consideration in green chemistry, tend to accumulate in lipids in living organisms, a process called bioaccumulation. Lipids can be valuable raw materials and fuels. A major kind of renewable fuel is made by hydrolyzing the long-chain fatty acids from triglycerides and attaching methyl groups to produce esters. This liquid product, commonly called biodiesel fuel, serves as a substitute for petroleum-derived liquids in diesel engines. The development and cultivation of plants that produce oils and other lipids is a major possible route to the production of renewable resources.

7.6: Nucleic Acids

Nucleic acids (Figure 7.7)are biological macromolecules that store and pass on the genetic information that organisms need to reproduce and synthesize proteins. The two major kinds of nucleic acids are **deoxyribonucleic acid**,**DNA**, which basically stays in place in the cell nucleus of an organism and **ribonucleic acid**, **RNA**, which is spun off from DNA and functions throughout a cell. Molecules of nucleic acids contain three basic kinds of materials. The first of these is a simple sugar, 2-deoxy-β-D-ribofuranose (deoxyribose) contained in DNA and β-D-ribofuranose (ribose) contained in RNA. The second major kind of ingredient consists of nitrogen-containing bases: cytosine, adenine, and guanine, which occur in both DNA and RNA, thymine, which occurs only in DNA, and uracil, which occurs only in RNA. The third constituent of both DNA and RNA is inorganic phosphate, PO_4^{3-}. These three kinds of substances occur as repeating units called **nucleotides** joined together in astoundingly long chains in the nucleic acid polymer as shown in Figure 7.7.

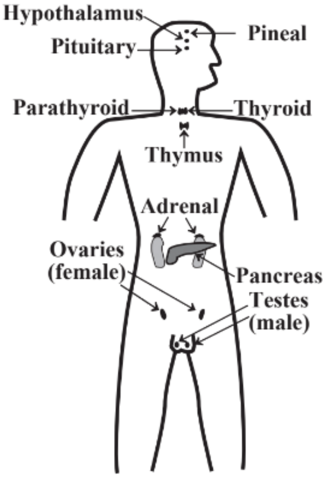


Figure 7.6. Location of important endocrine ductless glands that secrete hormones directly into the bloodstream in the human body. In contrast, exocrine glands including sweat, salivary, and mammary glands secrete hormones through ducts.In addition to secreting insulin into the bloodstream, the pancreas also functions as a ducted gland secreting pancreatic juice into the small intestine. This material contains digestive enzymes that help break down carbohydrate, protein, and fat molecules

The remarkable way in which DNA operates to pass on genetic information and perform other functions essential for life is the result of the structure of the DNA molecule. In 1953, James D.Watson, and Francis Crick deduced that DNA consisted of two strands of material counterwound around each other in a structure known as anα-helix (Figure 7.8), a remarkable bit of insight that earned Watson and Crick the Nobel Prize in 1962. These strands are held together by hydrogen bonds between complementary nitrogenous bases. Taken apart, the two strands resynthesize complementary strands, a process that occurs during reproduction of cells in living organisms. Indirecting protein synthesis, DNA becomes partially unravelled and generates a complementary strand of material in the form of RNA, which in turn directs protein synthesis in the cell.

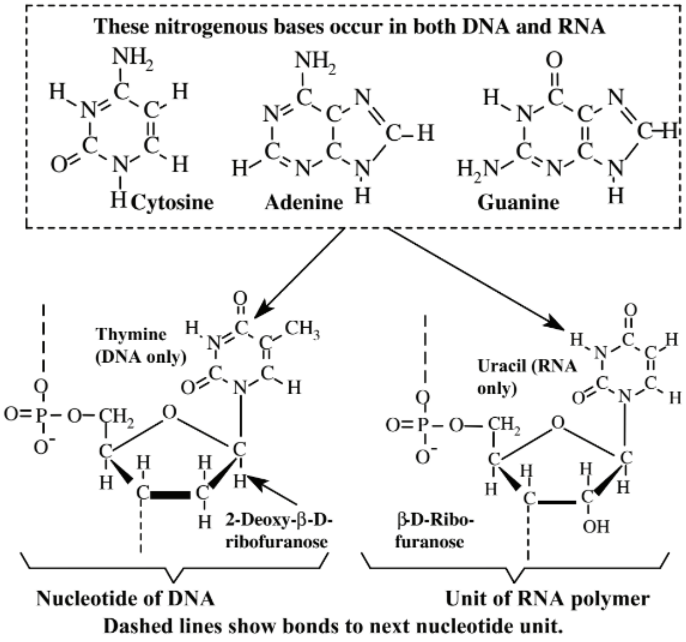


Figure 7.7. Basic units of nucleic acid polymers. These units act as a code in directing reproduction and other activities of organisms.

Consideration of nucleic acids and their function is very important in the development of green chemistry. One aspect of this relationship is that the toxicity hazards of many chemical substances result from potential effects of these substances upon DNA. Of most concern is the ability of some substances to alter DNA and cause uncontrolled cell replication characteristic of cancer. Also of concern is the ability of some chemical substances called **mutagens** to alter DNA such that undesirable characteristics are passed on to offspring.

Another important consideration with DNA as it relates to green chemistry is the ability that humans now have to transfer DNA between organisms, popularly called genetic engineering. An important example is the development of bacteria that have the DNA transferred from humans to make human insulin. This technology of recombinant DNA is discussed in more detail in Chapter 12.

7.7: Enzymes

Recall from Chapter 5, Section 5.5, that catalysts are substances that speed up a chemical reaction without themselves being consumed in the reaction. Catalysis is one of the most important aspects of green chemistry because the ability to make reactions go faster as well as more efficiently, safely, and specifically means that less energy and raw materials are used and less waste is produced. Biochemical catalysts called **enzymes** include some of the most sophisticated of catalysts. Enzymes speed up biochemical reactions by as much as ten- to a hundred million-fold. They often enable reactions to take place that otherwise would not occur, that is, they tend to be very selective in the reactions they promote. One of the greatest advantages of enzymes as catalysts is that they have evolved to function under the benign conditions under which organisms exist. This optimum temperature range is generally from about the freezing point of water (0°C) to slightly above body temperature (up to about 40°C). Chemical reactions go faster at higher temperatures, so there is considerable interest in enzymes isolated from microorganisms that thrive at temperatures near the boiling point of water (100°C) in hot water pools heated by underground thermal activity such as are found in Yellowstone National Park.

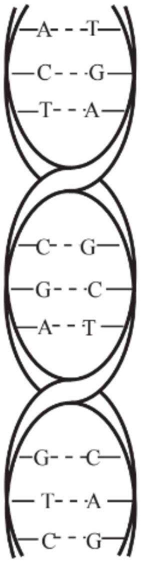


Figure 7.8. Representation of the double helix structure of DNA showing the allowed base pairs held together by hydrogen bonding between the phosphate/sugar polymer “backbones” of the two strands of DNA. The letters stand for adenine (A), cytosine (C), guanine (G), and thymine (T). The dashed lines, ---, represent hydrogen bonds.

Enzymes are proteinaceous substances. Their structure is highly specific so that they bind with whatever they act upon, a substance called a **substrate**. The basic mechanism of enzyme action is shown in Figure 7.9. As indicated by the figure, an enzyme recognizes a substrate by its shape, bonds with the substrate to produce an **enzyme-substrate complex**, causes a change such as splitting a substrate in two with addition of water (hydrolysis), then emerges unchanged to do the same thing again. The basic process can be represented as follows:

$$\text{enzyme} + \text{substrate} \leftrightarrows \text{enzyme-substrate complex} \leftrightarrows \text{enzyme} + \text{product} \tag{7.7.1}$$

Note that the arrows in the formula for enzyme reaction point both ways. This means that the reaction is **reversible**. An enzyme-substrate complex can simply go back to the enzyme and the substrate. The products of an enzymatic reaction can react with the enzyme to form the enzyme-substrate complex again. It, in turn, may again form the enzyme and the substrate. Therefore, the same enzyme may act to cause a reaction to go either way.

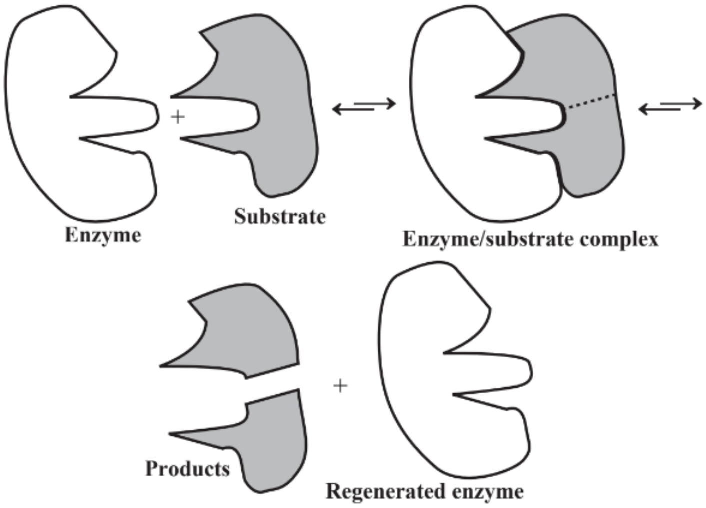


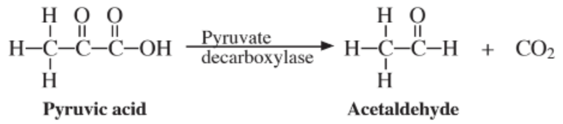
Figure 7.9. Representation of the “lock-and-key” mode of enzyme action which enables the very high specificity of enzyme-catalyzed reactions

In order for some enzymes to work, they must first be attached to **coenzymes**. Coenzymes normally are not protein materials. Some of the vitamins are important coenzymes.

The names of enzymes are based upon what they do and where they occur. For example, *gastric protease*, commonly called pepsin,is an enzyme released by the stomach (gastric), which splits protein molecules as part of the digestion process (protease). Similarly, the enzyme produced by the pancreas that breaks down fats (lipids) is called *pancreatic lipase*. Its common name is steapsin. In general, lipase enzymes cause lipid triglycerides to dissociate and form glycerol and fatty acids.

Lipase and protease enzymes are **hydrolyzing enzymes**, which enable the breakdown of high-molecular-mass biological compounds and add water, one of the most important types of the reactions involved in digestion of food carbohydrates, proteins, and fats. Recall that the higher carbohydrates humans eat are largely disaccharides (sucrose, or table sugar) and polysaccharides(starch). These are formed by the joining together of units of simple sugars, $C_6H_{12}O_6$, with the elimination of an H_2O molecule at the linkage where they join. Proteins are formed by the condensation of amino acids, again with the elimination of a water molecule at each linkage. Fats are esters which are produced when glycerol and fatty acids link together. A water molecule is lost for each of these linkages when a protein, fat, or carbohydrate is synthesized. In order for these substances to be used as a food source, the reverse process must be catalyzed by hydrolyzing enzymes to break down large, complicated molecules of protein, fat, or carbohydrate to simple, soluble substances which can penetrate a cell membrane and take part in chemical processes in the cell.

An important biochemical process is the shortening of carbon atom chains, such as those in fatty acids, commonly by the elimination of CO_2 from carboxylic acids. For example, *pyruvate decarboxylase* enzyme removes CO_2 from pyruvic acid,



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH \xrightarrow[\text{decarboxylase}]{\text{Pyruvate}} H{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}H + CO_2}$$

to produce a compound with one less carbon. It is by such carbon-by-carbon breakdown reactions that long chain compounds are eventually degraded to CO_2 in the body. Another important consequence of this kind of reaction is the biodegradation of long-chain hydrocarbons by the action of microorganisms in the water and soil environments.

Energy is exchanged in living systems largely by oxidation and reduction mediated by **oxidoreductase enzymes**. Cellular respiration is an oxidation reaction in which a carbohydrate, $C_6H_{12}O_6$, is broken down to carbon dioxide and water with the release of energy

$$\mathrm{C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O + energy} \tag{7.7.2}$$

Actually, such an overall reaction occurs in living systems by a complicated series of individual steps including oxidation. The enzymes that bring about oxidation in the presence of free O2 are called **oxidases.**

In addition to the major types of enzymes discussed above there are numerous other enzymes that perform various functions. **Isomerases** form isomers of particular compounds. For example, isomerases convert several simple sugars with the formula $C_6H_{12}O6$ to glucose, the only sugar that can be used directly for cell processes. **Transferase enzymes** move chemical groups from one molecule to another, **lyase enzymes** remove chemical groups without hydrolysis and participate in the formation of C=C bonds or addition of species to such bonds, and **ligase enzyme**s work in conjunction with ATP (adenosine triphosphate, a high-energy molecule that plays a crucial role in energy-yielding, glucose-oxidizing metabolic processes) to link molecules together with the formation of bonds such as carbon-carbon or carbon-sulfur bonds.

Enzymes are affected by the conditions and media in which they operate. Among these is the hydrogen ion concentration (pH). An interesting example is gastric protease which requires the acid environment of the stomach to work well but stops working when it passes into the much more alkaline medium of the small intestine. This prevents damage to the intestine walls, which would occur if the enzyme tried to digest them. Part of the damage to the esophagus from reflux esophagitis (acid reflux) is due to the action of gastric protease enzyme that flows back into the esophagus from the stomach with the acidic stomach juices. Temperature is critical for enzyme function. Not surprisingly, the enzymes in the human body work best at around 37°C (98.6°F), which is the normal body temperature. Heating these enzymes to around 60°C permanently destroys them. Some bacteria that thrive in hot springs have enzymes that work best at temperatures as high as that of boiling water. Other “cold-seeking” bacteria have enzymes adapted to near the freezing point of water.

Immobilized Enzymes in Green Chemistry

As noted above, enzymes in organisms have a variety of existing and potential uses in the practice of green chemistry. In many cases it is advantageous to isolate the enzyme used for a particular process from cells and use it outside the cellular environment. In a batch synthesis this can be done by mixing the enzyme with the reactants and allow it to catalyze the desired reaction making sure that optimum conditions of temperature and pH are maintained. This approach has several disadvantages. Enzymes are expensive and isolation of the enzyme from the reaction mixture is usually very costly and often not possible. Enzyme contamination of the product can cause difficulties.

The solution to the problem outlined above is often to employ **enzyme immobilization** that uses a two-phase system in which the enzyme is in one phase and the reaction occurs in another. Sequestration of the enzyme in a separate phase enables its re-use or continuous use in flow-through systems and prevents enzyme contamination of the products. Several major techniques have been employed for enzyme immobilization including (1) adsorption onto a solid, (2) covalent binding onto a separate phase, (3) entrapment in a separate phase, (4) confinement with a membrane that allows transport of reactants and products but retains the enzyme. Ideally the matrix holding the enzyme should be capable of holding the enzyme as well as being inert, physically strong, chemically stable, and capable of being regenerated. The most common materials used to hold enzymes have been porous carbon, ion-exchange matrices, clays, polymeric resins, hydrous metal oxides, and glasses.

The procedure for immobilization of an enzyme begins with mixing the enzyme and the solid materials under suitable conditions of pH and ionic strength, sometimes along with binding agents. The support holding the immobilized enzyme is then incubated for some time. Finally, excess enzyme and, where used, binding agents are washed off of the support.

Rather than isolating enzymes and immobilizing them on a support, living microorganism cells, usually those of bacteria, are often used. Two main categories of immobilization are employed, attachment and entrapment. The simplest kind of immobilization is aggregation cross-linking in which the microbial cells form networks that compose their own support. This approach is usually confined to batch processes. Otherwise the major kinds of attachment immobilization are covalent binding, binding on ion-exchangers, adsorption binding, and biofilm formation. Probably the most common form of biofilm reactor is the trickling filter used for wastewater treatment (see Chapter 9) in which growing bacteria and protozoa form a film over solid support material (usually rock) and the wastewater is sprayed over the biofilm. This enables contact of the immobilized microorganisms with both the biodegradable material in the wastewater and atmospheric oxygen. Entrapment of microorganisms may be on organic polymer, on inorganic polymer, or behind a semi-permeable membrane.

Use of living organisms as sources of immobilized enzymes offers the advantage of not having to isolate the enzyme and, in cases where the organism is reproducing, of continuously replenishing the enzyme. A disadvantage includes having to maintain conditions under which the organism is viable. Also, living cells harbor numerous enzymes so side-reactions and unwanted products can be a problem.

Effects of Toxic Substances on Enzymes

Toxic substances may destroy enzymes or alter them so that they function improperly or not at all. Among the many toxic substances that act adversely with enzymes are heavy metals, cyanide, and various organic compounds such as insecticidal parathion. Many enzyme active sites through which an enzyme recognizes and bonds with a substrate contain -SH groups. Toxic heavy metal ions such as Pb^{2+} or Hg^{2+} are “sulfur seekers” that bind to the sulfur in the enzyme active site causing the enzyme to not function. A particularly potent class of toxic substances consists of the organophosphate “nerve gases” such as Sarin that inhibit the acetylcholinesterase enzyme required to stop nerve impulses. Very small doses of Sarin stop respiration by binding with acetylcholinesterase and causing it to not work. Discussed further in Section 7.9 under the topic of toxicological chemistry, toxicity to enzymes is a major consideration in the practice of green chemistry.

7.8: Biochemical Processes in Metabolism

So far, this chapter has discussed the cells in which biochemical processes occur, the major categories of biochemicals, and the enzymes that catalyze biochemical reactions. Biochemical processes involve the alteration of biomolecules, their synthesis, and their breakdown to provide the raw materials for new biomolecules, processes that fall under the category of **metabolism**. Metabolic processes may be divided into the two major categories of **anabolism** (synthesis) and **catabolism** (degradation of substances). An organism may use metabolic processes to yield energy or to modify the constituents of biomolecules. Metabolism is discussed here as it affects biochemicals and in Chapter 12, Section 12.4, as it applies to the function of organisms in the biosphere.

Metabolism is a very important consideration in green chemistry and sustainability. Toxic substances that impair metabolism pose a danger to humans and other organisms and attempts are made to avoid such substances in the practice of green chemistry. Exposures to environmental pollutants that impair metabolism endanger humans and other organisms; the control of such pollutants is an important aspect of environmental chemistry. Metabolic processes are used to make renewable raw materials and to modify substances to give desired materials. The complex metabolic process of photosynthesis provides the food that forms the base of essentially all food webs and is increasingly being called upon to provide renewable raw materials for manufacturing.

Energy-Yielding Processes

The processing of energy is obviously one of the most important metabolic functions of organisms. The metabolic processes by which organisms acquire and utilize energy are complex generally involving numerous steps and various enzymes. Organisms can process and utilize energy by one of three major processes:

- **Respiration** in which organic compounds undergo catabolism
- **Fermentation**, which differs from respiration in not having an electron transport chain
- **Photosynthesis**, in which light energy captured by plant and algal chloroplasts is used to synthesize sugars from carbon dioxide and water

There are two major pathways in respiration. **Oxic respiration**(called aerobic respiration in the older literature) requires molecular oxygen whereas **anoxic respiration** (anaerobic respiration) occurs in the absence of molecular oxygen. Oxic respiration uses the **Krebs cycle** to obtain energy from the following reaction:

$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O + \text{energy} \tag{7.8.1}$$

About half of the energy released is converted to short-term stored chemical energy, particularly through the synthesis of **adenosine triphosphate**(**ATP**) shown in Figure 7.10

The highly energized ATP molecule is sometimes described as the “molecular unit of currency” for the transfer of energy within cells during metabolism. It releases its energy when it loses a phosphate group and reverts to adenosine diphosphate and other precursors. ATP is used by enzymes and proteins for cell processes including biosynthetic reactions (anabolism), cell division, and motility (such as occurs in moving protozoa cells). In so doing, ATP is continually being produced and reconverted back to its precursor species in an organism. Some studies have suggested that the human body processes its own mass in ATP during a single day! Whereas ATP is used for very short term energy storage and processing, for longer-term energy storage,glycogen or starch polysaccharides are synthesized, and for still longer-term energy storage, lipids(fats) are generated and retained by the organism.

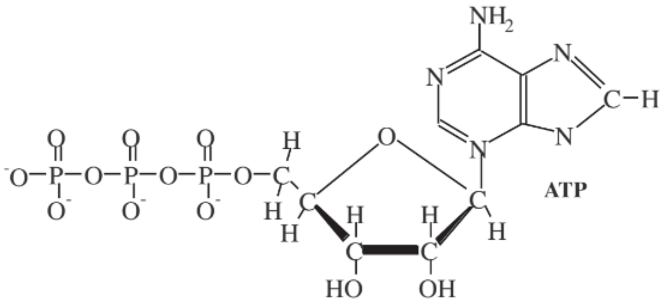


Figure 7.10. Adenosine triphosphate, a molecule strongly involved with energy transfer in living organisms.

As noted above, fermentation differs from respiration in not having an electron transport chain and organic compounds are the final electron acceptors rather than O2in the energy-yielding process. Many biochemical processes including some used to make commercial products are fermentations. A common example of fermentation is the production of ethanol from sugars by yeasts growing in the absence of molecular oxygen:

$$C_6H_{12}O_6 \rightarrow 2\,CO_2 + 2\,C_2H_5OH \tag{7.8.2}$$

Photosynthesis, is an energy-capture process in which light energy captured by plant and algal chloroplasts is used to synthesize sugars from carbon dioxide and water:

$$6\,CO_2 + 6\,H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{7.8.3}$$

When it is dark, plants cannot get the energy that they need from sunlight but still must carry on basic metabolic processes using stored food. Plant cells, like animal cells, contain mitochondria in which stored food is converted to energy by cellular respiration.

Nonphotosynthetic organisms depend upon organic matter produced by plants for their food and are said to be heterotrophic. They act as “middlemen” in the chemical reaction between oxygen and food material using the energy from the reaction to carry out their life processes Plant cells, which use sunlight as a source of energy and CO_2 as a source of carbon, are classified as **autotrophic**. In contrast, animal cells must depend upon organic material manufactured by plants for their food. These are called **heterotrophic** cells.

Biochemical conversions involving energy are very important in the practice of green chemistry and sustainability. The most obvious connection is the capture of solar energy as chemical energy by photosynthesis. As discussed in Chapter 15, photosynthetically produced biomass can serve as a source of chemically fixed carbon for the synthesis of chemical fuels including synthetic natural gas, gasoline, diesel fuel, and ethanol. A tantalizing possibility is to use recombinant DNA techniques to increase by several-fold the very low efficiency of photosynthesis by most plants. Fermentation has a strong role to play in sustainable energy development. As shown in Reaction 7.8.2, fermentation of glucose produces ethanol, which can be used as fuel.

Anoxic fermentation of biomass (abbreviated $\{CH_2O\}$) from sources such as sewage sludge or food wastes yields methane (natural gas) the cleanest-burning of all hydrocarbon fuels:

$$2\,(CH_2O) \rightarrow CH_4 + CO_2 \tag{7.8.4}$$

7.9: Biochemistry of Toxic Substances and Toxicological Chemistry

One of the more important aspects of biochemistry that is important in green chemistry is the way that organisms deal biochemically with toxic substances. There are two major aspects of this. One is the biochemical changes in toxic substances in an organism's system including the detoxification of such substances and in some cases the conversion of nontoxic compounds to toxic compounds. The second is the biochemical mode of action of toxic substances through which they exert a toxic effect. **Toxicological chemistry** is the science that deals with the chemical nature and reactions of toxic substances, including their origins, uses, and chemical aspects of exposure, fates, and disposal.[2] Toxicological chemistry addresses the relationships between the chemical properties and molecular structures of molecules and their toxicological effects. Figure 7.11 illustrates the definition of toxicological chemistry. This section discusses the biochemical aspects of toxicological chemistry. Toxicology, itself, and other details regarding toxicological chemistry are covered in Chapter 17.

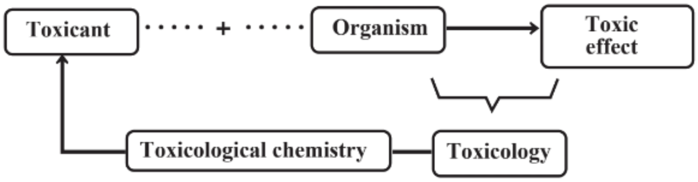


Figure 7.11. Toxicological chemistry is the biochemical science of toxic substances and their precursors. Toxicological chemistry relates the nature and reactions of these substances to toxicology

Biochemistry of Toxicants and **Protoxicants**

In some cases a toxic substance that enters into the system of a living organism is unchanged until it reacts to cause a toxic effect. This is the case with carbon monoxide, CO, which enters the bloodstream through the lungs and binds with blood hemoglobin to prevent oxygen transfer to tissues. In other case toxicants or their metabolic precursors (**protoxicants**) react in ways that may make them more toxic or that detoxify them and facilitate their elimination from the organism. **Xenobiotic compounds** are those that are normally foreign to living organisms. Some of the more toxic substances, such as the toxin produced by *Botulinus* bacteria or the venom of the deadly Australian inland taipan viper, are among the most toxic substances known. “Toxicant” is used here as a term to refer to toxic substances and their precursors including both xenobiotic materials and those of natural organisms. “The body” is used to refer to the human body, but also applies to other organisms as well.

Of particular importance in the metabolism of toxicants is **intermediary xenobiotic metabolism** which results in the formation of somewhat transient species that are different from both those ingested and the ultimate product that is excreted. Intermediary metabolites may have significant toxicological effects. Toxicants and protoxicants in general are acted upon by enzymes that normally act upon an **endogenous substrate**, a material that is in the body naturally. For example, flavin-containing monooxygenase enzyme acts upon endogenous cysteamine to convert it to cystamine, but also functions to oxidize xenobiotic nitrogen and sulfur compounds.

Toxicants undergo **biotransformation** as a result of enzyme action, usually Phase I and Phase II reactions defined below. Some nonenzymatic transformations are also important including bonding of compounds with endogenous biochemical species without an enzyme catalyst, hydrolysis in body fluid media, or oxidation/reduction processes.

The likelihood of enzymatic metabolism in the body depends upon the physical and chemical properties of the species. Highly polar compounds, such as those that form ions readily, are less likely to enter the body system and generally are quickly excreted. Therefore, such compounds are unavailable, or only available for a short time, for enzymatic metabolism. Volatile compounds, such as dichloromethane or diethyl ether, are expelled so quickly from the lungs that enzymatic metabolism is less likely. This leaves as the most likely candidates for enzymatic metabolic reactions **nonpolar lipophilic compounds**, those that are relatively less soluble in aqueous biological fluids and more attracted to lipid species. Of these, the ones that are resistant to enzymatic attack (PCBs, for example) tend to bioaccumulate in lipid tissue.

Xenobiotic species may be metabolized in many body tissues and organs. The liver is of particular significance because materials entering systemic circulation from the gastrointestinal tract must first traverse the liver. As part of the body's defense against the entry of xenobiotic species, the most prominent sites of xenobiotic metabolism are those associated with entry into the body, such as the skin and lungs. The gut wall through which xenobiotic species enter the body from the gastrointestinal tract is also a site of significant xenobiotic compound metabolism.

Phase I and Phase II Reactions

The metabolism of toxic substances may be divided into two phases. **Phase I reactions** normally consist of attachment of a functional group, usually accompanied by oxidation. For example, benzene, C_6H_6, (see Chapter 6, Section 6.2) is oxidized in the body by the action of the cytochrome P-450 enzyme system as shown in Figure 7.12.

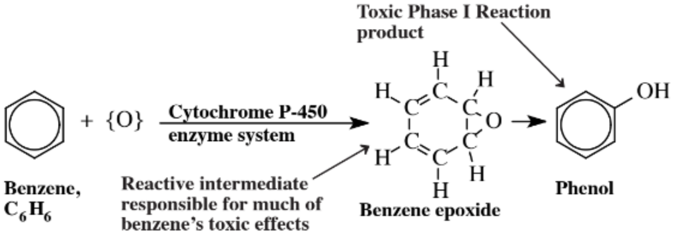


Figure 7.12. Phase I reaction of benzene to produce reactive intermediate benzene epoxide which rearranges to produce toxic phenol

The Phase I oxidation product of benzene is phenol, a toxic substance. A reactive intermediate in the process is benzene epoxide, which interacts with biomolecules to cause toxic effects. The phenol Phase I oxidation product of benzene may undergo a second reaction, a Phase II reaction in which it is bound with a conjugating agent that is endogenous to (produced naturally by) the body, such as glucuronide (Figure 7.13).

Although Phase I and Phase II reactions generally act to make xenobiotic substances more water soluble, more readily eliminated from the body, and less toxic, in some cases, the opposite occurs and metabolic processes make substances more toxic. Most known human carcinogens(cancer-causing agents) are actually produced by biochemical processes in the body from non-carcinogenic precursor substances.

Biochemical and Toxic Effects of Toxicants

Toxic substances, which, as noted above, are often produced by metabolic processes from nontoxic precursors, produce a toxic response by acting upon a **receptor** in the body. Typically, a receptor is an enzyme that is essential for some function in the body. As a consequence of the binding of the receptor to the toxicant there is a **biochemical effect**. A common example of a biochemical effect occurs when a toxicant binds to an enzyme such that the bound enzyme may be inhibited from carrying out its normal function. As a result of a biochemical effect, there is a response, such as a behavioral or physiological response, which constitutes the actual observed toxic effect. Acetylcholinesterase enzyme inhibited by binding to nerve gas Sarin may fail to stop nerve impulses in breathing processes, leading to asphyxiation. The phenomena just described occur in the **dynamic phase** of toxicant action as summarized in Figure 7.14.

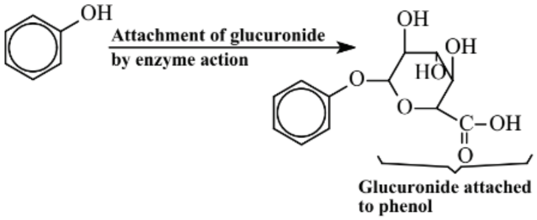


Figure 7.13. A Phase II reaction in which phenol is conjugated with glucuronide, an endogenous conjugating agent.

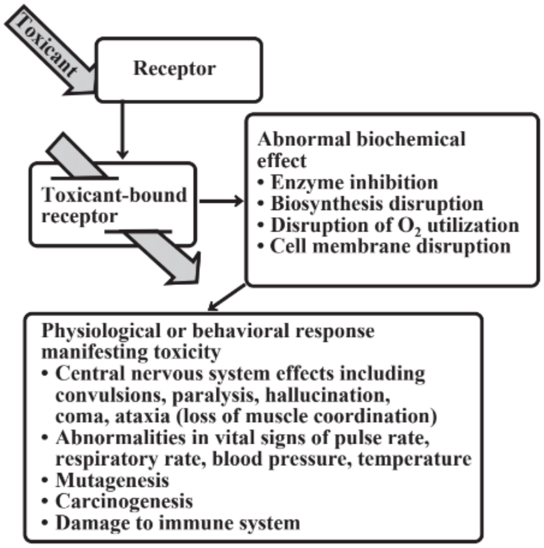


Figure 7.14. The dynamic phase of toxicant action in which a toxicant interacts with an endogenous receptor leading to biochemical changes that adversely affect an organism

Toxicological Chemistry and the Endocrine System The endocrine glands and the hormones they produce (see Section 7.5 and Figure 7.6) are important in the consideration of toxicological chemistry, green chemistry and sustainability. Of particular importance are substances that organisms get exposed to through their environment, food, and drinking water that have the potential to disrupt the crucial endocrine gland activities that regulate the metabolism and reproductive functions of organisms. **Hormonally active agents** exhibit hormone-like activity that may be detrimental. Most commonly these are estrogenic substances that act like the female sex hormone estrogen. Some of these survive water treatment processes. Discharged to receiving waters they affect aquatic organisms and potentially can get into water that humans drink. Among such substances are estrogen, an endogenous sex hormone; 17a-ethinylestradiol, an ingredient of oral contraceptives; and chemicals from industrial and consumer sources that mimic estrogen. Estrogenic substances from artificial sources are called **xenoestrogens** and include antioxidants, bisphenol A, dioxins, PCBs, phytoestrogens (from plants), some pesticides (chlordecone, dieldrin, DDT and its metabolites, methoxychlor, toxaphene), preservatives, and phthalic acid esters (butylbenzyl phthalate).

The practice of green chemistry minimizes the production and use of xenoestrogens and attempts to prevent their introduction into the environment. A particular need exists for the development of alternatives to xenoestrogenic bisphenol A and phthalate plasticizers. These substances improve the properties of plastics and as molecules much smaller than those in the plastic polymer tend to get into the environment and food chain. Modification of the plastic polymer formulation to give desired properties without the need for plasticizer additives would be especially desirable.

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2. Stanley E. Manahan, *Toxicological Chemistry and Biochemistry*, 3rd ed., Taylor & Francis/CRC Press, Boca Raton, Florida, 2002.

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Questions and Problems

Access to and use of the internet is assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be "right."

1. What are the basic building blocks of proteins, and how do they determine the primary structure of proteins?

2. What is meant by denaturation of proteins? Is it bad?

3. What are some major kinds of proteins?

4. What is the approximate simple formula of carbohydrates?

5. Fill in the blanks of the following pertaining to carbohydrates: Glucose is an example of a______________, sucrose is a ____________________________, and starch and cellulose areboth ____________________________.

6. How are lipids defined and how does this definition differ from that of other biomolecules?

7. What does DNA stand for? What are 6 specific ingredients of DNA?

8. Although lipids are defined by a physical property that they all share, what is a common characteristic of lipid structure?

9. From the structures given in Figure 7.5, what kind of functional group seems to be common in lipids?

10. How does the compatibility of lipids with organic substances, such as organochlorine compounds, influence the environmental behavior of such compounds?

11. What distinguishes RNA from DNA? How are they similar?

12. What are the three constituents of all basic units of nucleic acids?

13. Exposure of a person to toxic benzene can be estimated by measuring phenol in blood. Explain the rationale for such an analysis. Why is benzene epoxide not commonly determined to estimate benzene exposure?

14. Consider the toxicity of inhaled carbon monoxide in the context of Figure 7.14. Identify for carbon monoxide the receptor, the abnormal biochemical effect, and the physiological response manifesting toxicity.

15. What is the toxicological importance of lipids? How are lipids related to hydrophobic pollutants and toxicants?

16. What is the function of a hydrolase enzyme?

17. Match the cell structure on the left with its function on the right, below:

A. Mitochondria 1. Toxicant metabolism

B. Endoplasmic reticulum 2. Fills the cell

C. Cell membrane 3. Deoxyribonucleic acid

D. Cytoplasm 4. Mediate energy conversion and utilization

E. Cell nucleus 5. Encloses the cell and regulates the passage of materials into and out of the cell interior

18. The formula of simple sugars is $C_6H_{12}O_6$. The simple formula of higher carbohydrates is $C_6H_{10}O_5$. Of course, many of these units are required to make a molecule of starch or cellulose. If higher carbohydrates are formed by joining together molecules of simple sugars, why is there a difference in the ratios of C, H, and O atoms in the higher carbohydrates as compared to the simple sugars? What do these formulas suggest about the kind of enzyme that would be required to produce glucose from a higher carbohydrate such as cellulose?

19. What would be the chemical formula of a *tri*saccharide made by the bonding together of three simple sugar molecules?

20. The general formula of cellulose may be represented as $(C_6H_{10}O_5)_x$. If the molar mass of a molecule of cellulose is 400,000, what is the estimated value of$x$?

21. Glycine and phenylalanine can join together to form two different dipeptides. What are the structures of these two dipeptides?

22. Fungi, which break down wood, straw, and other plant material, have what are called“exoenzymes.” Fungi have no teeth and cannot break up plant material physically by force. Knowing this, what do you suppose an exoenzyme is? Explain how you think it might operate in the process by which fungi break down something as tough as wood.

23. The straight-chain alcohol with 10 carbons is called decanol. What do you think would be the formula of decyl stearate? To what class of compounds would it belong?

24. In what respect is an enzyme and its substrate like two opposite strands of DNA?

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CHAPTER OVERVIEW

8: The Five Environmental Spheres and Biogeochemical Cycle

“In addition to water, air, solid earth, and life, a fifth sphere of the environment must be considered, the anthrosphere consisting of the things made and used by humans. The anthrosphere has such a profound influence that we are now entering a new epoch, the anthropocene in which Earth’s environment will be largely determined by human activities.

8.1: Five Environmental Spheres
8.2: The Hydrosphere
8.3: The Atmosphere
8.4: The Geosphere
8.5: The Biosphere
8.6: The Anthrosphere
8.7: Cycles of Matter
Questions and Problems
Supplementary References

8.1: Five Environmental Spheres

In Section 1.2 it was noted that Earth's environment may be regarded as consisting of five spheres: (1) The **hydrosphere**, (2) the **atmosphere**, (3) the **geosphere**, (4) the **biosphere**, and (5) the **anthrosphere** (that part of the environment constructed and operated by humans). All of these spheres are closely interconnected and interactive, continuously exchanging matter and energy and influencing each other. Much of this interaction is through biogeochemical cycles in which biological, geochemical, aquatic, atmospheric, and, increasingly, anthrospheric processes act to exchange matter and energy among the five environmental spheres and determine Earth'senvironment. The next several chapters address these five environmental spheres and the cycles in which they are involved.

Consideration of the five environmental spheres and their interactions through biogeochemical cycles are very important in green chemistry, science, and technology as well as sustainability as a whole. Earth's natural capital (see Section 1.4) resides in the four "natural" spheres and is utilized (sometimes shamelessly exploited) and managed in the anthrosphere. The interfaces between spheres are particularly important for, among other reasons, they are where materials and energy are exchanged. As discussed in Section 1.2, one such interface is the one between the geosphere and the atmosphere where most plants grow that support life on Earth. Like most such interfaces, it is very thin compared to the spheres themselves, generally extending into the geosphere for only the meter or less penetrated by plant roots and into the atmosphere only to the height of the plants. The boundary between the anthrosphere and the atmosphere is where air pollutants from automobile engines and other sources enter the atmosphere. Many other examples of important interfaces could be given.

8.2: The Hydrosphere

Water, chemical formula H_2O, comprises the hydrosphere (Figure 8.1). As discussed in more detail in Chapter 9, although it has a simple chemical formula, water is actually a very complex substance largely because of the water molecule's polarity and ability to form hydrogen bonds. Water participates in one of the great natural cycles of matter, the **hydrologic cycle** illustrated in Figure 8.1. Basically the hydrologic cycle is powered by solar energy that evaporates water as atmospheric water vapor from the oceans and bodies of fresh water from where it may be carried by wind currents through the atmosphere to fall as rain, snow, or other forms of precipitation in areas far from the source. In addition to carrying water, the hydrologic cycle conveys energy absorbed as latent heat when water is evaporated by solar energy and released as heat when the water condenses to form precipitation.

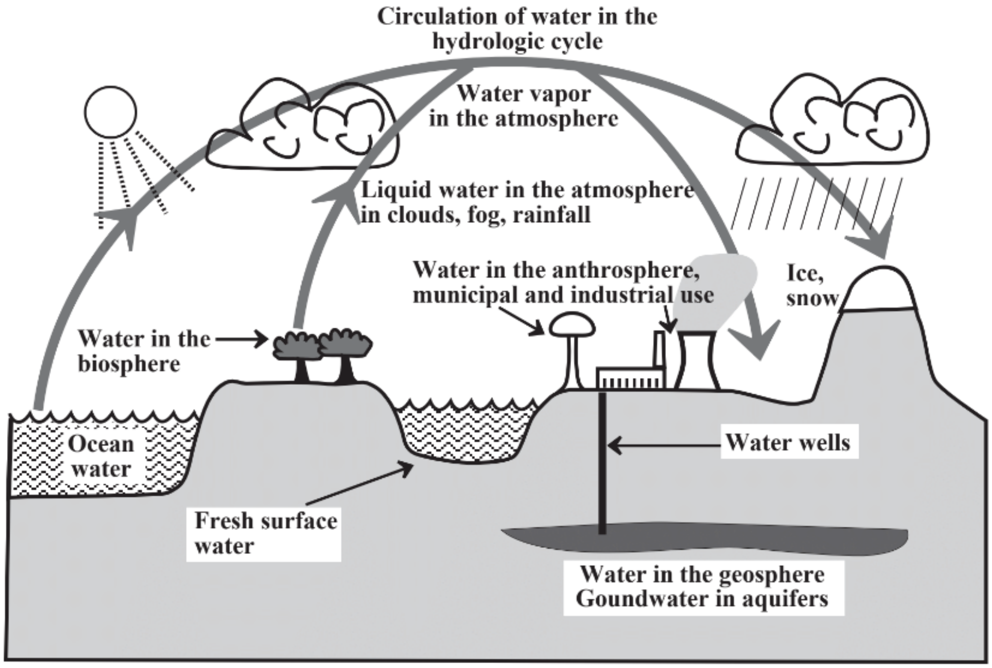

Figure 8.1. The hydrosphere overlaps strongly with all the other environmental spheres. This illustration shows water in bodies of water, underground as groundwater, in snow pack, in plants in the biosphere, as droplets and vapor in the atmosphere, and in water distribution systems and cooling towers in the anthrosphere. Water's cycle in the environment is the hydrologic cycle shown here in which solar energy evaporates water from the oceans, surface bodies of water, soil, and plants (transpiration) and the water in the atmosphere is carried for a distance (sometimes thousands of kilometers), falls back to Earth as precipitation, infiltrates in part into groundwater, moves on Earth's surface in rivers, back in part to the oceans, then evaporates to renew the cycle.

The hydrosphere is shown in Figure 8.1, which also illustrates its relationship to the other environmental spheres. A remarkable 97.5% of Earth's water is saltwater in the oceans. Of the remaining fresh water, 1.7% of Earth's total water is in polar ice and the Greenland icecap. This leaves only about 0.77% of Earth's water as fresh water for other than ocean-dwelling organisms and for use by humans. This fresh water occurs in natural lakes, rivers, impoundments made by humans, and underground as groundwater. At any given time a miniscule, but very important fraction is contained in the anthrosphere, such as in water distribution systems.

Water is the most widely used substance by organisms in the anthrosphere. Humans use water in their households for drinking, food preparation, cleaning, and disposal of wastes, drawing water from rivers, from impoundments made by damming rivers, and by pumping from underground aquifers. Moving water is one of the oldest forms of power harnessed by humans. Water wheels date back more than 2000 years and hydroelectric power is still the leading source of renewable energy. Hot water vapor (steam) is widely used for heat transfer in industry and in buildings and is the largest means of electrical power generation through the mechanism of steam turbines coupled to electrical generators.

Sustainability demands consideration of the water resource, shortages of which resulting from climate-induced droughts have caused severe problems for many organisms and declines of major civilizations. Devastating floods displace and even kill large numbers of people throughout the world and destroy homes and other structures. Severe droughts curtail plant productivity resulting in food shortages for humans and animals in natural ecosystems and often necessitating slaughter of farm animals. It is feared that both drought and the severity of occasional flooding will become much worse as the result of global warming brought on by rising carbon dioxide levels in the atmosphere (see Chapter 10, Section 10.6).

The maintenance of healthy and prosperous human populations requires consideration of both water quality and quantity. Waterborne diseases including cholera and typhoid have killed millions of people and these and others, especially dysentery, are problems in less developed areas lacking proper sanitation. The prevention of water pollution has been a major objective of the environmental movement and avoiding discharge of harmful water pollutant chemicals is one of the main objectives of the practice of green technology. Water supplies are a concern with respect to terrorism because of their potential for deliberate contamination with biological or chemical agents.

Since ancient times humans have built water reservoirs for water storage and dikes and dams for flood control. Such water management measures have enabled development of large populations in arid regions and in areas vulnerable to flooding. However, unusually severe, prolonged droughts do occur and in past times entire civilizations have been wiped out as a result. The effects of severe droughts are exacerbated by the fact that control of water supplies has enabled excessive growth in water-deficient areas. The Las Vegas metropolitan region of the U.S.and Mexico City in Mexico are examples of metropolitan regions that have outgrown the natural water capital available to them.

Floods cause hundreds of millions of dollars in damage to communities where construction of river dikes and impoundments have enabled agricultural and other developments in flood-prone areas that become overwhelmed by “hundred-year” flood events. Such an incident took place along the Missouri River in 1993 when a 500-year flood overwhelmed most of the protective structures. Failure of the protective systems caused much greater devastation than would otherwise have been the case when Hurricane Katrina destroyed much of New Orleans in 2005. Following the 1993 Missouri River flood, sensible actions were taken in some areas where farm property along the Missouri river was purchased by government agencies and allowed to revert to wildlife habitat in its natural state, which included periodic flooding. It would have been sensible for the future of New Orleans to move areas located below sea level and flooded by levee failure in 2005 to higher ground and to avoid trying to thwart the natural tendency of water to seek lower levels where humans may try to live.

Problems with water supply are discussed in Chapter 9. Figure 9.2 showing rainfall patterns in the continental U.S. reveals that the eastern continental U.S. receives generally adequate rainfall, although damaging droughts may still occur in that region. However, except for northern coastal regions, the western half of the continental U.S. is water-deficient. Water-deficient areas of theU.S. including southern California, Arizona, Nevada, and Colorado have exhibited some of the most rapid population growth in recent decades putting increasing pressure on limited water supplies and making the region vulnerable to prolonged severe droughts. Even much more severe water supply problems exist in other parts of the world, such as sections of Africa and the Middle East including the area of Palestine and Israel.

Damage to the Hydrosphere

Earth could have lost most of its water by now except for one very fortunate atmospheric feature, the very cold tropopause boundary at the upper part of the atmospheric troposphere. At a temperature well below the freezing point of water, this region converts water vapor to ice that remains in the troposphere and participates in the hydrologic cycle. Were this not the case, the water vapor would infiltrate the next higher atmospheric layer, the stratosphere, where highly energetic solar ultraviolet radiation would split H atoms off the H_2O molecules. These very light atoms and H_2 molecules formed from them would have diffused into space, leaving Earth with an arid Martian landscape. In fact, there is probably a net influx of water into Earth’s atmosphere from meteorites that are largely composed of water.

Although water is not destroyed on Earth, the hydrosphere certainly can suffer damage by human activities. One of the main ones of these is excessive utilization of water in arid regions. Withdrawal of irrigation water from rivers in arid regions has reduced some once mighty rivers to trickles by the time they reach the ocean. The water is not destroyed, but it evaporates and in some cases infiltrates to below ground.

Mexico City manifests one of the most serious problems of water over-use, the depletion of groundwater. This highly populous city was built on an old lake bed, and excessive pumping of ground water has caused land subsidence and damage to surface structures. In the U.S. wasteful use of groundwater is illustrated by the depletion of the High Plains Aquifer (Figure 8.2) commonly called the Ogallala aquifer. Largely composed of fossil water remaining from the last

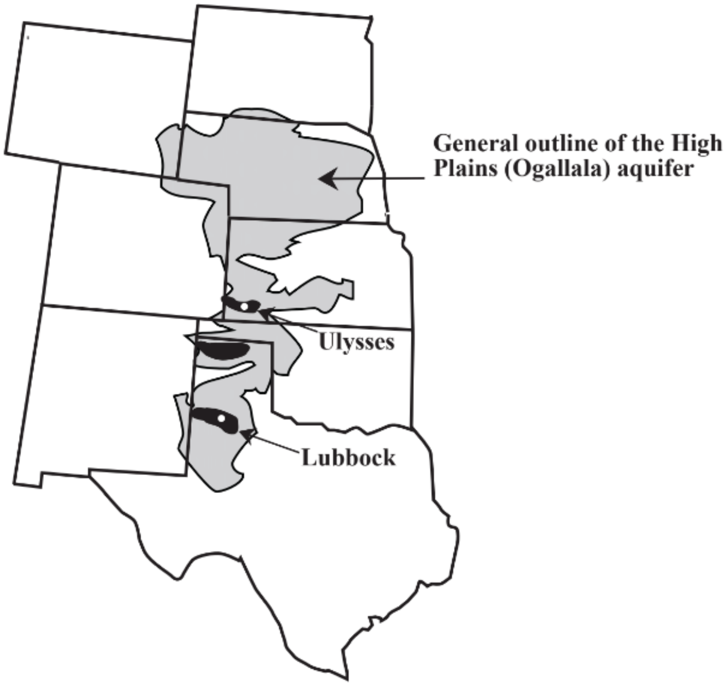

Figure 8.2. The water of the vast Ogallala aquifer, a precious resource remaining from the last Ice Age, has been recklessly exploited and depleted to grow water-intensive crops in semi-arid regions that do not normally support such crops. Areas outlined in black are those in southwestern Kansas and the Texas Panhandle where depletion has been especially severe.

Ice Age, the Ogallala aquifer lies beneath much of Nebraska, western Kansas, the Oklahoma and Texas panhandles, and small sections of eastern Wyoming, Colorado, and New Mexico. Although it is recharged from surface water in parts of Nebraska, it is largely composed of fossil water from the last Ice Age. It contains an astounding amount of water, enough to cover the entire United States to a depth of around 1.5 meters!

Since the 1940s, huge quantities of water pumped from the Ogallala aquifer have been used to irrigate corn and other crops not normally adapted to the High Plains region. As a result, the water table (level reached by water in a well drilled into an aquifer, Figure 8.3) has dropped dramatically, exceeding 50 meters in some areas, In the single decade beginning in 1995, the water level dropped by 6 meters in the middle of Kansas' irrigated corn belt around Ulysses, Kansas. Such unsustainable water depletion will force a shift from thirsty crops, such as corn, to those that require less water, such as milo.

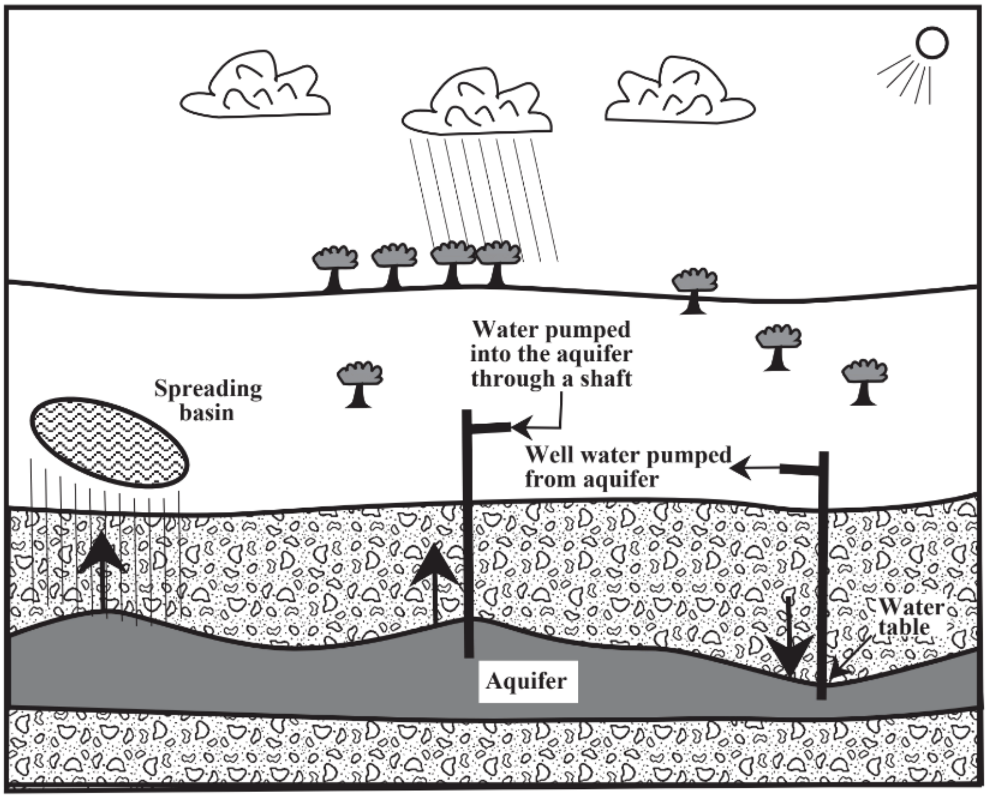

Figure 8.3. Water levels in an aquifer can be directly influenced by human activities. Water levels are lowered by withdrawal of water from wells. The recharge of aquifers can be aided by water infiltrating from spreading basins on the surface or by direct injection of water

The depletion of water supplies has numerous implications for sustainability. Clearly, the U.S. can meet its food demands without exploiting the Ogalla aquifer and other diminishing sources of water. A major thrust of the U.S. energy plan — such as it is — has been increased production of biofuels — ethanol from fermentation of glucose sugar derived from corn and biodiesel fuel from soybeans. The voracious consumption of irrigation water required to grow enough of these crops to make a significant difference in fuel resources is not sustainable. Some underground water supplies should be regarded as depletable resources and reserved for municipal water supplies and manufacturing, which require only a fraction as much water as does irrigation.

Sustaining the Hydrosphere

Fortunately, the solar-powered hydrologic cycle and the inexhaustible supply of water in Earth's oceans makes water one of nature's most renewable resources. Water is never really consumed or destroyed, although it may become so polluted or dispersed that its reclamation is impractical. Even water infiltrating into the ground may be regarded as recycled water because it renews groundwater sources. Although the thought of so doing has largely prevented efforts to completely recycle water that has been through domestic sewage systems, recycling of this water following purification will have to be practiced in some water-deficient areas in the future. In fact, recycling sewage water has long been the practice where municipalities take their water supplies from rivers into which other municipalities discharge treated wastewater. A very favorable development during the last 30 years is that the trend toward ever increasing water use that prevailed in the U.S. until about 1980 has leveled off due to more efficient irrigation and industrial processes and it appears that total utilization of water will remain relatively constant in the U.S into the future.

As exemplified by the exploitation of the Ogallala aquifer discussed above, human manipulation of the hydrosphere to provide water has often had adverse effects. However, application of the principles of green science and technology can enable supply of water to water-deficient areas without damaging the environment and even with enhancement of water quality. Unlike the over-utilized Colorado and Rio Grande rivers of the southwestern U.S., the enormous flow of the Mississippi River could be tapped for water-deficient areas. One scheme would be to divert a fraction of this flow near the mouth of the Mississippi where it discharges to the Gulf of Mexico and pump the water using abundant wind power to arid regions of the U.S. Southwest and northern Mexico. Mississippi River water retained for some time in constructed wetlands near the point of the diversion could undergo self-purification, collecting sediment that builds up land mass and removing nutrients that are now harmful to water quality in the Gulf of Mexico. Aquatic plants growing in the wetlands and thriving on fertilizer runoff from the upstream Mississippi watershed could remove nutrients that are now harmful to water quality in the Gulf of Mexico.

Groundwater recharge is another key to water sustainability that is being practiced in parts of the world. Most groundwater recharge occurs naturally, although it has been reduced by paving and surface modifications in the anthrosphere. Anthrospheric constructs on the surface can be designed to maximize recharge. For example, some paving surfaces in China have been made of porous materials that allow water to penetrate into the ground below. Two of the more active approaches to groundwater recharge are shown in Figure 8.3. One of these is water pumped into a shaft that extends underground and even to the aquifer itself. Surfaces of these conduits can become clogged with silt, bacterial growths, and other materials suspended in the recharge water and may have to be cleaned periodically. A spreading basin consists of a reservoir of water excavated into porous geospheric material from which water flows into the aquifer. An advantage is the purification of water that occurs through contact with mineral matter, but the process does not work well if aquifers are overlain by poorly pervious layers

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8.3: The Atmosphere

Illustrated in Figure 8.4, the atmosphere having a total mass of about 5.15×10^{15} tons is a layer of gases blanketing Earth that diminishes rapidly in density with increasing altitude. More than 99% of the atmosphere's mass is within 40 kilometers (km) of Earth's surface, with the majority of the air below 10 km altitude (compared to Earth's diameter of almost 13,000 km). A person exposed to air at the approximately 13,000 m altitude at which commercial jet aircraft fly could remain conscious for only about 15 seconds without supplementary oxygen. There is no clearly defined upper limit to the atmosphere, which keeps getting thinner with increasing altitude. A practical upper limit may be considered to be an altitude of about 1000 km above which airmolecules can be lost to space (a region called the exosphere).

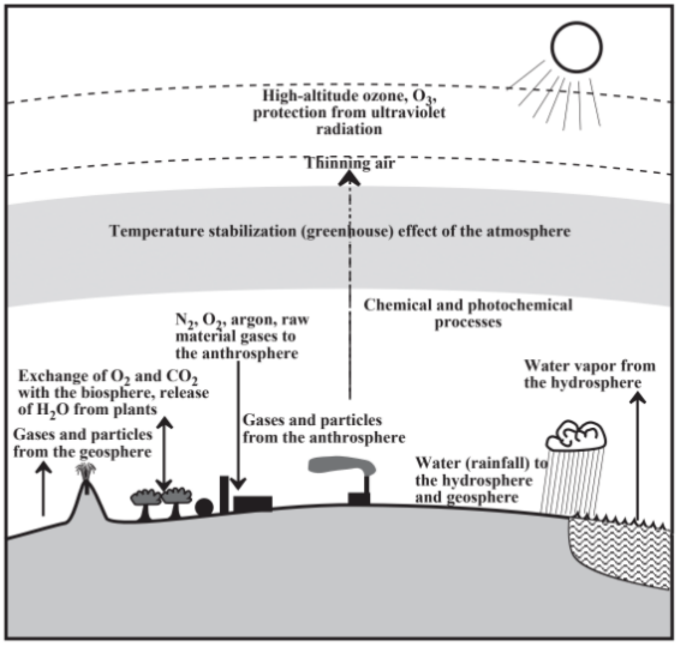

Figure 8.4. The atmosphere is a layer of gas, most of which is concentrated in a very thin region just above Earth's surface. It serves as a source of some essential materials, protects life on Earth from deadly electromagnetic radiation, transports water as part of the hydrologic cycle, participates in the carbon, oxygen, and sulfur cycles, and is an essential part of natural capital

The atmosphere nurtures life on Earth in many important respects. Some of the main ones of these are the following:

- The atmosphere constitutes much of Earth's natural capital because of its attributes listed below.
- The atmosphere is a source of molecular O_2 for all organisms that require it including humans and all other animals. In addition, pure oxygen, argon, and neon are extracted from the atmosphere for industrial uses.
- At approximately 0.039% carbon dioxide, CO_2, the atmosphere is the source of carbon that plants and other photosynthetic organisms use to synthesize biomass
- Consisting mostly of molecular N_2, the atmosphere serves as a source of nitrogen that is an essential component of protein and other biochemicals as well as a constituent of a variety of synthetic chemicals. Organisms "fix" this nitrogen in the biosphere chemically by the action of bacteria such as *Rhizobium* and it is fixed synthetically in the anthrosphere under much more severe conditions of temperature and pressure.
- The atmosphere acts as a blanket to keep Earth's surface at an average temperature of about 15°C at sea level and within a temperature range that enables life to exist(the "good" greenhouse effect).
- Earth's atmosphere absorbs very short wavelength ultraviolet radiation from the sun and space, which, if it reached organisms on Earth's surface, would tear apart the complex biomolecules essential for life. In this respect, the stratospheric ozone layer is of particular importance
- The atmosphere contains and carries water vapor evaporated from oceans that forms rain and other kinds of precipitation over land in the hydrologic cycle(Figure 8.1)

The atmosphere is 1–3% by volume water vapor, a level that is somewhat higher in tropical regions and lower in desert areas and at higher altitudes where condensation to liquid droplets and ice crystals removes water vapor. Exclusive of water vapor, on a dry basis air is 78.1% by volume nitrogen gas (N_2), 21.0% O_2, 0.9% noble gas argon, and almost 0.039% CO_2, a level that keeps increasing by a little more than 0.001% per year. In addition, there are numerous trace gases in the atmosphere at levels below 0.002% including ammonia, carbon monoxide, helium, hydrogen, krypton, methane, neon, nitrogen dioxide, nitrous oxide, ozone, sulfur dioxide, and xenon.

Figure 8.4 shows some of the main features and aspects of the atmosphere and its relationship to other environmental spheres. Except for a few aviators who fly briefly into the stratosphere, living organisms experience the lowest layer called the **troposphere** characterized by decreasing temperature and density with increasing altitude. The troposphere extends from surface level, where the average temperature is 15°C, to about 11 km (the approximate cruising altitude of commercial jet aircraft) where the average temperature is –56°C (the tropopause discussed in Section 8.2)

Above the troposphere is the **stratosphere** in which the average temperature increases from about –56°C at its lower boundary to about –2°C at its upper limit. The stratosphere is warmed by energy of intense solar radiation impinging on air molecules. Because this radiation can break the bonds holding O_2 molecules together, at higher altitudes the stratosphere maintains a significant level of O atoms and of ozone (O_3) molecules formed by combination of O atoms with O_2 molecules. Stratospheric ozone molecules are essential for the ability of humans and other organisms to exist on Earth's surface because of their ability to filter out damaging ultraviolet radiation before it can penetrate to Earth's surface. Although the stratosphere's ozone is spread over many km in altitude, it is commonly called the **ozone layer**. If all this ozone that is so essential for life were in a single layer of pure ozone at conditions near Earth's surface, it would be only about 3 millimeters thick! Some classes of chemical species, especially the chlorofluorocarbons or Freons formerly used as refrigerants, are known to react in ways that destroy stratospheric ozone, and their elimination from commerce has been one of the major objectives of efforts in achieving sustainability.

Above the stratosphere are the atmospheric mesosphere and thermosphere. which are relatively less important in the discussion of the atmosphere. Radiation energetic enough to tear electrons away from atmospheric molecules and atoms reaches these regions giving rise to a region containing ions called the **ionosphere.**

Earth's atmosphere is crucial in absorbing, distributing, and radiating the enormous amount of energy that comes from the sun. A square meter of surface directly exposed to sunlight unfiltered by air would receive energy from the sun at a power level of 1,340 watts. Called the **solar flux**, this level of power impinging on just one square meter could power an electric iron or thirteen 100-watt light bulbs plus a 40-watt bulb! If one considers Earth's cross-sectional area, the rate of total incoming solar energy is huge. Incoming solar radiation is in the form of electromagnetic radiation, which has a wavelike character in which shorter wavelengths are more energetic. The incoming radiation in the form electromagnetic radiation centered in the visible wavelength region with a maximum intensity at a wavelength of 500 nanometers (1 nm = 10^{-9}m) is largely absorbed and converted to heat in the atmosphere and at Earth's surface.

On average, the incoming solar energy must be balanced with heat energy radiated back into space; otherwise Earth would have melted and vaporized long ago. The outbound heat energy radiates into space as infrared radiation between about 2 micrometers and 40 μm (1 μm = 10^{-6} m)with a maximum intensity at about 10 μm). This energy is delayed on its outward path by being re-absorbed by water molecules, carbon dioxide, methane, and other minor species in the atmosphere. This has a warming (greenhouse) effect that is very important in sustaining life on Earth. As discussed in Chapter 10, anthrospheric discharges of greenhouse gases, especially carbon dioxide and methane, are likely causing an excessive greenhouse effect, which will have harmful effects on global climate.

Climate

Largely determined by conditions in the atmosphere, **climate** is crucial to the well-being of humans and other organisms on Earth. **Weather** refers to such factors as rain, wind, cloud cover, atmospheric pressure, and temperature whereas climate involves these conditions over a long period of time such as the warm, low-humidity weather that prevails in southern California or the cool, generally rainy conditions of Ireland. **Meteorology** is the science of the atmosphere and weather and climate is addressed by **climatology.**

Much of the driving force behind weather and climate is due to the fact that the incoming flux of solar energy is very intense in regions around the equator and very low in polar regions due to the angles at which the solar flux impinges Earth in these regions. Heated equatorial air tends to expand and flow away from the equatorial regions, creating winds and carrying with it large quantities of energy and water vapor evaporated from the oceans. As the air cools, water vapor condenses forming precipitation and warming the air from heat released when water goes from a vapor to a liquid. This process is the driving force behind hurricanes and typhoons which can result in torrential rainfalls and damaging winds.

Meteorological phenomena have an important influence on air pollution. An important example occurs with temperature inversions in which a layer of relatively warm air confines a surface layer of somewhat cooler, more dense stagnant air close to the ground. Hydrocarbons and nitrogen oxides confined in the stagnant air mass are acted upon by solar energy to cook up the noxious mixture of ozone, oxidants, aldehydes and other unpleasant materials that constitute photochemical smog.

Winds are important in air pollution. The lack of substantial wind is required for the formation of photochemical smog. Sulfur dioxide emitted to the atmosphere may be relatively innocuous near the point of discharge but transformed to harmful acid rain as it is carried some distance by wind. That is the reason that New England and parts of Canada can be afflicted with acid rain from sulfur dioxide given off by coal-fired power plants some distance away in the Ohio River Valley.

Climate and sustainability go hand-in-hand. Favorable climate conditions and a relatively unpolluted atmosphere are important parts of natural capital. A favorable climate is required to maintain food productivity. One of the greatest concerns with the emission of excessive amounts of greenhouse gases to the atmosphere is warming that will result in catastrophic drought in formerly productive agricultural regions leading to much reduced food production and even widespread starvation.

Anthrospheric Influences on the Atmosphere

Human activities in the anthrosphere strongly influence the atmosphere and have enormous potential to affect Earth’s environment as a whole. Photochemical smog with its destructive ozone and other oxidants along with other pollutants and visibility-obscuring atmospheric particulate matter results when nitrogen oxides and reactive hydrocarbons, largely from internal combustion vehicle engine exhausts, are emitted to the atmosphere from the anthrosphere. The sulfur dioxide and nitrogen oxide precursors to strong sulfuric and nitric acids in acid rain come from anthrospheric activities associated with fossil fuel combustion and other sources such as roasting of sulfide metal ores. Because of factors such as these, one of the most important aspects of sustainability is the construction and operation of the anthrosphere in ways that preserve the quality of the atmosphere. One of the important aspects of green chemistry is to use products and processes that do not contribute to damage to the atmosphere.

8.4: The Geosphere

As illustrated in Figure 8.5, the **geosphere** is the solid Earth (which sometimes is not so solid when earthquakes or volcanic eruptions occur). The geosphere is an enormous source of natural capital. It provides the platform upon which most food is grown and is the source of plant fertilizers, construction materials, and fossil fuels that humans use. As part of its natural capital, the geosphere receives large quantities of consumer and industrial wastes. Past and current practices of using the geosphere as the anthrosphere's waste dump are ultimately unsustainable. As shown in Figure 8.5, the geosphere interacts strongly with the hydrosphere, atmosphere, biosphere, and anthrosphere. Managing and preserving Earth's natural capital are of utmost importance to sustainability.

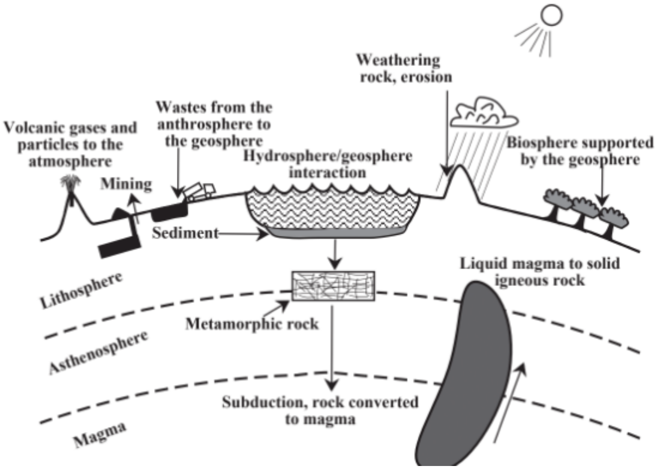

Figure 8.5. The geosphere. The "solid earth" consists of a surface layer of rock about 100 km thick on average floating on top of molten magma. Rock cycles occur within the geosphere. It is an enormous source of natural capital including essential minerals and provides a thin surface of soil upon which most food is grown

Earth is in the shape of a geoid defined by the levels of the oceans and a hypothetical sea level beneath the continents. It is slightly pear-shaped rather than being a perfect sphere because of differences in gravitational attraction in different parts of Earth. Although humans have flown hundreds of thousands of km into space, they have been unable to penetrate more than a few km into Earth's crust.

The geosphere is a layered structure most of which is hot enough to melt rock. Earth's core is a huge ball of iron at a temperature above the normal melting point of iron, but solid due to the enormous pressure that it is under. Above this core is the **mantle** composed of rock and ranging in depth between 300 km and 1,890 km. The deeper inner mantle, though hot enough for the rock to be liquid under ordinary pressures is solid because of the enormous pressure to which it is subjected. On top of the inner mantle is the outer mantle at a depth between 10 km and 300 km composed of hot molten rock called **magma**. Floating on the magma is the solid **lithosphere** composed of relatively strong rock, varying in thickness from just a few to as much as 400 km, averaging about 100 km. The transition layer between the molten magma and the lithosphere is the **athenosphere** composed of hot rock that is relatively weak and plastic. Earth's **crust** is the outer layer of the lithosphere, which is only 5-40 km thick.

Introduced to much controversy in the mid-1900s, the theory of **plate tectonics** views Earth'ssurface as consisting of huge lithospheric plates upon which the continents and Pacific Ocean rest, behaving as units. Earth's crust is a dynamic system in which the lithospheric plates move relative to each other by, typically, a few centimeters per year. When abrupt plate movement occurs, an earthquake results. Magma coming to the surface along plate boundaries results in emissions of hot and molten rock, ash, and gases in the form of **volcanoes**.

There are three kinds of boundaries between tectonic plates

- **Divergent boundaries** on ocean floors between tectonic plates that are moving apart are where hot magma undergoes upwelling and cooling to form new solid lithospheric rock, creating ocean ridges.
- **Convergent boundaries** where plates move toward each other forcing matter downward into the asthenosphere in subduction zones, eventually to form new molten magma and in some cases forcing matter upward to produce mountain ranges
- **Transform fault boundaries** where two plates move laterally relative to each other creating fault lines along which earthquakes occur

The conditions outlined above drive the **tectonic cycle**. In this cycle, there is upwelling of molten rock magma at the boundaries of divergent plates. This magma cools and forms new solid lithospheric material. At convergent boundaries, solid rock is forced downward and melts from the enormous pressures and contact with hot magma at great depths, reforming magma. This cycle and the science of plate tectonics explain once puzzling observations of geospheric phenomena including the opening and spreading of ocean floors that create and enlarge oceans, the movement of continents relative to each other, formation of mountain ranges, volcanic activity, and earthquakes.

Earth's Composition

Characterized by definite chemical composition and crystal structure, about 2000 known minerals compose Earth. Most rocks in the crust are composed of only about 25 common minerals. With a composition of 49.5% oxygen and 25.7% silicon, Earth's crust is largely composed of chemical compounds of these two elements with smaller amounts of aluminum, iron, carbon, sulfur, and other elements. Other than aluminum and iron, only about 1.6% of Earth'scrust consists of the kinds of rock that must serve as important resources of metals, phosphorus required for plant growth, and other essential minerals. Careful management of this resource of essential minerals is one of the primary requirements for sustainability.

As molten magma penetrates to near the top of Earth's crust then cools and solidifies, it forms igneous rock. Exposed to water and the atmosphere, igneous rock undergoes physical and chemical changes in a process called **weathering**. Weathered rock material carried by water and deposited as sediment layers may be compressed to produce secondary minerals, of which clays are an important example. Molded and heated to high temperatures to make pottery, brick, and other materials, clays were one of the first raw materials used by humans and are still widely used today.

A part of the crust crucial for the existence of humans and most other non-aquatic life forms is the thin layer of weathered rock, partially decayed organic matter, air spaces, and water composing **soil** (see Chapter 11) that supports plant life. Were Earth the size of a geography classroom globe, the average thickness of the soil layer on it would be only about the size of a human cell! The to player of soil that is most productive of plants is topsoil, which is often only a few centimeters thick in many locations, or even non-existent where poor cultivation practices and adverse climatic conditions have led to its loss by wind and water erosion. The conservation of soil and enhancement of soil productivity are key aspects of sustainability (see Chapter 11).

The Geosphere in Relation to Other Environmental Spheres

Virtually all things and creatures commonly regarded as parts of Earth's environment are located on, in, or just above the geosphere. Major segments of the hydrosphere including the oceans, rivers, and lakes rest on the geosphere, and groundwater exists in aquifers underground. Water dissolves minerals from the geosphere that nourish aquatic life. These minerals and rock particles eroded by moving water from the geosphere are deposited in layers and transformed into rock again. The atmosphere exchanges gases with the geosphere. For example organic carbon produced by photosynthetic plants from atmospheric carbon dioxide may end up as soil organic matter in the geosphere, and the photosynthetic processes of plants growing on the geosphere put elemental oxygen back into the atmosphere. The majority of biomass of organisms in the biosphere is located on or just below the surface of the geosphere. Most structures that are parts of the anthrosphere are located on the geosphere, and a variety of wastes from human activities are discarded to the geosphere. Modifications and alterations of the geosphere can have important effects on other environmental spheres and vice versa.

8.5: The Biosphere

Composed of living organisms and the materials and structures that they produce, the **biosphere** is one of the five major environmental spheres. The nature of the biosphere and its essential role in sustainability are the topics of Chapter 13. **Biochemistry**, the chemistry that occurs in the biosphere, is discussed in Chapter 7. The biosphere is of obvious importance to the discussion of soil and agriculture in Chapter 12. Aspects of the biosphere are important in sustainability covered in other chapters of the book.

The living organisms that compose the biosphere are the topic of the science of **biology**. The classes of biomolecules that make up these organisms are outlined in Chapter 7. They include proteins that are the basic building blocks of organisms, carbohydrates made by photosynthesis and metabolized by organisms for energy, lipids (fats and oils), and the all-important nucleic acids(DNA, RNA), genetic materials which define the essence of each individual organism and act as codes to direct protein biosynthesis and reproduction. Hierarchical organization is a characteristic of living organisms in the progression of biomolecules < living cells < organs < organisms < the biosphere, itself. Organisms carry out metabolic processes in which they chemically alter substances to obtain energy and to synthesize new biomass. An essential function of organisms is reproduction, and their young undergo various stages of development. Through their DNA organisms express heredity, and modifications of DNA cause mutations.

Although an imperfect system of classification, organisms are regarded as belonging to several kingdoms. Three of these are organisms capable of existing as single cells, but often occurring in colonies of undifferentiated cells clumped together: (1) Archaebacteria without defined cell nuclei that do not require oxygen or light and often exist in extreme environments such as hot springs; (2) eubacteria without defined cell nuclei including heterotrophs that metabolize organic material, cyanobacteria that obtain energy through photosynthesis, and members that obtain their energy by mediating reactions of inorganic matter; and (3) protists consisting of single-celled organisms that have defined cell nuclei enclosed by a nuclear membrane and often have animal-like features, such as moveable hair-like flagella that enable the organisms to move in water. At more complex levels are generally multicelled plantae (plants) and animalia (animals), as well as fungi including yeasts, molds, and mushrooms.

Several terms are used to describe organisms and their place in ecosystems. A **population** of organisms consists of a group of the same species. Groups coexisting in the same location makeup a **community**. Interacting communities and their physical environment make up an **ecosystem**, all of which grouped together constitute the entire biosphere. The basis of any ecosystem is its **productivity**, the ability to produce biomass, usually through photosynthesis in which organisms remove carbon dioxide from the atmosphere and fix it in the form of organic matter that is further converted by biochemical processes to proteins, fats, DNA, and other life molecules. These biomolecules constitute the basis of the whole ecosystem food chain upon which the remainder of the organisms in the food chain depend for their existence. In water, the most biomass at the base of the food chain is produced by algae, photosynthetic phytoplankton growing suspended in water. Some protozoa and some bacteria also have photosynthetic capabilities. The major photosynthetic organisms in terrestrial ecosystems are plants growing in soil.

The outline of the main features of the biosphere are shown in Figure 8.6. For the most part the biosphere is anchored by dominant plant species that are the major producers of biomass. The dominant plant species may also modify the physical environment in ways that facilitate the existence of other species. The big trees dominant in a rain forest obviously form an environment to which other organisms adapt, for example, by providing safe nesting places for birds. The shade provided by the trees makes up a microclimate and a degree of shelter at ground level in which certain kinds of organisms can thrive. Lichen, a synergistic combination of fungi and photosynthetic algae that grow on the surface of rocks weather the rocks to eventually produce soil in which other plants can grow.

The biosphere has undergone massive evolutionary and climate-related changes over millions of years. Much more rapid and sometimes dramatic changes have been caused by human influences. Arguably the most notable of these took place after Columbus discovered the Americas in 1492. Separated by vast oceans, the biospheres of the Eastern and Western hemispheres had evolved largely independent of each other. As humans introduced organisms from one hemisphere to the other an often spectacular phenomenon called ecological release took place as populations of some species exploded when they were introduced into regions free of their natural predators. The Bluegrass State of Kentucky got its name from the prolific growth of this grass introduced from Europe; clover from Europe also grew rapidly in the New World. Newly introduced peachtrees grew so well in the Carolinas and Georgia that fears were expressed over the potential development of a “peach tree wilderness.” Some regions of Peru were inundated with newly introduced mint. It is possible that a human population explosion in parts of Africa was made possible by productive corn from the Western Hemisphere enabling the removal of millions of people from the continent into slavery without depleting Africa’s population. Originating in the Andes Mountains of South America, the potato became a staple of the diet in

Ireland. When the catastrophic *Phytophthora infestans* fungal blight decimated the crop in the 1840s, Ireland lost half its population to starvation and emigration. Tragically, smallpox introduced to North America by Europeans decimated Native American populations, reducing populations of some tribes by 90%.

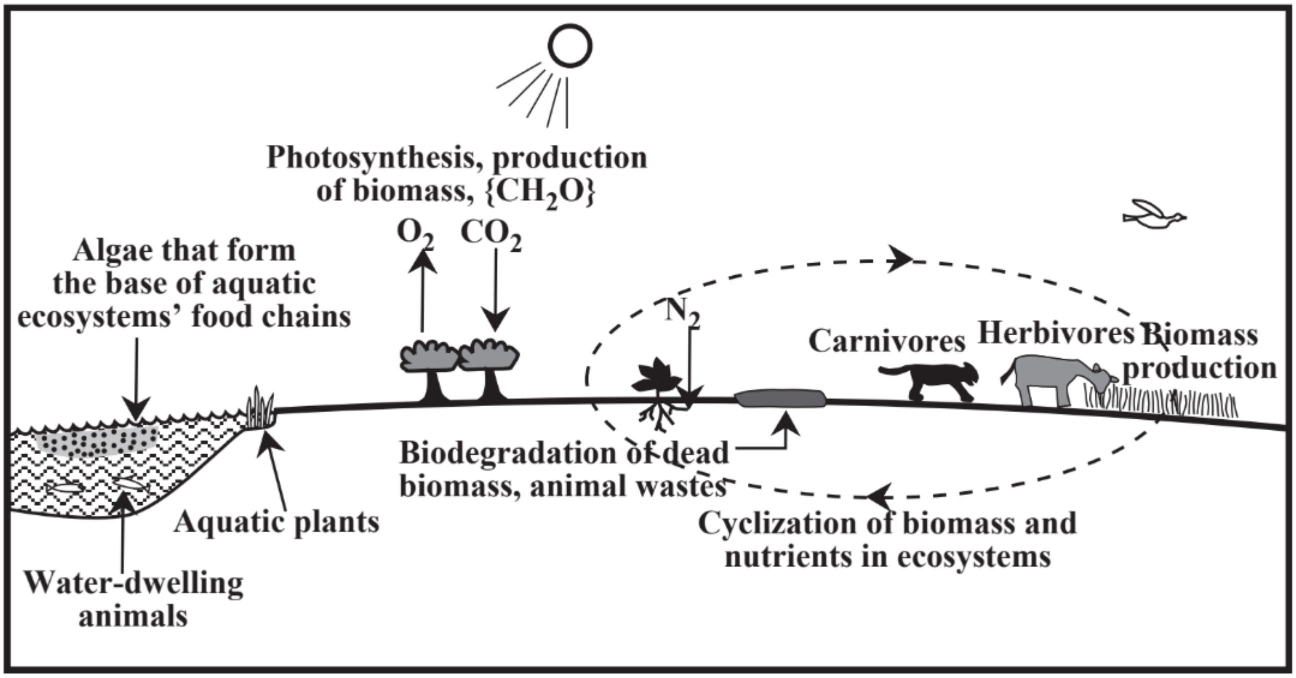

Figure 8.6. Organisms occur within ecosystems in the biosphere where they interact with each other and their enviroment. Ecosystems have evolved in a manner that enables the most efficient utilization of energy and matter with complete recycling of biomass and nutrients. Ecosystems are based upon photosynthetic plants and algae that produce the biomass that anchors the ecosystems, in the process removing carbon dioxide from the atmosphere and returning oxygen. Nitrogen-fixing bacteria, such as those that grow on the roots of leguminous plants, convert elemental nitrogen from the atmosphere to biochemically bound nitrogen. Fungi and bacteria degrade dead biomass, a process that returns nutrients to the ecosystem.

The biosphere has significant effects on the other environmental spheres and *vice versa*. Materials generated in the biosphere are used in the anthrosphere; wood is one such material. Biological productivity is largely determined by conditions of geospheric soil. The availability of the hydrosphere's water largely determines kinds and populations of organisms. Fertilizers and pesticides produced in the anthrosphere have a strong influence on biological productivity in agriculture. Shielding organisms from pollutants, wastes, and toxic substances generated in the anthrosphere is a high priority in environmental protection. The design and operation of the anthrosphere strongly influence the nature of the biosphere and its productivity, especially in the agricultural sector.

The biosphere largely determines Earth's environment. The atmosphere's oxygen was generated by photosynthetic bacteria eons ago. Lichen communities of synergistically growing algae and fungi act upon geospheric rock forming soil that supports plant life. The anthrosphere of less industrialized societies has been largely a product of the biosphere in which the human residents have existed. Massive herds of bison provided food, robes, and the material for the teepee dwellings of North American Plains Native Americans. The availability and kinds of wood have largely determined the nature of dwellings constructed in many societies. More than 2000 years ago, domesticated animals harnessed to carts, wagons, and plows provided humans with mobility and the source of power used to cultivate soil. Many societies, including the Amish farmers in the U.S., still use horses, donkeys, mules, oxen, and water buffalo for land cultivation and transport of goods. One of the basic tenets of green chemistry and sustainability is the use of materials from the biosphere to replace those produced from scarce, expensive petroleum.

In achieving sustainability humans have much to learn from the organisms in the biosphere which over millions of years have developed essential tools of survivability. An important aspect is the ability to thrive and be productive under the mild, safe conditions under which organisms may exist, conditions which are most desirable for green chemical synthesis and other sustainable activities. Even the conditions under which some thermophilic bacteria thrive in the thermal hot springs of Yellowstone National Park are mild compared to the much higher temperature, high-pressure conditions required in many chemical syntheses. The intolerance of living organisms to toxic substances provides valuable lessons regarding which substances should be avoided in the practice of green chemistry.

Important lessons in the development of sustainable systems of industrial ecology (Chapter13) are provided by the biosphere. Over hundreds of millions of years of evolution organisms in the biosphere have had to evolve sustainable ecosystems for their own survival, completely recycling materials and enhancing their environment. In contrast, humans have behaved in ways that are unsustainable with respect to their own existence, exploiting nonrenewable resources and fouling the environment upon which they depend for their own survival. The complex, sustainable ecosystems in which organisms live sustainably in relationships with each other and their surroundings serve as models for anthropogenic systems. By taking lessons from the biosphere and its long-established ecosystems, humans can develop much more sustainable systems of industry and commerce.

A crucial respect in which the biosphere is a key to achieving sustainability is its ability to perform photosynthesis and synthesis of specialized materials. Using carbon dioxide from the atmosphere and energy from the sun, organisms produce biogenic materials in a much greener, safer, more sustainable manner than the manner in which materials are produced in the anthrosphere. Furthermore, organisms are particularly well adapted to make a variety of complex and specialized materials that are very difficult or impossible to make by purely chemical means.

8.6: The Anthrosphere

Although some authorities object to recognizing the things that people make, modify, and use as a separate environmental sphere — the **anthrosphere**—as a distinct environmental sphere, it is essential to consider it in the achievement of sustainability. Just a look around us shows the dwellings, buildings, roads, airports, factories, power lines and numerous other things constructed and operated by humans as visible evidence of the existence of the anthrosphere on Earth (see Figure 8.7). The anthrosphere and its influences are so obvious and even intrusive that the Nobel Prize-winning atmospheric chemist Paul Crutzen has argued convincingly that Earth is undergoing a transition from the holocene geological epoch to a new one, the **anthropocene**. This is occurring because human activities are now quite significant compared to nature in their impact on Earth'senvironment and are changing Earth's fundamental physics, chemistry, and biology. There is concern that, especially through changes in global climate, activity in the anthrosphere will detrimentally alter Earth's relatively stable, nurturing environment and produce one that is much more challenging to human existence.

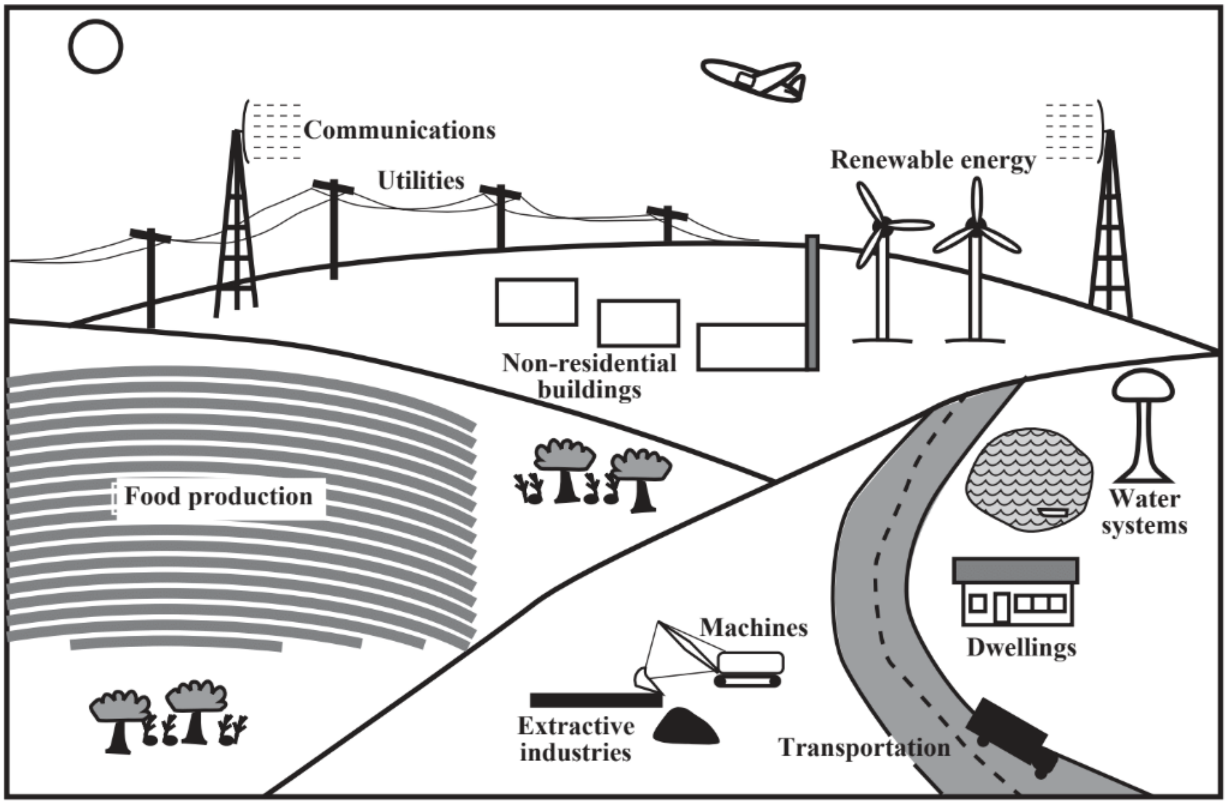

Figure 8.7. There are many aspects to the anthrosphere as illustrated by the examples in this figure. It is tied closely with the other environmental spheres

It is not completely accurate to believe that pre-industrial humans had little influence on the biosphere and ecosystems. The grazing habits of excessive numbers of goats bred by humans form eat and milk centuries ago contributed to the transformation of formerly productive grasslands of the Middle East and North Africa to deserts. Some pre-Columbian native South Americans created their unique anthrosphere by building terraces, draining wetlands, and constructing raised agricultural fields to grow a variety of food crops. As much as one third of the Midwestern prairies first encountered by early European settlers in the present day U.S. were created through the pyromaniacal tendencies of Native Americans who burned forests to create grasslands that supported game animals. Subsequently, forestation, largely with European tree varieties, often followed in the paths of the first non-native settlers. Compared to the modern industrial era, however, the impact of humans until just a few centuries ago was comparatively benign. Particularly with the development of fossil fuel resources and the large machines powered by these fuels, during the last approximately 200 years, humans have built a pervasive anthrosphere that is having massive environmental impact.

The boundaries between the anthrosphere and the other environmental spheres are sometimes blurred. Most of the anthrosphere including buildings, highways, and railroads is anchored to the geosphere. Gardens that adorn the anthrosphere are planted on geospheric soil and the flowering plants in them are part of the biosphere. Farm fields are modifications of the geosphere, but the crops raised on them are part of the biosphere. Coal mines are burrowed into the anthrosphere. Ships move over ocean waters in the hydrosphere and airplanes fly through the atmosphere.

There are many distinct segments of the anthrosphere as determined by a number of factors including where and how humans dwell; the movement and distribution of goods; the provision of services; the utilization of non-renewable materials; the provision of renewable food, fiber, and wood; the collection, conversion, and distribution of energy; and the collection, treatment, and disposal of wastes. With these factors in mind it is possible to list a number of specific things that are parts of the anthrosphere as shown in Figure 8.7. These include dwellings as well as other structures used for manufacturing, commerce, education, and government functions. Utilities include facilities for the distribution of water, electricity, and fuel, systems for the collection and disposal of municipal wastes and wastewater (sewers), and — of particular importance to sustainability, — systems for materials recycle. Transportation systems include roads, railroads, and airports, as well as waterways constructed or modified for transport on water. The anthrospheric segments used in food production include cultivated fields for growing crops and water systems for irrigation. A variety of machines, including automobiles, trains, construction machinery, and airplanes are part of the anthrosphere. The communications sector of the anthrosphere includes radio transmitter towers, satellite dishes, and fiber optics networks. Oil and gas wells are employed for extracting fuels from the geosphere and mines are excavated into the geosphere for removing coal and minerals.

The Crucial Infrastructure

A critical part of the anthrosphere may be classified as **infrastructure**. Infrastructure is generally considered to be parts of the anthrosphere used by large numbers of people in common. It consists of utilities, facilities and systems essential to a properly operating society. Physical components of the infrastructure include electrical power generating facilities and distribution grids, communications systems, roads, railroads, air transport systems, airports, buildings, water supply and distribution systems, and waste collection and disposal systems. A very important part of infrastructure is non-physical, composed of laws, regulations, instructions, and operational procedures. Because they are used in common by many people, crucial parts of the infrastructure are in the public sector; other segments are privately owned and operated. For example, major airports are almost always publicly owned whereas the aircraft that serve them are generally owned by private corporations.

Consider a computer operating system as infrastructure. The use of the system enables a computer to run programs for word processing, record keeping, calculation, drawing, communication, and other common computer operations. The operating system enables the computer to properly record, store, correlate, and output the products of the programs that it operates. By analogy, the infrastructure of the anthrosphere facilitates infrastructure activities including acquisition and processing of materials, the conversion of materials to manufactured items, and the distribution of such items. Crash-prone computer systems that are outdated or poorly designed in the first place cause lost productivity and general distress to the computer user. Similarly, an outdated, cumbersome, poorly designed, worn-out anthrospheric infrastructure causes economic systems and societies to operate in a very inefficient manner that is inconsistent with sustainability. Catastrophic failure can result as has occurred with cascading breakdowns of electrical power grids or failure of wastewater treatment systems resulting in discharge of sewage to streams.

Deterioration of the infrastructure is a continuing concern. One of the greatest problems is corrosion, a chemical process in which metals, such as the steel that composes bridge girders, tend to revert to the state in which they occur in nature (in the case of steel, rust). Human negligence, misuse and vandalism can all cause premature loss of infrastructure function. A major concern with terrorism is potential damage to infrastructure including cybercrime that could cripple electrical distribution systems. Infrastructure problems frequently begin with improper design. Sustainability requires that elements of the infrastructure be properly designed, maintained, and protected to avoid the expense and material and energy required to rebuild infrastructure if it fails before its expected lifetime is up.

To date much of infrastructure has been dedicating to thwarting what nature does naturally, often a losing proposition in the long run. A prime example consists of levees constructed along rivers which work well until overwhelmed by extraordinarily heavy precipitation events. Much more consideration must be given to sustainability and the maintenance of environmental quality in the development of infrastructure. Examples include highly effective waste treatment systems with recovery of materials and energy from wastes, high-speed rail systems to replace inefficient movement of people and freight by private carriers, and electrical systems that use wind power to the maximum extent possible.

The Sociosphere

The **sociosphere** is the societal organization of people including their governments, laws, cultures, religions, families, and social traditions and is a critical part of infrastructure. A well functioning sociosphere enables people to lead good lives within a sustainable environment and economic system. Largely because of disfunctional social systems, the quality of life and the environment in some countries with substantial resources, especially of petroleum, is often sub-standard. Societies in countries with dictatorial, corrupt governments that do not nurture human rights are not beneficial in the maintenance of sustainability. Sustainability and quality of life are also not well served by anti-government creeds that reject the role of well-functioning governments in implementing sensible well-administered laws and regulations designed to protect the environment and maintain sustainability.

An important consideration in the sociosphere is the science of **economics**, which describes the production, distribution, and use of income, wealth, and materials (commodities). Much of economics as it is usually practiced is inconsistent with the development of sustainability upon which functional economic systems must ultimately depend. Economic value has traditionally been measured in terms of financial and material possessions with emphasis on growth and with an arrow view of the environment. Earth has been largely regarded as a part of the economic system from which materials may be extracted, which is to be “developed” with structures and other artifacts of the anthrosphere, and into which wastes are to be discarded. Such an approach is putting an unacceptable strain on environmental support systems and Earth’s natural capital. Amore enlightened economic view regards Earth’s natural capital as an endowment. As with financial endowments, Earth’s endowment of natural capital should be nurtured, with only a portion of its income spent for immediate needs and the rest devoted to enhancing the natural capital. Therefore, it is essential for sustainability that economics be viewed as a part of Earth’sgreater environmental system, rather than viewing the environment as a subsection of a world economic system. Instead of defining wealth in material possessions it should be measured in terms of well-being and satisfaction with life, operating within rules that promote and require sustainability.

The Human Microsociosphere

The immediate environment in which humans carry out their daily activities may be regarded as a human microsociosphere. For many people recent years have seen a marked change in this microenvironment as the consequence of a flood of electronic devices including personal computers, cellular telephones, and other devices that flood individuals with information and communications. Some psychological studies have suggested that this deluge of information is changing human behavior, not necessarily in beneficial ways. Many people engage in multitasking, for example by texting or talking on cell phones while working or performing other tasks. The consequences of this can even be deadly as happens when people get into automobile accidents while talking or — worst of all — texting on a cell phone. Some people have several computers and screens at their workplace and attempt to follow several streams of information simultaneously. It is the feeling of some reputable neuroscientists that this kind of activity forces the human brain to function in ways that it has not evolved to handle making multitaskers more stressed, impatient, impulsive, and forgetful. Extreme cases have been documented of people who fall asleep with a laptop computer on their chest and whose first action after waking up is to connect to the internet.

Despite the benefits of modern computer and communications technology, the “always-plugged-in existence” that many people now lead has a definite downside. Not the least of these harmful effects can be upon human social interaction in which the major kind of interaction is through a computer rather than with other human beings. On the other hand, e-mail and other modes of electronic communication have made it possible for people to stay in constant, virtually instantaneous contact and to expand their circle of human contact, even if it is over a computer screen. The challenge of dealing with the kinds of problems discussed here is expected to be most acute for the increasing numbers of people who work from home on computers.

8.7: Cycles of Matter

The physical connections among the environmental spheres are largely through cycles of matter. Involving physical processes, chemical reactions, and biochemical processes, they are called **biogeochemical cycles**. They are commonly named for the major element involved in each, usually an essential organism nutrient including carbon, nitrogen, oxygen, sulfur, and phosphorus. A particularly important cycle is the hydrologic cycle of water shown in Figure 8.1. In Figure 8.5 aspects of the **rock cycle** are shown in which molten rock solidifies, undergoes weathering, maybe carried by water and deposited as sedimentary rock, is converted to metamorphic rock by heat and pressure, and is eventually buried at great depths and melted to produce molten rock again. Anthrospheric processes are also very much involved in the important cycles of matter such as the input of chemically fixed nitrogen synthesized from atmospheric N_2 in the nitrogen cycle.

The two major parts of biogeochemical cycles are the **reservoirs** in which matter is contained for some time and the **conduits** through which matter and energy are moved. Oceans, the atmosphere, parts of Earth's crust, and organisms are reservoirs of matter. The atmosphere acts as a conduit to carry water vapor in the hydrologic cycle and streams carry sedimentary matter in the rock cycle. **Endogenic cycles**, of which the phosphorus cycle is an example, are those that occur below or directly on the surface of the geosphere without a significant atmospheric component; most biogeochemical cycles are **exogenic** cycles in which the atmosphere serves as a conduit and often as a reservoir.

Figure 8.8 illustrates one of the key biogeochemical cycles, the carbon cycle. An important reservoir of carbon is in the atmosphere as carbon dioxide. Photosynthetic processes by plants extract significant amounts of carbon from the atmosphere and fix it as biological carbon in the biosphere. In turn, animals and other organisms in the biosphere release carbon dioxide back to the atmosphere through the respiration processes by which they utilize oxygen and food for energy production. More carbon dioxide is released to the atmosphere by the combustion of biological materials such as wood and fossil fuels including coal and petroleum. Carbon dioxide from the atmosphere dissolves in water to produce dissolved carbon dioxide and inorganic carbonates. Solid carbonates, particularly limestone, dissolve in bodies of water to also produce dissolved inorganic carbon. Respiration of organic matter by organisms in water and sediments also produces dissolved inorganic carbon species in water. Large amounts of carbon are held in the geosphere. The major forms of this carbon are fossil carbon of ancient plant origin held by fossil fuels, such as coal and petroleum, and inorganic carbon in carbonate

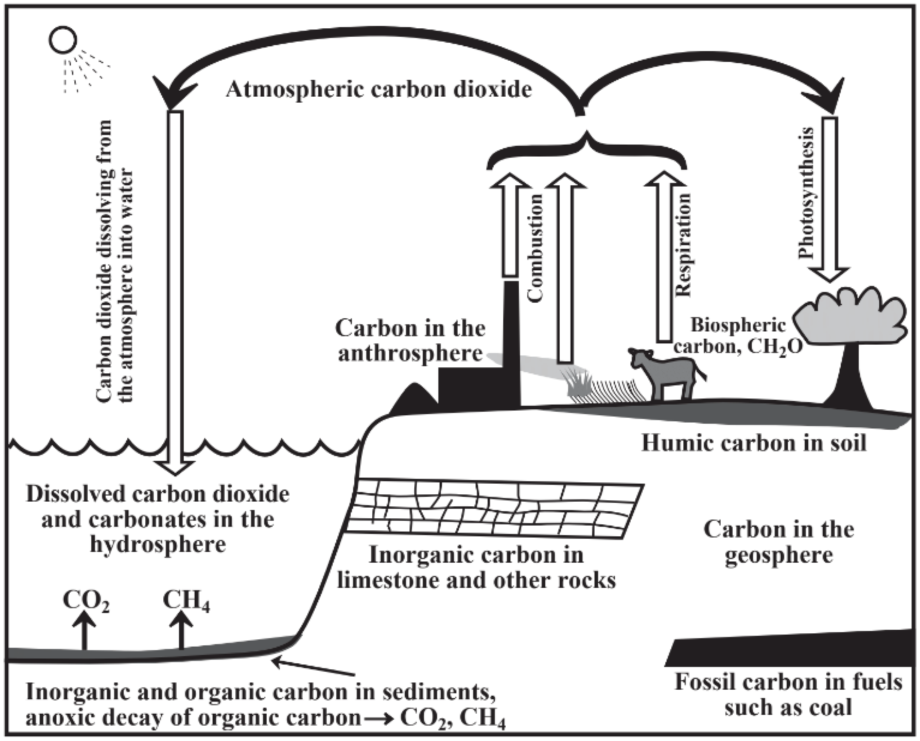

Figure 8.8. The carbon cycle showing the various reservoirs and conduits of carbon species in the environment. Because some important carbon compounds contain oxygen and elemental oxygen is released to the atmosphere by the photosynthetic process that fixes carbon from atmospheric carbon as biomass, the carbon cycle is closely related to the oxygen cycle.

rocks, especially limestone. Organic carbon from partially degraded plant material is present as humic material in soil, a source that is added to by organisms breaking down plant biomass from the biosphere.

The carbon cycle is extraordinarily important in maintaining sustainability because a major part of it is the fixation of carbon from highly dilute atmospheric carbon dioxide into biomass by photosynthesis carried out by green plants. Biomass is a source of food, chemical energy, and raw materials and the carbon cycle contains the main pathway by which solar energy is captured and converted to a form of energy that can be utilized by organisms and as fuel.

Other important cycles of matter are linked to the carbon cycle. The oxygen cycle describes movement of oxygen in various chemical forms through the five environmental spheres. At 21% elemental oxygen by volume, the atmosphere is a vast reservoir of this element. This oxygen becomes chemically bound as carbon dioxide by respiration processes of organisms and by combustion. The reservoir of atmospheric oxygen is added to by photosynthesis. Oxygen is a component of biomass in the biosphere and most rocks in Earth's crust are composed of oxygen-containing compounds. With its chemical formula of H_2O, water in the hydrosphere is predominantly oxygen.

In addition to the carbon and oxygen cycles described above, three other important life-element cycles are those of nitrogen, sulfur, and phosphorus:

•**Nitrogen cycle**: Biochemically bound nitrogen is essential for life molecules including proteins and nucleic acids. Although the atmosphere is about 80% by volume elemental N_2, this molecule is so stable that it is difficult to split it apart so that N can combine with other elements. This process is performed in the anthrosphere by the synthesis of NH_3, from N_2 and H_2 over a catalyst at high temperatures and very high pressures. Furthermore, air pollutant NO and NO_2 form from the reaction of N_2 and O_2 under the extreme conditions in internal combustion engines. In contrast, some bacteria, including *Rhizobium* bacteria growing on the roots of legume plants, convert atmospheric nitrogen to nitrogen compounds under the very mild conditions just below the soil surface. Plants convert nitrogen in NH_4^+ and NO_3^- to biochemically bound N. As part of the nitrogen cycle, biochemically bound nitrogen is released as NH_4^+ by the biodegradation of organic compounds. The nitrogen cycle is completed by microorganisms that use NO_3^- as a substitute for O_2 in energy-yielding metabolic processes and release molecular N_2 gas to the atmosphere. Other than nitrogen fixation in the anthrosphere and formation of nitrogen oxides in the atmosphere from lightning discharges, most transitions in the nitrogen cycle are carried out by organisms, especially microorganisms.

•**Sulfur cycle**: The sulfur cycle includes both chemical and biochemical processes and involves all spheres of the environment. Chemically combined sulfur enters the atmosphere as pollutant H_2S and SO_2 gases, which are also emitted by natural sources including volcanoes. Large quantities of H_2S are produced by anoxic microorganisms degrading organic sulfur compounds and using sulfate, SO_4^{2-}, as an oxidizing agent and discharged to the atmosphere. Globally, a major flux of sulfur to the atmosphere is in the form of volatile dimethyl sulfide, (CH_3S), produced by marine microorganisms. The major atmospheric pollutant sulfur compound is SO_2 released in the combustion of sulfur-containing fuels, especially coal. In the atmosphere, gaseous sulfur compounds are oxidized to sulfate, largely in the forms of H_2SO_4 (pollutant acid rain) and corrosive ammonium salts (NH_4HSO_4) which settle from the atmosphere or are washed out with precipitation. The geosphere is a vast reservoir of sulfur minerals including sulfate salts $(CaSO_4)$, sulfide salts (FeS), and even elemental sulfur. Sulfur is a relatively minor constituent of biomolecules, occurring in two essential amino acids, but various sulfur compounds are processed by oxidation-reduction biochemical reactions of microorganisms.

•**Phosphorus cycle**: Unlike all the exogenous cycles with an atmospheric component discussed above, the phosphorus cycle is endogenous with no significant participation in the atmosphere. It is an essential life element and ingredient of DNA as well as ATP and ADP through which energy is transferred in organisms. Dissolved phosphate in the hydrosphere is an essential nutrient for aquatic organisms, although excessive phosphate may result in too much algal growth causing an unhealthy condition called eutrophication. Phosphorus is abundant in the geosphere, especially as the mineral hydroxyapatite, chemical formula $Ca_5OH(PO_4)_3$. Significant deposits of phosphorus-rich material have be enformed from the feces of birds and bats (guano).

Questions and Problems

Access to and use of the internet is assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be "right."

1.Observations such as heavy clouds, sometimes torrential rains, and humid air might lead to the conclusion that the atmosphere is a major reservoir of water. Using internet resources, find out if this is true and compare the amount of water in Earth's atmosphere to that in the oceans.

2.Suggest a role played by the tropopause in the hydrologic cycle. Without the tropopause, would Earth even have a hydrologic cycle?

3. Water of the Colorado River of the U.S. is essentially fully committed for irrigation and municipal water supplies. What fraction of the Mississippi River discharge would be equivalent to the amount of water used from the Colorado River?

4. Argon and neon are byproducts of the production of another important industrial product. What is the main process of which these two gases are byproducts?

5. It is stated in this chapter that if the stratospheric ozone layer were in a pure layer of ozone at Earth's surface, the layer would be only about 3 millimeters thick. According to the ideal gas law, a mole of gas occupies 22.4 liters at a temperature of 273 K and a pressure of 1 atmosphere, very close to average conditions at sea level. Using this information calculate a reasonable estimate of the total mass of ozone in the ozone layer.

6. Although the ozone layer mentioned in the preceding question is a very good thing and even essential for human life, where in the atmosphere is ozone detrimental? Explain.

7. Long before humans were able to reach the atmospheric region of the ionosphere scientists observed the reception of radio waves transmitting over long distances far beyond line-of-sight, a "skipping" effect that enabled (at times, with luck) short wave transmissions across the Atlantic. The hypothesis was that the signals were bouncing off a layer of ions many kilometers up in the atmosphere. They also observed that longer distance transmission was possible at night. From this information suggest how ions are formed in the ionosphere and why it raises during nightime.

8. What is a common air pollutant that is associated with the sulfur cycle?

9. Some large volcanic eruptions cause significant global cooling whereas the climatic effects of other, equally large eruptions are negligible. Very little, if any of the cooling is caused by volcanic ash ejected to the atmosphere, large as the amounts of ash may be. Give a plausible explanation for these observations.

10. Soil is formed over very long periods of time beginning with igneous rock. Explain why soil forms faster in wet, temperate climates subjected to seasonal changes than it does in hot, dry regions where it may be largely absent.

11. What lessons are offered by the biosphere for the development of workable systems of industrial ecology?

12. What process in the anthrosphere is most closely analogous to photosynthesis by plants and algae in the biosphere? Explain

13. Consider your computer as a system of industrial ecology. What is its infrastructure? To which parts of an industrial ecosystem is it analogous? Consider how word processing, data, and graphics were handled in the days when typewriter, calculator, and paper were the instruments of choice and suggest how a computer recycles data as compared to those times.

14. Look up the definition of economics, especially if one can be found in older textbooks. Suggest an alternate definition that is consistent with sustainability and the preservation of Earth's natural capital.

15. Since about 1980 the classification of organisms such as the generally recognized kingdoms of organisms has undergone significant change. Suggest a development that has enabled this change to occur.

16. What are plankton? What kind of plankton are especially important for aquatic ecosystems?

17. By around 1800 one form of renewable energy was dominant in the generation of power for applications such as grinding grain for flour and sawing wood, but was not usable during the coldest winter months. Suggest the source of power and why it was not usable during winter.

18. Suggest the major aspects of the silicon cycle. Is it exogenous or endogenous? Does it have a biospheric component?

Supplementary References

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CHAPTER OVERVIEW

9: Water - the Ultimate Green Substance

“Although the wastewater from Mexico City that the farmers in Mexico’s Mezquital valley use for irrigating their crops is a foul concoction that sometimes causes boils and other ailments to those who contact it, the farmers that use it are concerned that a new drainage and treatment system may remove nutrients and enable recycle of water back to the city depriving them of the irrigation water upon which their livelihoods depend.

9.1: H_2O - Simple Formula, Remarkable Molecule
9.2: Occurrence, Availability , and Utilization of Water on Earth
9.3: Water Chemistry
9.4: Water Pollution
9.5: Greening of Water - Purification Before Use
9.6: Wastewater Treatment
9.7: Advanced Wastewater Treatment and Recycling
9.8: The Many Uses of Water
9.9: Hot Water - Pressurized Subcritical Water
9.10: Supercritical Water
Literature Cited
Questions and Problems
Supplementary References

9.1: H_2O - Simple Formula, Remarkable Molecule

Water composes the hydrosphere, which is described and discussed in Section 8.2. This chapter enlarges upon that discussion and the crucial role of water in the environment. In this chapter and elsewhere in the book the term **natural water** is used in reference to water that occurs in the environment in comparison to water in the anthrosphere, such as water in municipal water distribution systems. Water has a special place in living organisms and the environment. The quality and availability of water are of the utmost importance to humans and the environment. Although scarce and badly polluted in many parts of the world, water is arguably the most recyclable of the substances that compose Earth's green capital and it is accurately described as the ultimate green substance.

This chapter addresses major aspects of the sustainability of water. The first of these is water pollution, which degrades water quality and can make it unfit for use or to support life. The second major area addressed is how water quality can be maintained and enhanced, largely through various water treatment processes. A third major area is water pollution prevention and a fourth is recycling of the water resource which is arguably nature's most recyclable material.

The chemical formula of water, H_2O, is probably the best known of all compounds. This simple formula represents a substance that is unique and complex in its behavior. These special properties are due to the molecular structure of the H_2O molecule represented in Figure 9.1. There are four pairs of electrons in the outer electron shell of the O atom in the H_2O molecule, two of which compose the bonds between the H and O atoms and two of which are lone pairs. The distribution of these pairs as far apart as possible around an imaginary sphere representing the outer electron shell of the O atoms results in the two H-O bonds being located at an angle rather than a straight line. The side of the molecule with the two H atoms has a partial positive charge and the side with the two non-bonding pairs has a partial negative charge, so the molecule is polar. This polarity and the ability of the H atoms on one molecule to form hydrogen bonds to O atoms on other molecules determine the remarkable chemical and physical diversity of water.

Especially because of their hydrogen bonding capability, water molecules are strongly attracted to each other. This means that a large amount of heat energy must be put into a mass of water to enable the molecules to move more rapidly as the temperature is raised. This gives water a very high **heat capacity**. A very large amount of energy must be put into a mass of ice to break the hydrogen bonds holding the molecules in place in the solid as it melts and an equally large amount of heat energy is released when liquid water freezes. Thus water has a very high **latent heat of fusion**. Even more energy per unit mass is required to convert liquid water to vapor (steam) and an equal amount of energy is released when water vapor condenses to liquid. This means that water has a very high **heat of vaporization**.

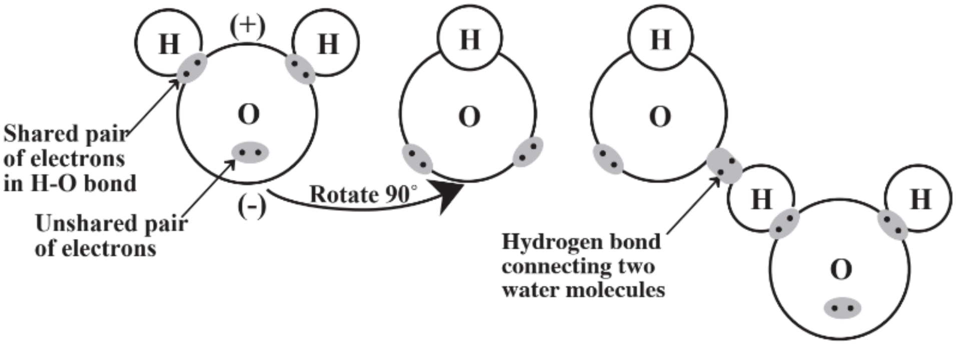


Figure 9.1. Representation of the polar nature and hydrogen bonding capability of the water molecule that give it unique properties that determine its essential role in living organisms and the environment.

The ability of water to absorb, release, and store heat is crucial to its role in the environment and its practical uses.[1] Water's high heat capacity stabilizes temperatures of organisms and geographical areas. Steam produced in a boiler can be transferred through insulated pipes to remote locations and condensed to release heat. The heat released when atmospheric water condenses warms the surrounding air and is the driving force behind tropical storms. Europe owes its relatively mild weather despite its northern latitudes to heat carried by water across the North Atlantic Ocean from the Gulf of Mexico. As the water releases heat and cools along the European coasts, its density increases and it flows at lower ocean depths back to the Gulf of Mexico to repeat the cycle. Water's high latent heat of fusion stabilizes temperatures of bodies of water at water's freezing point ($0^\circ C$).

In addition to those listed above, there are other unique and environmentally important qualities of water. It is an excellent solvent, especially for ionic substances, making it important in the transport of nutrients and wastes in the biosphere and in the dissolution, transport, and deposition of minerals in the geosphere. Water has a very high surface tension, a controlling factor in physiology and a property involved in formation of drops in rainfall. The temperature/density relationship of water causes bodies of water to become stratified (see Figure 9.4), a property that strongly affects the chemical behavior of water in stratified bodies of water. The fact that the maximum density of water occurs as a liquid at 4°C means that solid ice floats. If that were not the case, bodies of water in northern climates would become frozen solid with only a surface layer thawing during the summer. Water is largely transparent to visible light, which can penetrate the liquid to some depth and enable photosynthetic phytoplankton and some bottom-rooted plants in shallow water regions to carry out photosynthesis and produce the biomass that is the basis of aquatic food chains (see Section 8.5).

9.2: Occurrence, Availability , and Utilization of Water on Earth

Much of Earth’s approximately 1.4 billion cubic kilometers (1.4×109km3) water that is not chemically bound circulates through the hydrologic cycle represented in the illustration of the hydrosphere shown in Figure 8.1. About 97.6% of this water is salt water in oceans. Of the approximately 33 million km^3 of water remaining, 86.9% is in the solid form in snowpack, ice and glaciers; 12.0% is accessible water under ground (groundwater), 0.37% is in freshwater lakes, reservoirs, and ponds; 0.31% is in saline lakes; 0.19% is soil moisture; 0.19% is in biospheric organisms; 0.039% is in the atmosphere as vapor and cloud droplets; 0.011% is in wetlands; and only 0.0051% constitutes the water in all Earth’s rivers, streams, and canals. Therefore, a remarkably small percentage of Earth’s water is relatively available for use, a major factor in the sustainability of this crucial part of Earth’s natural capital.

Fresh surface water and groundwater are the major sources for human use. Desalinated seawater is a growing source of fresh water in some areas that do not have access to this valuable resource. Most seawater desalination plants are in the Middle East, an arid region with generally abundant sources of energy that can be used for desalination. The world’s largest desalination plant is the Jebel Ali multi-stage flash distillation unit in the United Arab Emirates that can produce 300 million cubic meters of potable water per year. There are significant resources of brackish (saline) groundwater throughout the world. In many cases this water has a lower salt content than seawater making it easier and more economical to desalinate.

A major concern regarding water’s availability is its uneven distribution with respect to time and location. Some areas experience tremendous rainfall and flooding during wet (monsoon)seasons with dry conditions in between. Whereas these fluctuations are predictable and compensation may be made for them, greater problems occur with long-term droughts. Regions of Africa are periodically afflicted with droughts that last for several years, killing crops and animals and inflicting great hardship on the people in the region. Evidence from tree rings indicates a pre-Columbian drought of almost three centuries duration in what is now the southwestern U.S.! Uneven geographic distribution of water occurs throughout the world and is illustrated for the continental U.S. in Figure 9.2. It is seen that precipitation is generally adequate in the eastern part of the country, although damaging droughts do occur in this region. However, the western continental U.S. has a shortage of precipitation with essentially permanent drought conditions in some regions including Nevada, Arizona, and southern California. The problem is exacerbated by the popularity of these regions as areas in which people want to live and the demands that they put on limited water resources.

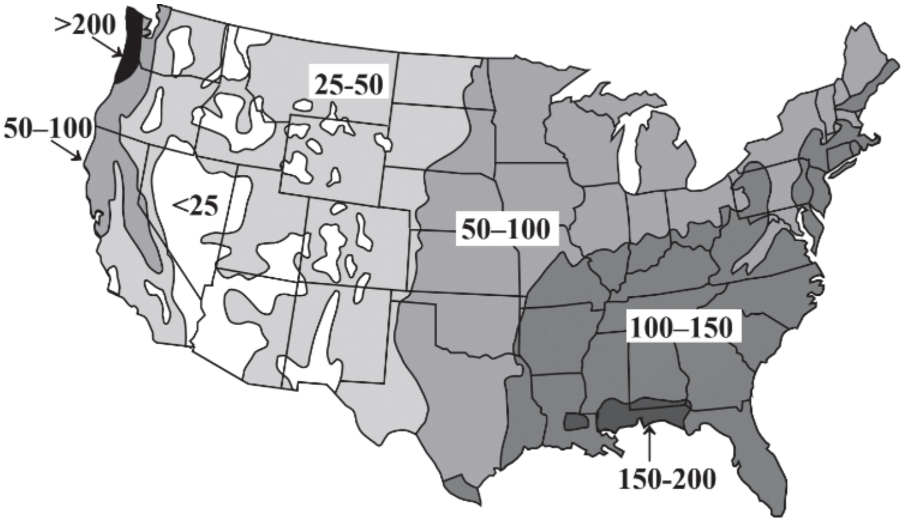


Figure 9.2. Distribution of average annual rainfall in the continental United States, amounts in centimeters per year.

Surface Streams of Water

A major source of water is surface water that flows in streams and rivers. The areas of land upon which precipitation falls to provide flows of surface water is called the **watershed**. Insofar as water utilization is concerned, watersheds constitute one of the most important connections between the geosphere and the hydrosphere; the nature of the watershed largely determines the quantity and quality of water available for human use. A good watershed retains water for a significant length of time, which reduces flooding, allows for a steady flow of runoff water, and maximizes recharge of water into groundwater reservoirs (aquifer recharge, Figure 9.3). Measures employed to enhance watershed quality include minimization of cultivation and forest cutting, especially on steeply sloping sections of watershed, construction of terraces and waterways planted to grass on cultivated land to minimize erosion and accumulation of sediment, construction of small impoundments on feeder streams of the watershed, and of course minimization of pollution such as from herbicides.

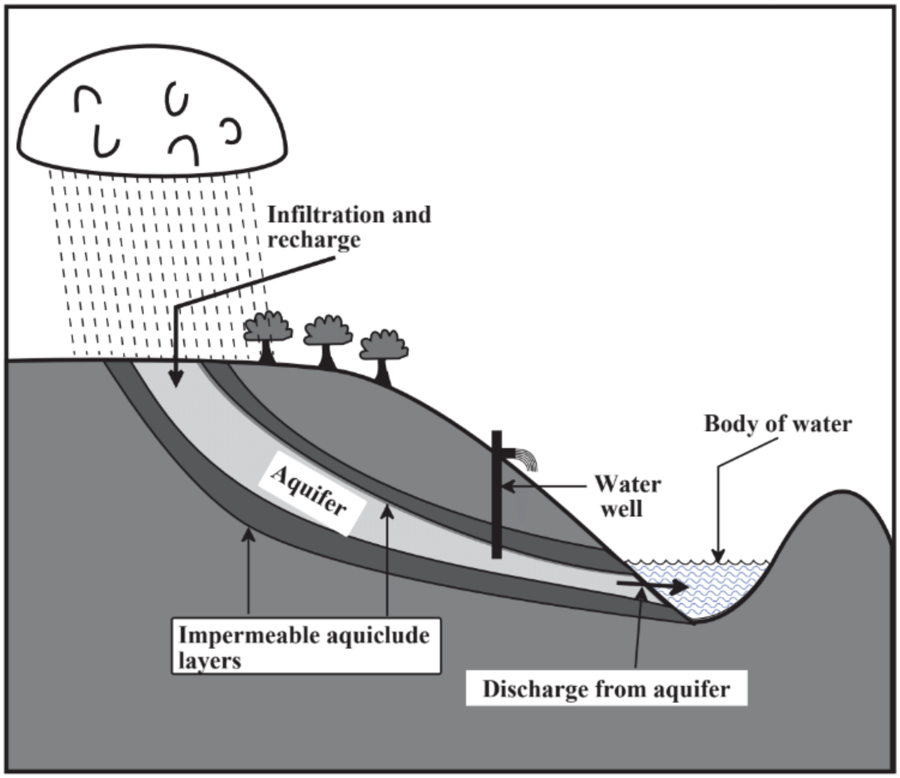


Figure 9.3. Illustration of groundwater in aquifers in the geosphere. Groundwater enters aquifers from surface water in recharge zones and is discharged through springs or pumped out through wells.

An important aspect of streams that affects water utilization and quality is their ability to mobilize sedimentary materials through erosion, transport materials along with stream flow, and deposit them as solids. Normally it is desirable for streams used as a source of water to have minimal sedimentary material, which has to be removed during water treatment.

Most rivers, once free flowing and unimpeded by human intervention, have been modified by humans to generate power, for water supply, and reduce effects of flooding. Beginning with impoundment of water from the Owens Valley in northern California and extending to the Feather, Sacramento, and Colorado rivers, Los Angeles' voracious thirst for water is served by a vast system of dams, canals, and tunnels. Diversion of water from the Owens valley has turned a formerly productive agricultural area into one of limited agricultural use. Many of the adverse effects of water diversion have resulted from dams built to confine rivers. As a result of dam construction many once beautiful river valleys have been covered with water and productive farmland in river valleys has been lost. For example, the beautiful Hetch-Hetchy Valley in Yosemite National Park in California has been inundated since the early 1900s by construction of a dam built to provide water and hydroelectric power to San Francisco. Serious proposals are now being considered to remove the dam and restore the valley to its former beauty.

Standing Bodies of Water

Much of the water that humans use comes from standing bodies of water including natural lakes and reservoirs constructed by placing dams on rivers. **Wetlands** are bodies of water shallow enough to support the growth of bottom-rooted plants. **Estuaries** form where fresh river water flows into oceans. They have unique physical, chemical, and biological properties because of the mixing of fresh water and saltwater. Wetlands and estuaries are important breeding grounds for a number of organisms and it is crucial that they be preserved. Many wetland areas have been drained for agricultural land and an important effort in conservation is their preservation and restoration.

An important characteristic of a lake or reservoir that develops during the summer as a result of the temperature/density behavior of water is **stratification**, shown in connection with water chemistry in Figure 9.4. Exposed to atmospheric oxygen and light, the top layer, the epilimnion, normally has a significant concentration of dissolved oxygen and is **oxic**. Photosynthetic algae thrive in the epilimnion and during daylight produce O2 by photosynthesis. Isolated from atmospheric oxygen, the hypolimnion located in the bottom regions of the body of water becomes **anoxic** as O_2 is consumed by bacteria. Chemically oxidized species including CO_2, NO_3-, and SO_4^{2-} predominate in the epilimnion and chemically reduced species such as CH_4, NH_4^+, and H_2S are found in the hypolimnion. During fall in temperate climates, cooling of the epilimnion causes it to become more dense and to sink resulting in **overturn** of the body of water. This phenomenon tends to stir up sedimentary material and release nutrients from the sediment into the water.

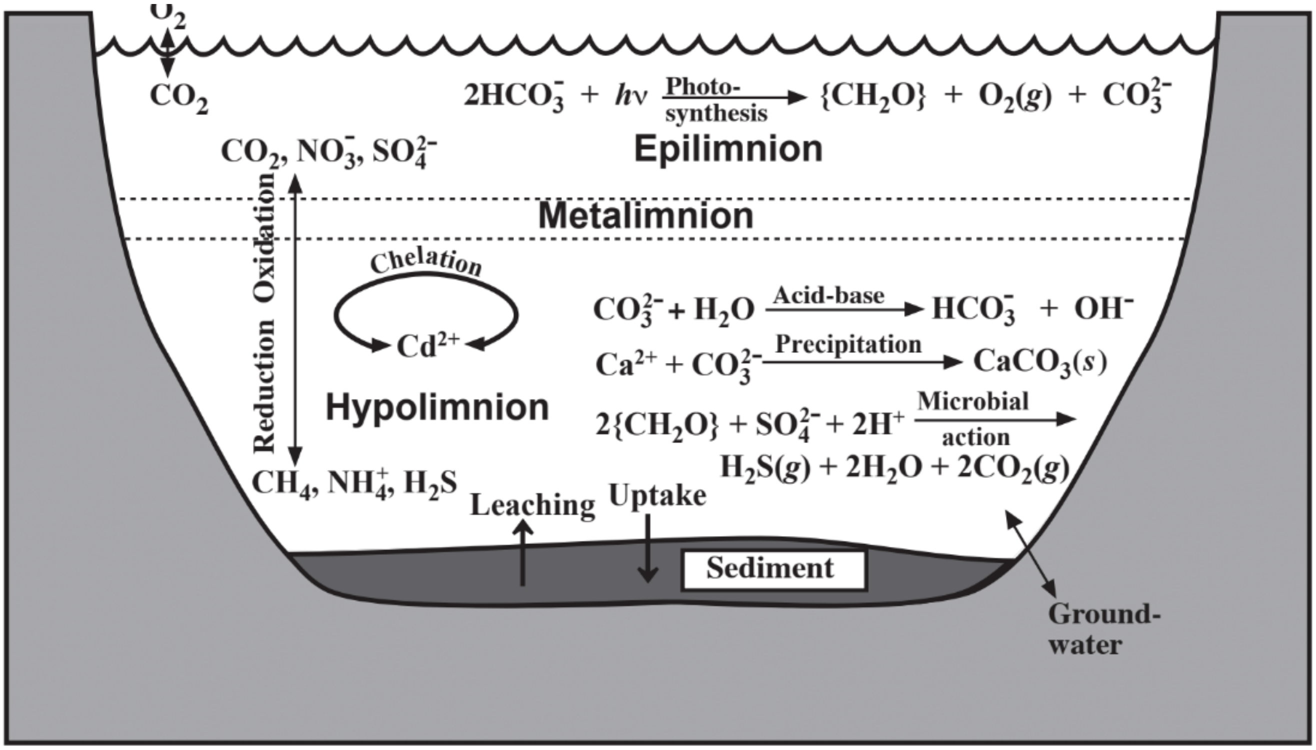


Figure 9.4. Water chemistry as affected by stratification of a body of water in which a warmer, less dense layer of water in the epilimnion resides above a cooler, more dense hypolimnion. This stratification prevents oxygen from penetrating to lower depths where chemically reduced species (CH_4, NH_4^+, H_2S) predominate. In the oxic epilimnion chemically oxidized species (CO_2, NO_3^-, SO_4^{2-}) are present.

Groundwater

Figure 9.3 illustrates the pathway of groundwater into **aquifers** from precipitation falling on a watershed and infiltrating the aquifer through a recharge zone. The zone of saturation consists of the geospheric rock and soil layers in which all the pores are filled with water, the top of which defines the water table. The fraction of the aquifer formation consisting of pores is the **porosity** and the ability of the formation to allow movement of water is its **permeability**. Generally, high permeability and high porosity are desirable properties of aquifer formations that allow relatively large amounts of water to be withdrawn through water wells drilled into the aquifers. The quality of groundwater is strongly affected by its contact with mineral formations in the geosphere. Infiltration through rock and sand purifies water filtering out microorganisms and suspended solids. Contact with geospheric solids largely determines the chemical composition of water by adding desirable levels of dissolved Ca^{2+} ion and alkalinity and sometimes undesirable solutes such as sodium chloride.

Artesian Wells

Artesian aquifers are those confined by dense clay or shale such that water flows naturally from an **artesian well** drilled into them. The name comes from the Roman city of Artesum at the site of the French town of Artois known for the free-flowing water from wells dug in the Middle Ages. Artesian wells are often highly prized sources of water. Some modern day bottling companies have leased or purchased sites of artesian wells and advertise their product as artesian water, although it does not differ in quality from pumped well water. Many artesian wells have lost their free-flowing qualities because of depletion of their water resource.

9.3: Water Chemistry

Some of the chemical and biochemical phenomena that occur in water are illustrated in Figure 9.4.[2] Physically, the body of water shown is stratified during summer months with a warmer, less dense epilimnion floating over a colder, more dense hypolimnion, with little mixing between the two. The epilimnion is in contact with the atmosphere and has a significant content of dissolved oxygen. Therefore, oxidized inorganic species predominate in the epilimnion. The hypolimnion is anoxic because microorganisms consume all the dissolved O_2 in it and it is not in contact with the atmosphere. Reduced inorganic species predominate in the hypolimnion. A major factor in the chemistry of this system is the biochemical photosynthetic production of organic matter represented $\{CH_2O\}$. Organic matter is a biochemical reducing agent and when it sinks into the hypolimnion it is oxidized by microorganism-mediated processes that, for example, reduce NO_3^- and SO_4^{2-} to NH_4^+ and H_2S, respectively. Two important microbially-mediated oxidation-reduction reactions of$\{CH_2O\}$ are reaction with dissolved O_2,

$$(\mathrm{CH_2O}) + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \tag{9.3.1}$$

which depletes dissolved oxygen in water making the hypolimnion anoxic and methane fermentation,

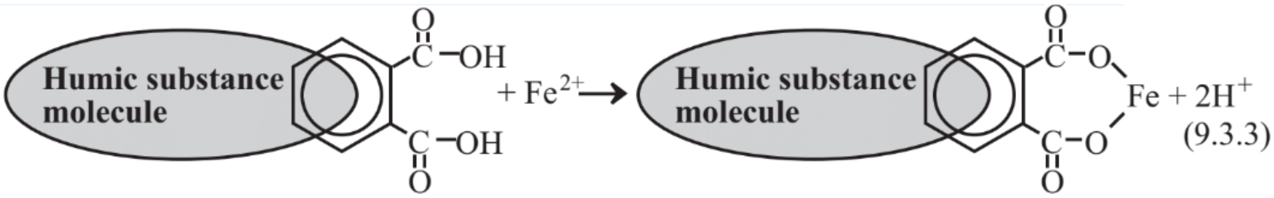
$$2\,(\mathrm{CH_2O}) \rightarrow \mathrm{CH_4} + \mathrm{CO_2} \tag{9.3.2}$$

which produces combustible methane gas. The ability of $\{CH_2O\}$ to react with dissolved O_2 is a measure of the potential of water to become depleted in the oxygen needed by fish and other aquatic organisms and is expressed as **biochemical oxygen demand**, **BOD**, an important water quality parameter.

The photosynthetic biochemical production of biomass results in some important chemical reactions. As illustrated in Figure 9.4, algae use dissolved HCO_3^- ion as a carbon source and in so doing produce carbonate ion, CO_3^{2-}. Two additional reactions of carbonate ion are shown in Figure 9.4. One is its hydrolysis reaction with H_2O molecules back to HCO_3^- with production of OH^- ion. This makes the water basic, an important aquatic acid-base reaction. A second reaction of carbonate is that with dissolved Ca^{2+} to produce solid $CaCO_3$, an important precipitation reaction in water that has been responsible for formation of large deposits of limestone.

All major oxidation-reduction reactions in natural water are carried out by microorganisms acting as catalysts and extracting energy released by the reactions. An example shown in Figure 9.4 is the biochemical reduction of SO_4^{2-} to H_2S. in which sulfate acts as an oxidizing agent to oxidize biomass ($\{CH_2O\}$) in the absence of molecular O_2. Taking place in the hypolimnion and sediments, this reaction is responsible for the foul odor of hydrogen sulfide in some bodies of water and swamps.

Another important phenomenon in natural water and wastewater is the formation of metal chelates in which metal ions are bound in two or more places by organic substances. Humic substances produced by the partial biodegradation of biomass are complex large organic molecules with numerous aromatic ring structures containing oxygen in functional groups including carboxyl (-CO2H) and phenolic hydroxyl (-OH). These groups can lose H+to produce negatively charged groups capable of bonding with metal ions as shown below for the chelation of Fe^{2+} ion:



(9.3.3)

The most important humic substances in water are the lower-molecular-mass fulvic acids. These species tend to chelate Fe^{2+} ion producing a yellow material called *gelbstoffe* (German for "yellow stuff.)" Metal ions bound with fulvic acid are hard to remove from water and, since iron is a very undesirable water impurity, drastic measures such as destruction of the fulvic acid with chlorine may be required to remove the chelated iron.

Phase Interactions in Aquatic Chemistry

Figure 9.4 illustrates the process of exchange of dissolved solutes in water with sediments. Interactions between water and solid, gas, and other liquid phases are very important in aquatic chemistry. Aquatic biochemical processes involve exchange of materials between water solution and cells of microorganisms. For example, when photosynthesis occurs in water (Figure 9.4), dissolved HCO_3^- ion is transferred into a cell of floating photosynthetic phytoplankton for conversion to biomass. As a product of this reaction gaseous O_2 is released from the cell, some of it dissolving in water and some floating to the top as O_2 bubbles. As noted above, the CO_3^{2-} ion generated as a byproduct of photosynthesis reacts with dissolved Ca^{2+} ion to produce solid $CaCO_3$. The reverse process occurs when bacterially-produced dissolved carbon dioxide reacts with solid calcium carbonate.

$$\mathrm{CO_2(aq) + H_2O + CaCO_3(s) \rightarrow Ca^{2+}(aq) + 2\,HCO_3^-(aq)} \tag{9.3.3}$$

to put calcium ion and bicarbonate ion into solution. Both of these species are important in water. The Ca^{2+} ion is responsible for **water hardness**, named for a tendency to form precipitates with soap anions that are useless for cleaning, and HCO_3^- is **water alkalinity**, the ability to neutralize acids.

A particular kind of phase that interacts with water consists of colloidal particles, which are very small particles of the order of a micrometer in size that are suspended in water. There are three kinds of colloidal particles as shown in Figure 9.5. Many significant materials exist as colloidal particles in water including bacterial and algal cells, clay minerals, soap, and a variety of pollutants. The behavior of colloids is intermediate between that of true solutions and bulk materials such as those in sediments. This behavior is strongly influenced by the very high surface-to-volume ratio of colloids. Aggregation of colloidal particles is an important and often challenging aspect of water treatment, for example in the settling and separation of microorganisms involved in the biological treatment of wastewater.

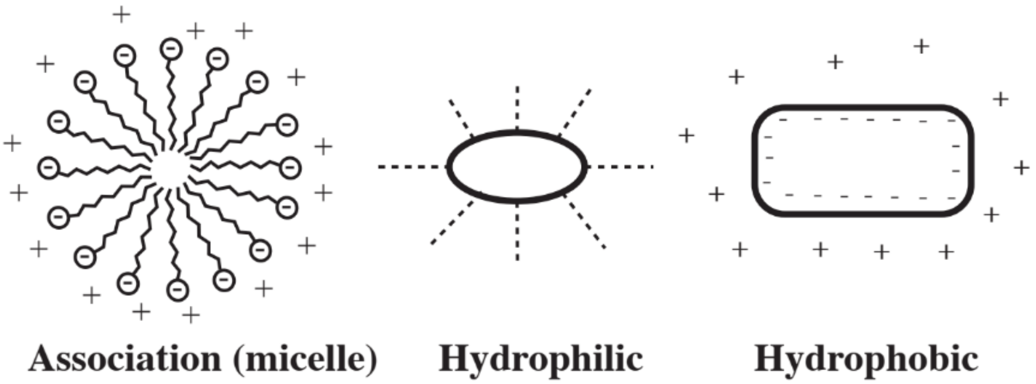


Figure 9.5. Representation of three kinds of colloidal particles in water. Association colloids are composed of micelles in which long hydrocarbon chains on fatty acid anions cluster in the center of the colloid and the anionic functional groups on the ends of the hydrocarbon chains are located around the periphery of the micelle in contact with water. Soap forms association colloids in water. Hydrophilic colloids are materials such as proteins or bacterial cells that are stabilized by their bonding to water. Hydrophobic colloids are repelled by water, but are stabilized by their electrical charges which prevent them from aggregating together.

Acid-Base Phenomena in Water

Natural water almost always contains acids capable of releasing H^+ ion and may contain solutes that can accept H^+ ion and thus act as bases. The most common acidic substance in water is dissolved CO_2, which may enter water from the atmosphere or in higher concentrations as a product of the microbial decay of organic matter. Dissolved carbon dioxide produces H^+ ion by the following reaction with water:

$$\mathrm{CO_2(aq) + H_2O \leftrightarrows H^+ + HCO_3^-} \tag{9.3.4}$$

The double arrows denote that the reaction is reversible. Since carbon dioxide is a weak acid, the equilibrium of the reaction lies to the left as expressed by the following acid dissociation constant in which pK_{a1}= -logK_{a1}:

$$\backslash \mathrm{K}_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = 4.45 \times 10^{-7} \quad pK_{a1} = 6.35 \tag{9.3.5}$$

The HCO_3^- ion can also lose H^+:

$$\mathrm{HCO_3^- \leftrightarrows H^+ + CO_3^{2-}} \tag{9.3.6}$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11} \quad pK_{a2} = 10.33 \tag{9.3.7}$$

Otherwise pure water in equilibrium with air contains some dissolved CO_2 from the atmosphere, which is 390 parts per million CO_2 by volume. Solubility calculations can be used to show that the dissolved carbon dioxide concentration water, $[CO_2(aq)]$, in equilibrium with air is 1.276×10^{-5} M (moles/liter). When each CO_2 reacts with H_2O, one H^+ and one HCO_3^- areproduced. Substitution into the equilibrium constant expression Equation 9.3.6 leads to $[H^+] = 2.38\times10^{-6}$ M, pH = 5.62, slightly more acidic than neutral pH 7. Therefore, rainwater is naturally slightly acidic. Natural water with a pH less than 5.62 likely contains pollutant strong acid, most commonly H_2SO_4 from acid rain.

Most water that has been in contact with the geosphere contains alkalinity, the ability to react with H^+ ion and neutralize acidity. Generally alkalinity is due to the presence of HCO_3^- ion which undergoes the following reaction with H^+ ion:

$$\mathrm{HCO_3^- + H^+ \rightarrow CO_2 + H_2O} \tag{9.3.8}$$

Alkalinity is normally introduced into water by the reaction of dissolved CO_2 with $CaCO_3$ mineral as shown in Reaction 9.3.4. Because of the presence of alkalinity, most natural waters such as those used to supply municipal water systems are slightly basic with a pH around 8 rather than being slightly acidic like rainwater.

9.4: Water Pollution

Water receives a number of different kinds of pollutants and moving water is one of the main pathways of pollutant transport. Water pollutants are of concern for a variety of effects. These include general water quality, toxicity, effects on aquatic organisms, esthetics, eutrophication, and water oxygen levels. Some of the main categories of water pollutants are discussed here.

Several kinds of pollutants are detrimental to water that is a source of water supply. **Taste**, **odor**, and **color** are caused by a variety of impurities. **Sediments** require removal and sometimes special measures are needed to coagulate and settle colloidal suspended matter. Acidity, alkalinity, and salinity at excessive levels are water pollutants.

Some pollutants are picked up by water as a natural consequence of its use in municipal water systems, which take in potable water fit to drink and discharge wastewater. One of the main ones of these consists of sewage including human wastes, food wastes, and other substances that get into water through bathrooms and kitchens. A major component of these water pollutants consists of biodegradable organic matter, abbreviated here as $\{CH_2O\}$ and commonly called **biochemical oxygen demand**, **BOD**, which rapidly depletes receiving water of its dissolved oxygen by the following microbially-mediated process:

$$(CH_2O) + O_2 \rightarrow CO_2 + H_2O \tag{9.4.1}$$

Another class of pollutants picked up in municipal water systems and produced in the biodegradation of sewage is composed of **algal nutrients**, primarily nitrogen (NH_4^+, NO_3^-), phosphates ($H_2PO_4^-$, HPO_4^{2-}), and potassium (K^+). Rather than being toxic, these materials cause algae to grow in excess in receiving waters producing too much biomass which degrades as shown in Reaction 9.4.1 and depletes the dissolved oxygen in the water, a process called **eutrophication**. **Detergents** are common pollutants in municipal wastewater and can be harmful because of their content of **surfactants** (basically, the ingredient that lowers water surface tension making it“wetter”) and **builders** added to assist detergent action, formerly a major source of phosphates in wastewater.

A variety of trace **inorganic compounds** can be water pollutants. These include algal nutrients and salts responsible for excess acidity, alkalinity, and salinity mentioned above. Other inorganic pollutants include odorous hydrogen sulfide (H_2S), oxygen-demanding sulfite (SO_3^{2-}),and, in rare cases from mineral processing waste, highly toxic cyanide, CN^-. Trace levels of a variety of elements can be undesirable pollutants. Especially significant of these are toxic **heavy metals** including lead, cadmium, and mercury and metalloid arsenic. **Organically-bound metals** are undesirable. As noted in Section 9.3, iron bound with humic substances causes water color and is particularly difficult to remove. **Methylated forms** of mercury and arsenic (those containing a $-CH_3$ group bound to the element) can be mobilized from sediments and get into water. Dimethylmercury, $Hg(CH_3)_2$, is particularly toxic and undergoes biomagnification through the food chain, accumulating in fish tissue. In addition to the methylated compounds, other **organometallic compounds** made synthetically can be troublesome toxic water pollutants. Until it was banned, tetraethyl lead used as a gasoline additive could get into water and more recently organotin compounds used in biocidal paints to prevent growth of organisms on ship hulls have been toxic to sediment-dwelling organisms.

In some cases **radionuclides** occur as water pollutants. Leakage of radioactive tritium, a form of hydrogen, has gotten into water from reactors. The radionuclide of most concern usually is radium from natural sources and a number of groundwater sources of water have been discontinued because of the presence of radium.

A variety of **organic compounds** occur as water pollutants. These include industrial chemicals, petroleum products (especially significant in light of the notorious 2010 leak from the Deepwater Horizon oil spill that dumped as much as 5 million gallons of crude oil into the Gulf of Mexico and caused billions of dollars in pollution damage to the Gulf and its shore areas), polychlorinated biphenyls (PCBs, now banned from manufacture but still sometimes encountered, especially in sediments), and dioxin. **Pesticides** are common water pollutants of which **herbicides** such as atrazine are a concern because of their widespread application to land. Some organic water pollutants call for particular attention because of their potential biological activity and toxicity. **Carcinogens** are an obvious case. **Pharmaceuticals** and their metabolites have emerged as a concern and are currently one of the "hottest" areas of water pollution research. A wide variety of these get into wastewater and sometimes into water supplies, though in minuscule quantities.

9.5: Greening of Water - Purification Before Use

From the air the San Marcos/ Cazones River near the city of Poza Rica, Mexico, has a beautiful green color. But this river's water is not what normally would be chosen as a water source (although by necessity it is so used), the reason being that its appearance denotes a major pollution problem because its green color indicates excessive growth of plants and algae (eutrophication) in the river, nourished by untreated sewage and other wastes discharged into it. This chapter discusses keeping water green, not in color but in terms of water quality.

For most uses water requires treatment. The processes used to treat water are generally similar for municipal, commercial, or industrial uses. This section addresses the major treatment processes applied to water supplies.

Municipal Water

The first steps in water treatment are usually physical, blowing air through it (aeration) and sedimentation to allow solids to settle from the water. Another benefit of water aeration is the oxidation of soluble Fe^{2+}, a very undesirable pollutant that causes staining of bathroom fixtures and clothing, to solid $Fe(OH)_3$, which settles from the water. A benefit of the formation of this gelatinous solid is that it acts as a **coagulant** that binds with colloidal impurities entrained in the water and causes them to settle. Another physical process to which municipal water is usually subjected is **filtration** to filter out solids. Filtration is usually over sand filters, but activated carbon, a form of carbon treated at high temperatures with steam or carbon dioxide to create pores and give it an enormous internal surface area, may be used as a filtration medium to remove organic substances.

Some water sources have too much dissolved Ca^{2+} (water hardness) that forms precipitates with soap and deposits solid $CaCO_3$ in pipes. Normally the dissolved calcium is present as calcium bicarbonate in which the anion present with Ca^{2+} is bicarbonate, HCO_3^-. Curiously, the method for removing this calcium is to add more calcium in the form of lime, $Ca(OH)_2$, a basic substance that converts the HCO_3^- to CO_3^{2-} and removes the dissolved calcium as solid $CaCO_3$ according to the following reaction:

$$\mathrm{Ca^{2+}(aq) + 2\,HCO_3^-(aq) + Ca^{2+}(aq) + 2\,OH^-(aq) \rightarrow 2\,CaCO_3(s) + 2\,H_2O} \tag{9.5.1}$$

The final step in water purification is **disinfection**, commonly by the addition of elemental chlorine gas, which reacts with water,

$$\mathrm{Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-} \tag{9.5.2}$$

to produce disinfectant HOCl that kills virus and bacteria in water. Hypochlorite salts of HOCl including NaOCl and $Ca(OCl)_2$ can also act as disinfectants. Chlorine and hypochlorites can react with low concentrations of added ammonia to produce chloramines such as NH_2Cl that remain in the water distribution system and maintain residual disinfection In the presence of residual organic matter such as humic substances, elemental chlorine may form potentially toxic chloroform, $HCCl_3$, and a class of related substances commonly called trihalomethane compounds. To prevent these compounds from forming, a common practice is the use of chlorine dioxide, ClO_2, which does not produce trihalomethanes. Chlorine dioxide is too dangerously reactive to move and too unstable to store so it is made on site by the reaction of sodium chlorite with elemental chlorine:

$$\mathrm{2\,NaClO_2(s) + Cl_2(g) \rightarrow 2\,ClO_2(g) + 2\,NaCl} \tag{9.5.3}$$

Therefore, potentially dangerous chlorine dioxide is prepared only when needed, in the quantities needed, where needed, which is in keeping with the best practice of green chemistry and technology.

Green Ozone

A greener alternative to chlorine-based water disinfectants in many respects is ozone, O_3. Pumped into water, this form of oxygen kills pathogens without producing the undesirable byproducts made by chlorine and it is actually more effective than chlorine in killing viruses. Ozone is produced from oxygen in air by a high-voltage electrical discharge through dried air as illustrated in Figure 9.6. The lifetime of ozone in water is short, so a small amount of chlorine must usually be added to ozonated water to maintain disinfection in the water distribution system.

Disinfection of water by ozonation is a virtually ideal example of green chemical practice. The only raw material is universally available air, which is free. Ozone is produced only where it is needed as it is needed, without byproducts. The ozone does not persist in water, decomposing to elemental oxygen. There is very little likelihood of producing harmful disinfection byproducts with ozone.

Water for Commercial and Industrial Use

A wide range of water quality is required for water destined for commercial and industrial use and for economic reasons the water is treated only as needed for its intended application. Water used for cooling generally requires little treatment, the main requirement being that it is wet. At the other end of the scale water used in the semiconductor industry has to be hyperpure. Pathogens obviously must be removed for water employed in food processing and corrosive and scale-forming contaminants must be removed from boiler feedwater.

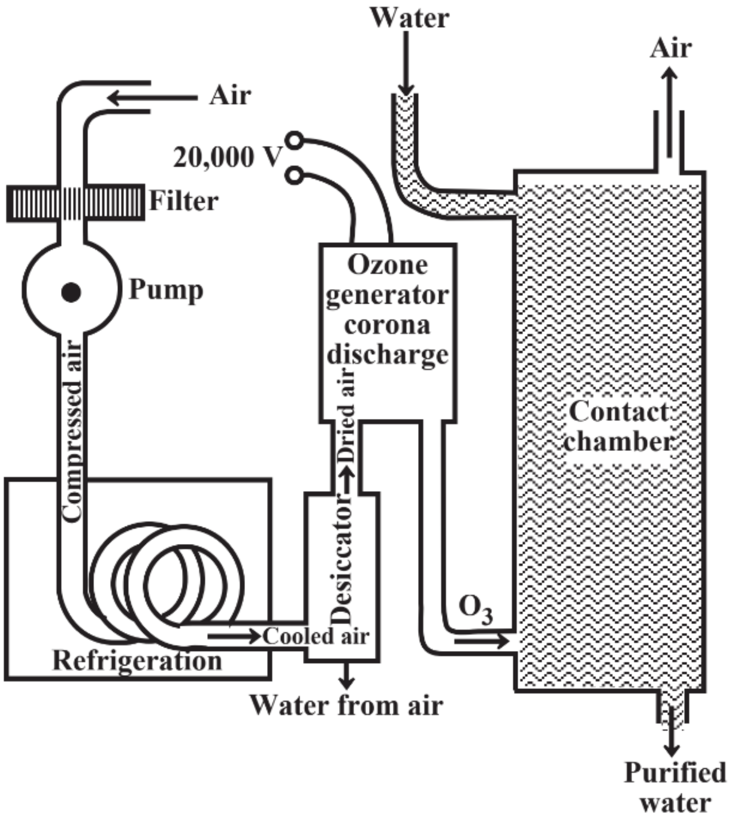


Figure 9.6. A water disinfection system based upon ozone produced by an electrical discharge through chilled, dried air followed by pumping the ozonated air through water.

The same treatment processes described above for municipal water are applied to water destined for commercial and industrial use. Some other treatment steps commonly applied to commercial and industrial water supplies include the following:

- Addition of precipitants such as Na_3PO_4 to remove Ca^{2+} and prevent formation of $CaCO_3$
- Addition of dispersants to prevent scale formation
- Adjustment of pH by addition of acid or base
- Disinfection to remove pathogens and addition of biocides to prevent microbial growths
- Addition of coagulants followed by filtration to remove suspended colloidal material
- Treatment with activated carbon to remove organics
- Deionization to remove salts
- Reverse osmosis to remove salts

For economic and conservation reasons significant amounts of water used for commercial and industrial applications are recycled as discussed in Section 9.7. Such water is often subjected to **sequential use** for applications that require successively lower quality, the last use before discharge requiring the lowest quality of water. In some cases water leaving a facility may be applied to grass or golf courses or used for irrigation.

9.6: Wastewater Treatment

Although there are many kinds of wastewater depending upon where the water has been used, the most common wastewater treatment is applied to sewage consisting of water that has been through a municipal water distribution system. The most common contaminant of municipal wastewater consists of biodegradable organic matter, abbreviated $\{CH_2O\}$, usually biological material from human wastes or biomass flushed down the drain by garbage disposal grinders. When this biodegradable matter gets into the receiving waters where sewage effluent ultimately ends up, its biodegradation consumes dissolved oxygen as shown in Reaction 9.3.1. As noted in Section 9.3, biochemically degradable matter in water is said to exert a biochemical oxygen demand, BOD. The main objective of municipal wastewater treatment is reduction of BOD.

There are three main categories of sewage treatment: (1)primary treatment to remove solid objects, grit, and grease, (2) secondary treatment to reduce BOD, and (3) tertiary treatment to further refine the quality of the effluent water. Primary treatment is essentially self-explanatory and tertiary (advanced) treatment is addressed in more detail in Section 9.6 which discusses treatment of wastewater for recycling. The following is a brief discussion of secondary wastewater treatment.

Normally biological treatment with microorganisms is employed to remove BOD in secondary wastewater treatment. In fixed film bioreactors this is accomplished with a film of bacteria and protozoa immobilized on a support so that the microorganisms are alternatively exposed to wastewater and to air. One way in which this is done is with a trickling filter consisting of rocks coated with microorganisms onto which wastewater is drained from a rotating pipe with holes along the bottom edge. A second means is with microorganism-coated disks that rotate on a shaft so that half of each disk is immersed in water and the other half exposed to air at any given time.

The most widely used means of secondary wastewater treatment is the **activated sludge process** shown in Figure 9.7. In this process, biomass is degraded in a tank containing a relatively large mass of microorganisms kept suspended by air pumped into the bottom of the tank. This air serves as a continually renewed source of dissolved molecular oxygen in the water. In the aeration tank biodegradable organic material is acted upon by the microorganisms to produce biomass and carbon dioxide. As part of this process organically bound nitrogen, sulfur, and phosphorus are largely converted to simple inorganic species, such as NH_4^+ from organic nitrogen. The treated wastewater exits the tank after an appropriate residence time and goes to a settling basin in which the suspended mass consisting largely of bacterial and protozoal biomass called sewage sludge(now often given the less offensive term of biosolids) settles and the treated water is discharged. The settled sewage sludge is then pumped back to the front of the aeration tank to provide a constant high population of biodegrading organisms in the tank. As the process progresses, the mass of sewage sludge increases and the excess is transferred to an anoxic digester where it remains for some time and generates methane (CH_4) by anoxic fermentation in the absence of oxygen. The methane is used as a fuel and can be employed to run engines that power the plant. Spent sludge accumulates in the anoxic digester and requires disposal. The “greenest” means of disposal is to spread it onto farmland as fertilizer. Often it is incinerated, which requires significant amounts of supplemental fuel because the sludge has such a high water content.

9.7: Advanced Wastewater Treatment and Recycling

Advanced or tertiary water treatment is applied to the effluent from secondary wastewater treatment facilities. Such treatment is becoming more common in part because water from secondary treatment often contains sufficient BOD to cause problems in receiving waters and contains excessive levels of algal nutrients, especially phosphate, that results in excess algae growth and eutrophication, a condition in which algal biomass accumulates in excess, then decays and depletes water of dissolved oxygen. The other reason for advanced wastewater treatment is that wastewater can be a readily available water source that is potentially easier to bring up to drinking water standards compared to seawater or brackish groundwater. A major barrier to complete water reuse is public opposition to the idea of using water that once was sewage although that is exactly what is done in cases where cities draw their water supplies from rivers downstream from where other cities have discharged treated wastewater.

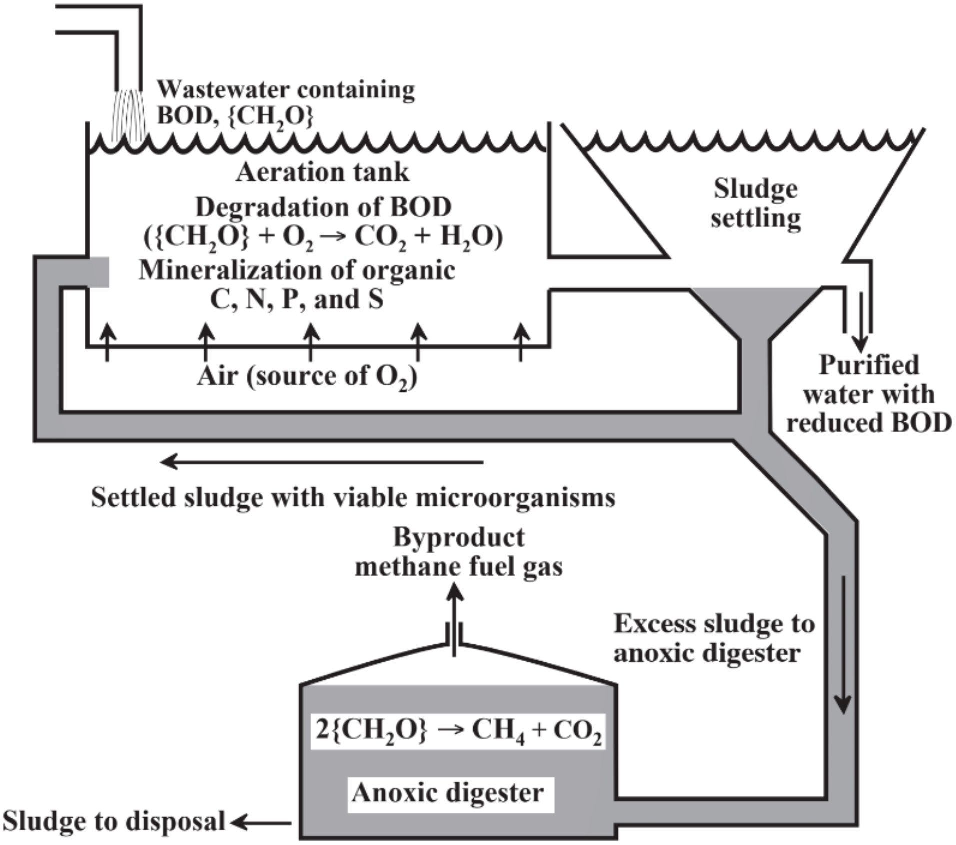


Figure 9.7. An activated sludge wastewater treatment facility

Most of the water treatment processes discussed so far in this chapter can be used for advanced wastewater treatment. The two major contaminants that need to be removed from such water are organics including BOD and salts including algal nutrient ions containing phosphorus or nitrogen. Also of concern are pathogens including virus and waste pharmaceuticals and their byproducts. Much of the BOD is in the form of residual suspended solids that can be removed by filtration processes. Filtration over beds of sand has long been used to purify water. More recently filtration with membranes that remove extremely small particles has become much more popular. Nanofiltration through membranes with pores 0.1–5 nanometers (nm) in size can even remove viruses from water, a step that is very important for recycling water from sewage sources. Filters with even smaller pores are used for **reverse osmosis** treatment of water (Figure 9.8) which removes salt ions including algal nutrients with a semipermeable membrane that attracts pure water but rejects ions. Reverse osmosis produces a concentrated brine product that requires disposal.

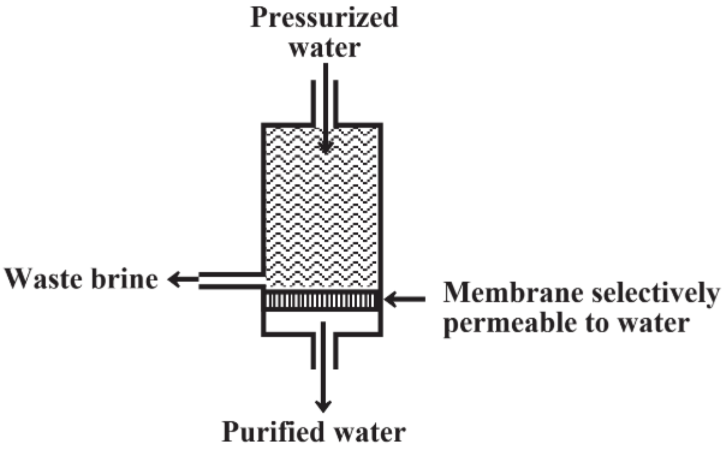


Figure 9.8. A reverse osmosis system for the removal of ions and other impurities from water. Membrane filtration processes that employ filters with larger pores are used to remove a variety of contaminants from water.

Figure 9.9 shows a system for reuse of water capable of producing drinking water from sewage. It illustrates the major kinds of treatment processes that can be employed and the applications of the water product. Taking effluent from a secondary sewage treatment plant, this system takes advantage of nature’s inherent ability to purify water by first placing the water in a constructed wetlands. Plants and algae grow profusely in the nutrient-rich wastewater effluent, and their biomass can be harvested for energy production. Water from the wetlands can percolate into underground aquifers or can even be pumped into aquifers where contact with mineral formations further purifies the water. Water leaving the wetlands can be used without additional treatment for irrigation or other non-potable applications, such as cooling water. For household or other uses requiring a higher purity product, the water can be treated with activated carbon to remove organics and subjected to membrane filtration processes to remove small particulate contaminants and some kinds of large-molecule solutes and pathogens, including virus. To remove dissolved salts, reverse osmosis may be employed. Ultraviolet irradiation of the water can be used to destroy pharmaceuticals and their metabolites. The final water product can then be introduced into a municipal water system.

The 275 million liter/day Groundwater Replenishment System of the Orange County Water District in southern California, which cost $481 million and went into operation in late 2007, is the world’s largest water plant designed to produce potable quality water from treated sewage effluent. The water from this system is not currently used for municipal water supply but is pumped into underground aquifers to serve as a future source of drinking water and to prevent infiltration of saline ocean water into the aquifers. The operation of this plant is expected to serve as a model for similar plants around the world.

9.8: The Many Uses of Water

Beyond its well known domestic uses and for irrigation, water has many applications. A renewable, sustainable green resource, next to air water is the cheapest and most universally available raw material and, because it is totally renewable, it is the greenest of raw materials. Here are addressed just a few of the huge number of water-based technologies.

Many of water's uses come from its unique physical properties, especially as they relate to water's extraordinarily high capacity to absorb and release heat energy. At 100°C,a very high 40.7kilojoules/mole (kJ/mol) is required to change liquid water to steam and a correspondingly large amount of heat is released when steam condenses to liquid water, the highest heat of vaporization of any common substance. Advantage is taken of this characteristic by vaporizing water in a boiler, moving it as steam, and condensing it back to liquid, a very effective means of moving heat energy from one place to another, such as for heating multiple buildings on a university campus, for example. Some European cities use such a **district heating** system to heat residential houses and apartments, often with boilers fueled in part by municipal refuse. The high heat of fusion for ice enables the use of solid water to absorb heat.

Steam is a very effective **working fluid** to convert heat energy to mechanical energy. This used to be done with piston engines including those on steam locomotives, but is now performed by steam turbines. Steam is produced in **water-tube** boilers in which liquid water is evaporated inside 2-8 cm diameter tubes around which hot combustion gases are circulated. Water drums for water storage and steam drums for steam storage are isolated from the fire to prevent an explosion in case they rupture, which would happen if their contents got into the firebox.

An interesting application of steam which greatly facilitates the sustainable use of wood is **steam explosion pulping** of wood in which wood is heated with pressurized steam at 180°C to 210°C. This step is followed by very rapid decompression such that the wood literally explodes releasing wood fibers that can be used in numerous applications including making paper pulp and fiber board. The cellulose in the fibers can be treated to produce sugars that can be fermented to produce alcohol.

An important consideration in producing steam for any purpose is the prevention of scaling, fouling, and corrosion, which generally requires very pure and carefully treated water. The best source of such water is the steam itself, which is condensed for **makeup water** to return to the boiler. The feed water to a boiler is treated to remove contaminants that can cause solid buildup in the boiler tubes. Phosphate salts are added to remove dissolved calcium and magnesium (hardness) by reactions such as the following:

$$5\,\mathrm{Ca}^{2+}(\mathrm{aq}) + 3\,\mathrm{PO}_4^{3-}(\mathrm{aq}) + \mathrm{OH}^-(\mathrm{aq}) \longrightarrow \mathrm{Ca}_5\mathrm{OH}(\mathrm{PO}_4)_3(\mathrm{s}) \tag{9.8.1}$$

The removal of silicon from boiler feedwater is required because it can carry over with steam and cause damaging deposits of SiO_2 on turbine blades. Both dissolved carbon dioxide and oxygen are corrosive. Hydrazine can be used to remove traces of residual oxygen by the following reaction:

$$\mathrm{N}_2\mathrm{H}_4 + \mathrm{O}_2 \rightarrow 2\,\mathrm{H}_2\mathrm{o} + \mathrm{N}_2 \tag{9.8.2}$$

Anticorrosive agents, such as cyclohexylamine are added to boiler feedwater.

Videos of floodwaters uprooting structures and carrying them away attest to water's ability to transmit mechanical energy. Advantage is taken of this capability by using jets of pressurized water to harvest sand and gravel from river beds and to mine and process some kinds of minerals.

The greatest use of moving water's mechanical energy is the application of **waterpower**. Employed for many centuries as a renewable energy source, waterpower is the oldest source of non-animal energy harnessed, for example, by waterwheels powering grain-grinding applications or sawmills. Energy may be harvested from water flowing downhill from a dammed stream and from rising and falling ocean tides. The greatest current use of moving water is for **hydroelectric power** to run electricity generators. The U.S. now has about 100,000 megawatts of hydroelectric capacity (a large fossil-fueled or nuclear power plant typically has a capacity of 1000 MW). This capacity could be doubled by using all available sites in the U.S., including Alaska for hydroelectric power, although this will not happen for economic and environmental reasons. A useful adaptation of hydroelectric power is **pumped storage** in which turbines are reversed to pump water to containment structures at higher elevations during periods of low electricity demand and the stored water is used to run turbines attached to electrical generators when demand is high.

Water power affords economic and environmental advantages including a free source of "fuel" and the lack of emissions or ash, making waterpower one of the "greenest" sources of energy. Problems may arise under extreme drought conditions when water is simply unavailable.

Unfortunately, the vast reservoirs required for most waterpower developments destroy free-flowing rivers and are detrimental to fish migration, such as that required for salmon reproduction. Most potentially remaining available sites are in remote regions from which the transfer of electricity to population centers requires massive power lines, which also present environmental problems. Because of this there is now a trend toward dismantling dams to restore normal stream flow, the esthetics of river valleys and gorges, and wildlife habitat. (Sediments accumulated in reservoirs, some of which contain hazardous material, can be released when dams are removed and cause problems downstream.) New technologies have also been developed that utilize the power of moving water in river beds without the need for dams.

Water as a Solvent

Water is an extraordinarily good solvent for a variety of materials and its solvent properties can be enhanced with suitable additives, especially surfactants that reduce its surface tension making it a powerful cleaning agent. Mixed with suspended lubricants, water is very useful as a lubricant and cooling agent, such as in metal-stamping operations. Substitution of appropriately treated water for organic solvents, which generally come from nonrenewable petroleum and are expensive, has extended water’s use for washing small parts, such as electronic constituents. As a solvent for chemical reactants, water serves as a medium for many chemical synthesis and processing applications. Substances can be purified by dissolving them in water, then evaporating some of the water off to leave a purified form of the substance; some salts are purified by this means.

Water is useful for its chemical properties and is a chemical ingredient for a number of industrial chemical reactions. It is required for the hardening of Portland Cement to make concrete. It can be used as the reagent in treating some kinds of hazardous wastes by hydrolysis. Water serves as a source of elemental hydrogen used as a fuel in fuel cells and as a raw material in making some chemicals, such as ammonia. Elemental hydrogen is generated along with oxygen gas when a direct electrical current is passed through water that has been made conducting by the addition of a salt. Hydrogen is produced at the negatively charged cathode when electrons (*e*-) are added to molecules of water,

$$2\,H_2O + 2\,e^- \rightarrow H_2(g) + 2\,OH^- \tag{9.8.3}$$

and oxygen is generated at the positively charged anode by the removal of electrons from water:

$$2\,H_2O \rightarrow O_2(g) + 4\,H^+ + 4\,e^- \tag{9.8.4}$$

The net reaction is simply the following:

$$2\,H_2O \rightarrow 2\,H_2(g) + O_2(g) \tag{9.8.5}$$

The process is certainly an example of green chemistry because the only reagent is water and the only byproduct is oxygen gas, which has a number of uses or can be released harmlessly to the atmosphere. In Iceland, hydrogen gas made by the electrolysis of water generated from abundant hydroelectric and geothermal sources of electricity is used to fuel automobiles.

9.9: Hot Water - Pressurized Subcritical Water

As described in Section 9.10, water heated above its critical temperature of 374.4°C and kept under very high pressure reaches a special state called supercritical fluid. However, at temperatures above its normal boiling temperature of 100°C but below those required to reach the supercritical state, the properties of liquid water change markedly. Whereas the dielectric constant of liquid water at 25°C is 78, that of pressurized subcritical water at 205°C is 33, the same as methanol at 25°C. At temperatures between 100 °C and 205°C, water behaves like a mixture of water and methanol and becomes a much more effective solvent for organic substances. Such superheated water has a number of uses such as extracting organic materials from plant biomass, extracting pollutant organic materials from contaminated soil and sediments, and as a reaction medium for organic chemical reactions. The decrease in dielectric constant of water and the increase in solubility of substances at higher temperatures means that the solubilities of some substances in superheated water may be orders of magnitude higher than in water at 25°C.

A potentially useful application of pressurized hot water is its application as a medium along with pressurized O_2 in which organic substances are oxidized. This procedure has been used to make oxygenated products from organics as refractory as coal. It has also been used as a means of destroying oxidizable pollutants in water. For example, the organic matter in sewage can be removed by reaction with O_2 in superheated water.

9.10: Supercritical Water

At temperatures exceeding 374.4°C and an extremely high pressure of at least 217.7 atm (217.7×normal atmospheric pressure) the distinction between liquid water and vapor vanishes and water enters a special physical state called a **supercritical fluid**. As a supercritical fluid, water no longer has the abundance of hydrogen bonds that give liquid water its special properties and that make it such a good solvent for ionic materials; instead, it becomes a good solvent for organic materials. The properties of supercritical water can be changed over a wide range by varying temperature and pressure and conditions can be attained in which the water is completely miscible with nonpolar compounds while retaining its ability to solubilize ions and polar species. Varying the pressure on supercritical water can change its density continuously from gaslike to liquid-like with a corresponding variation in the properties of the fluid. Although the conditions required to maintain water as a supercritical fluid are very severe and require special equipment, its ability to substitute for organic solvents make supercritical water very useful for a number of purposes, such as a medium for organic synthesis reactions. Even when compressed to a density equal to that of liquid water, supercritical water has a low viscosity. This is important for chemical processes because it increases mass transfer and rates of diffusion in diffusion-controlled processes.

Supercritical water has enormous potential as a solvent medium and catalytic material for chemical reactions. Its high temperature is conducive to pyrolysis, it promotes the hydrolysis of compounds in which molecules are cleaved with addition of H_2O, and in the presence of O_2 and other oxidants it is a strongly oxidizing medium. Careful tuning of temperature, pressure, and oxidant levels enables supercritical water to facilitate partial oxidation of organic materials such asthe partial oxidation of methane to produce methanol:

$$\mathrm{CH_4} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CH_3OH} \tag{9.10.1}$$

Whereas methane must be moved by pipeline or as an extremely cold cryogenic liquid, which is hard to do from some of the remote regions where natural gas is found, methane converted to liquid methanol can be shipped in large tankers and used as a motor fuel or in fuel cells.

Oxygen, like other common inorganic gases, is completely miscible with supercritical water under extreme pressures, which increases its capability to act as an oxidant in chemical synthesis and waste destruction. Supercritical water is an excellent medium in which to use dissolved molecular oxygen to oxidize organic wastes including chlorinated compounds to carbon dioxide, water, and inorganic halides (chloride ion). The process is facilitated by the ability of supercritical water under certain conditions to act as a good solvent for organic wastes such as polychlorinated biphenyls (PCBs).

Under the extreme pressure and temperature conditions of around 30 km in the geosphere water is likely to be supercritical. In the presence of supercritical water at these depths, minerals may behave much differently compared to their behaviors under normal conditions, especially with respect to their dissolution and precipitation behavior. There is also evidence to suggest that chemical processes may form methane under these conditions leading to a non-biological pathway for hydrocarbon formation.

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Questions and Problems

Access to and use of the internet is assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be "right."

1. Look up proposals to restore the Hetch-Hetchy Valley in Yosemite National Park to its former state. How might this affect water supply to parts of California? What might be some benefits of restoration of this valley to its former state?

2. Look up and explain the significance of the name Mulholland in relationship to water. How did Mulholland affect history?

3. Paradoxically, pollution by a strong acid such as HCl of groundwater in contact with limestone ($CaCO_3$) can lead to an increase in the alkalinity of the water. Using chemical reactions, explain how this may occur.

4. Tests can be performed on water that show the presence of biochemical demand (BOD) and other tests that chemically oxidize organic matter to produce CO_2 can show total organic carbon (TOC). Applied to a particular sample of water, these two tests showed relatively high TOC and relatively low BOD. What does this say about the nature of the organic pollutants in the water?

5. Agricultural fertilizer normally adds nitrogen, phosphorus, and potassium to soil. Explain how fertilizer runoff into a body of water can lead eventually to increased biochemical oxygen demand pollution.

6. The development of the flameless atomic absorption analysis for mercury enabled very sensitive tests for this element around 1970 and showed suprisingly high levels of this toxic element in some fish samples. The inorganic chemistry of mercury suggests that mercury compounds should precipitate and settle into sediments where they are unavailable to fish. What, then was the explanation for the high mercury levels found in some fish around 1970?

7. Phosphate in the form of $H_2PO_4^-$ and HPO_4^{2-} ions is the substance usually removed from secondary sewage effluent to prevent excessive algal growth and eutrophication in receiving waters. Of several possible algal nutrients, why is phosphate chosen? Show with a chemical reaction the most common means of removal.

8. Membrane filtration processes can be very effective in removing residual BOD from secondary wastewater effluent. What does this suggest regarding the nature of contaminants responsible for the BOD?

9. By doing some search on the internet, gather information regarding the use of wastewater for irrigation. Is this a practice that is used and if so where does it usually take place? What are some of the benefits? What are some of the risks?

10. In Section 9.2 information is given about the total amounts of water on Earth and how much of it is in the solid form as ice, snowpack, and glaciers. Information is available on the internet regarding the heat of fusion of ice and the rate at which energy reaches Earth from the sun. From this information, estimate the length of time required to melt all of Earth's solid water if all the solar flux received by Earth could go to that purpose.

11. Water is used for both its special solvent properties and its ability to absorb, transfer, and release heat energy. Explain on the basis of the characteristics of the water molecule how these two uses are related.

12. How far back into history does the use of waterpower go? Which civilizations were the first to use it? Explain why during the mid-1800s waterpower development slowed, only to start growing rapidly around the late 1800s and early 1900s.

13. What is Plaster of Paris? Show with a chemical reaction how water is employed as a chemical reagent in making objects from Plaster of Paris

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CHAPTER OVERVIEW

10: Blue Skies for a Green Environment

“We are absolutely dependent upon the atmosphere for materials essential to life and for protection from the hostile environment of outer space. This marvelous canopy over us is really very thin and fragile. If Earth were the size of a classroom geography globe, virtually all of the mass of the atmosphere would be contained in a layer about the thickness of the varnish on the globe!

10.1: More Than Just Air to Breathe
10.2: The Gas Laws
10.3: The Protective Atmosphere
10.4: Atmospheric Chemistry and Photochemical Reactions
10.6: The Enormous Importance of Climate
10.7: Atmospheric Particle Pollutants
10.8: Pollutant Gaseous Oxides
10.9: Acid Rain
10.10: Miscellaneous Gases in the Atmosphere
10.11: Photochemical Smog
10.12: Natural Capital of the Atmosphere
10.5: Energy and Mass Transfer in the Atmosphere
Questions and Problems
Supplementary References

10.1: More Than Just Air to Breathe

A Sea of Gas

We live and breathe in the **atmosphere**, a sea of gas consisting primarily of elemental O_2 and N_2. The fundamental properties of gases determine the properties of the atmosphere. Recall that gases consist of molecules and (in the case of noble gases) atoms with large amounts of space between them. The gas molecules are in constant, rapid motion, which causes gases to exert pressure. The motion of gas molecules becomes more rapid with increasing temperature. This motion also means that gas molecules move by a process called **diffusion**. The relationships among the amount of gas in moles, its volume, temperature, and pressure can be calculated by the gas laws discussed in Section 10.2.

Whereas seawater in the ocean has a well-defined volume and a distinct surface, the same cannot be said for the mass of gases comprising the atmosphere. Although most of the atmosphere is within a few kilometers of Earth's surface, there is no distinct point at higher altitude where the atmosphere ends. Instead, air becomes progressively thinner with increasing altitude. This is noticeable to humans who have traveled to higher altitudes on mountains where the thinner air makes breathing more difficult. Indeed, climbers who scale the highest mountain peaks commonly carry oxygen to aid breathing.

Atmospheric Composition

What is air? At our level, it is a mixture of gases of uniform composition, except for water vapor, which composes 1-3% of the atmosphere by volume, and some of the trace gases, such as pollutant sulfur dioxide. On a dry basis, air is 78.1% (by volume) nitrogen, 21.0% oxygen, 0.9% argon, and 0.04% carbon dioxide. Normally, air is 1–3% water vapor by volume. Trace gases at levels below 0.002% in air include ammonia, carbon monoxide, helium, hydrogen, krypton, methane, neon, nitrogen dioxide, nitrous oxide, ozone, sulfur dioxide, and xenon.

By a wide margin, oxygen and nitrogen are the most abundant gases in the atmosphere. Because of the extremely high stability and low reactivity of the N_2 molecule, the chemistry of atmospheric elemental nitrogen is singularly unexciting, although nitrogen molecules are the most common "third bodies" that absorb excess energy from atmospheric chemical reactions, preventing the products of addition reactions in the atmosphere from falling apart. Oxides of nitrogen actively participate in atmospheric chemical reactions. Elemental nitrogen is an important commercial gas extracted from the atmosphere by nitrogen-fixing bacteria and in the industrial synthesis of ammonia.

Oxygen is a reactive species in the atmosphere that reacts to produce oxidation products from oxidizable gases in the atmosphere. Two such species that are particularly important are sulfur dioxide gas, SO_2, and pollutant hydrocarbons. Molecular O_2 does not react with these substances directly but only indirectly through the action of reactive intermediates, especially **hydroxyl radical**, HO•.

A crucially important atmospheric chemical phenomenon involving oxygen is the formation of stratospheric ozone, O_3. The formation of this gas in the stratosphere is discussed in Section2.13 and shown by Reactions 2.13.1 and 2.13.2.

Oxygen in the atmosphere is consumed in the burning of hydrocarbons and other carbon-containing fuels. It is also consumed when oxidizable minerals undergo chemical weathering, such a

$$4\,\mathrm{FeO} + \mathrm{O_2} \rightarrow 2\,\mathrm{Fe_2O_3} \tag{10.1.1}$$

All of the oxygen in the atmosphere was originally placed there by photosynthesis shown by

$$\mathrm{CO_2} + \mathrm{H_2O} + h\nu \rightarrow (\mathrm{CH_2O}) + \mathrm{O_2} \tag{10.1.2}$$

where $\{CH_2O\}$ is a generic formula representing biomass

Unlike molecular oxygen, which can undergo direct photodissociation in the stratosphere, the very stable N_2 molecule does not encounter ultraviolet radiation sufficiently energetic to cause its photodissociation at altitudes below 100 km. However, nitrogen dioxide, NO_2, readily undergoes photodissociation in the troposphere.

$$\mathrm{NO_2} + h\nu \rightarrow \mathrm{NO} + \mathrm{O} \tag{10.1.3}$$

to generate highly reactive O atoms. These in turn can attack hydrocarbons in the atmosphere, leading to the formation of photochemical smog discussed later in this chapter.

10.2: The Gas Laws

The behavior of gases in the atmosphere is governed by several fundamental **gas laws** which are covered briefly here. In using these laws, it should be kept in mind that the quantity of gas is most usefully expressed in numbers of moles. There are many units of pressure, but the most meaningful conceptually is the **atmosphere** (atm) where 1 atmosphere is the average pressure of air in the atmosphere at sea level. (Air has pressure because of the mass of all the molecules of air pressing down from the atmosphere above; as altitude increases, this pressure becomes less.) For calculations involving temperature, the **absolute** temperature scale is used in which each degree is the same size as a degree Celsius (or Centigrade, the temperature scale used for scientific measurements and for temperature readings in most of the world), but zero is 273 degrees below the freezing point of water, which is taken as zero on the Celsius scale. Three important gas laws are the following:

> **Avogadro's law:** At constant temperature and pressure the volume of a gas is directly proportional to the number of moles; doubling the number of moles at a constant temperature and pressure doubles the volume.
>
> **Charles' law:** At constant pressure the volume of a fixed number of moles of gas is directly proportional to the absolute temperature (degrees Celsius +273) of the gas; doubling the absolute temperature at constant pressure doubles the volume.**Boyle's law:**
>
> At constant temperature the volume of a fixed number of moles of gas is inversely proportional to the pressure; doubling the pressure halves the volume.

These three laws are summarized in the **general gas law** relating volume (V), pressure (P), number of moles (n), and absolute temperature (T) expressed as

$$\mathrm{PV{=}nRT} \tag{10.2.1}$$

where R is a constant.

Mathematical calculations involving the gas laws are simple. One of the most common such calculations is that of changes in volume resulting from changes in pressure, temperature, or moles of gas. The parameter that does not change is the constant R. Using subscripts to represent conditions before and after a change yields the following relationship:

$$R=\frac{P_1V_1}{n_1T_1}=\frac{P_2V_2}{n_2T_2} \tag{10.2.2}$$

This equation can be arranged in a form that can be solved for a new volume resulting from changes in P, n, or T

$$V_2=V_1\times\frac{n_2T_2P_1}{n_1T_1P_2} \tag{10.2.3}$$

As an example, calculate the volume of a fixed number of moles of gas initially occupying 12.0 liters when the temperature is changed from 10°C to 90°C at constant pressure. In order to use these temperatures, they must be changed to absolute temperature by adding 273°. Therefore, T_1=10° + 273° = 283° , and T_2= 90° + 273° = 363°. Since n and P remain constant, they cancel out of the equation yielding

$$V_2=V_1\times\frac{T_2}{T_1}=12.0L\times\frac{363^\circ}{283^\circ}=15.4L \tag{10.2.4}$$

As another example consider the effects of a change of pressure, holding both the temperature and number of moles constant. Calculate the new volume of a quantity of gas occupying initially 16.0 L at a pressure of 0.900 atm when the pressure is changed to 1.20 atm. In this case, both n and T remain the same and cancel out of the equation giving the following relationship:

$$V_2=V_1\times\frac{P_1}{P_2}=16.0L\times\frac{0.900\text{ atm}}{1.20\text{ atm}}=12.0L \tag{10.2.5}$$

Note that an increase in temperature *increases* the volume and an increase in pressure *decreases* the volume.

10.3: The Protective Atmosphere

The atmosphere is the air around and above us. We know we must have air to breathe. A human deprived of air's life-giving oxygen for just a brief time will lose consciousness, and within a few minutes will die. But air is far more than just a source of oxygen. That is because it protects Earth's organisms in ways that are absolutely essential for their existence. One major protective function is to act as a blanket to keep us warm. It does that by reabsorbing the infrared radiation by which Earth radiates the energy that it receives from the sun. By delaying the exit of this energy into outer space, the average temperature of Earth's surface remains at about 15°C at sea level, though much colder at certain times and places and significantly warmer at others. Without this warming effect, plants could not grow and most other known organisms could not exist. The second protective function of the atmosphere is absorption of very short wavelength ultraviolet solar radiation. Were this radiation to reach our level, it would tear apart biomolecules, making it impossible for most life forms to exist.

Although one might get the impression that the atmosphere is very thick, it is "tissue thin" compared to Earth's diameter. Consider a corporate jet aircraft cruising at 35,000 feet (about 6.6miles or 10.7 kilometers). In the unlikely event of sudden, catastrophic loss of pressure in the pressurized cockpit, the pilot has only about *15 seconds* to grab an oxygen mask before losing consciousness (the passengers in the cabin have an equally short time, but it is more important for the pilot to stay conscious and dive to a lower altitude). The reason for this is that virtually all the air in the atmosphere is below the altitude of around 11 km. By way of comparison, Earth'sdiameter is almost 13,000 km.

The altitude at which high-flying jet aircraft cruise marks the upper limit of the lowest of several layers of the atmosphere, the **troposphere**, which extends from sea level to about 11 km (Figure 10.1). As anyone who has driven to the top of Pike's Peak or some other mountain knows, the troposphere gets cooler with increasing altitude, from an average temperature of 15°C at sea level to an average at 11 km of -56°C. Above the layer of the troposphere, however, atmospheric temperature increases to an average of -2°C at 50 km altitude. The layer above the troposphere is the **stratosphere**, which is heated by the absorption of intense ultraviolet radiation from the sun(Figure 10.2). There is virtually no water vapor in the stratosphere, and it contains ozone, O3, and O atoms as the result of ultraviolet radiation acting upon stratospheric O2. Beyond the stratosphere are layers called the mesosphere and thermosphere, but they are relatively less important in the discussion of the atmosphere.

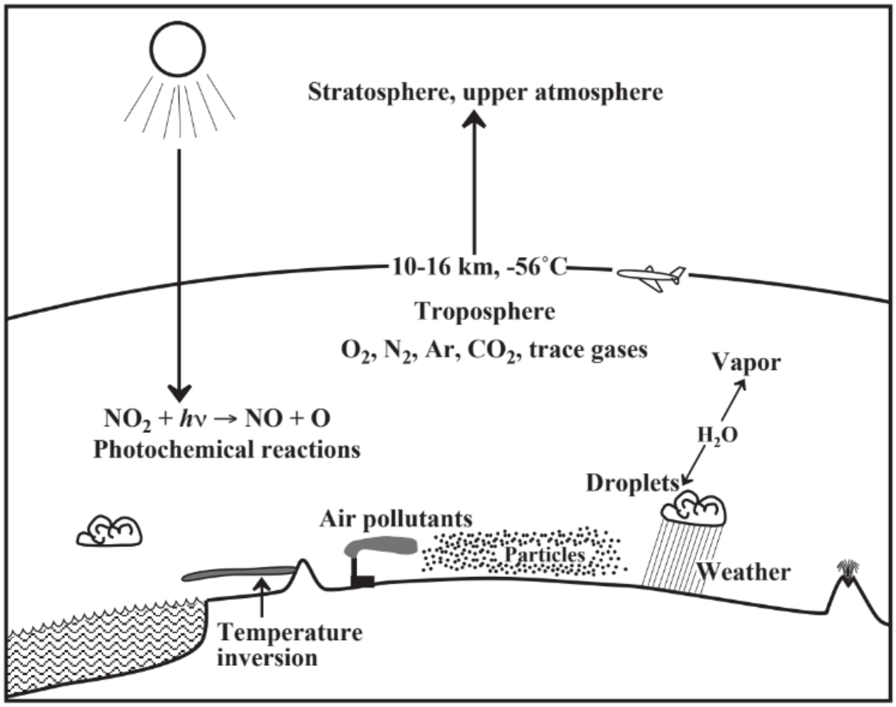

Figure 10.1. The troposphere is the very thin layer of the atmosphere closest to Earth, containing most of the atmosphere's air and water vapor. It is the source of oxygen, carbon dioxide, nitrogen, and water used by living organisms and as raw materials for manufacturing. With the important exception of stratospheric ozone destruction, it is where most air pollution phenomena occur

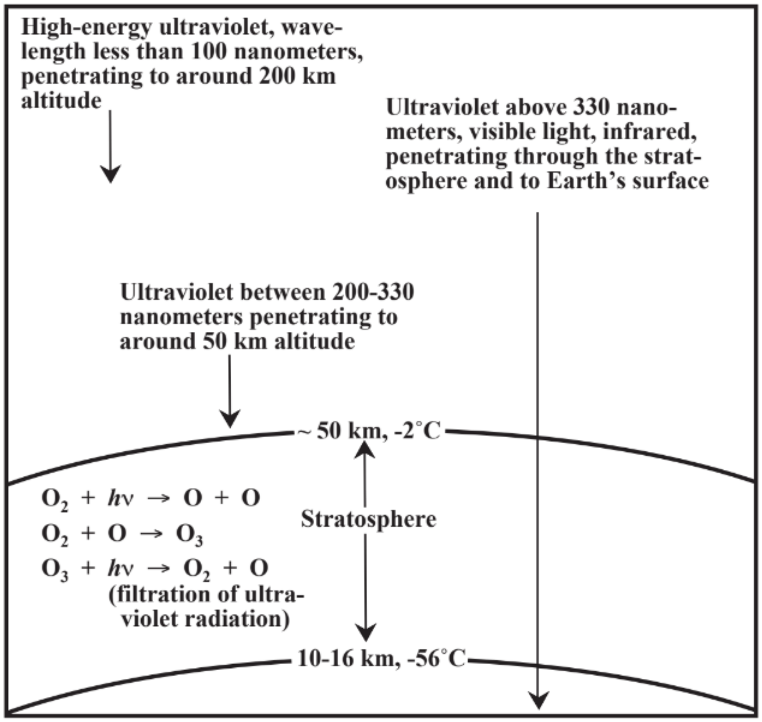

Figure 10.2. The upper atmosphere including the stratosphere and regions beyond is particularly important in the absorption of radiation that would make life impossible if it reached Earth's surface. The layer of ozone, O3, in the stratosphere is of the utmost importance and one that is subject to damage from anthropogenic species released into the atmosphere

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10.4: Atmospheric Chemistry and Photochemical Reactions

Atmospheric chemistry describes chemical processes that occur in the atmosphere. One notable aspect of atmospheric chemistry is that it occurs in the gas phase where molecules are relatively far apart, so a molecule or a fragment of a molecule may travel some distance before bumping into another species with which it reacts. This is especially true in the highly rarefied regions of the stratosphere and above.

A second major aspect of atmospheric chemistry is the occurrence of **photochemical reactions** that are initiated when a photon (essentially a packet of energy associated with electromagnetic radiation) of ultraviolet radiation is absorbed by a molecule. The energy of a photon, E, is given by E =*h*ν where *h* is Planck’s constant andνis the frequency of the radiation. Electromagnetic radiation of a sufficiently short wavelength breaks chemical bonds in molecules, leading to the formation of reactive species that can participate in reaction sequences called **chain reactions.**

An example of an important chain reaction sequence that begins with photochemical dissociation of a molecule is the one that occurs when chlorofluorocarbons get into the stratosphere. Chlorofluorocarbons are given the trade name of Freons and consist of carbon atoms to which are bonded fluorine and chlorine atoms. Noted for their extreme chemical stability and low toxicities, they were once widely used as refrigerant fluids in air conditioners, as aerosol propellants for products such as hair spray, and for foam blowing to make very porous plastic or rubber foams. Dichlorodifluoromethane, CCl_2F_2, was used in automobile air conditioners. Released to the atmosphere, this compound remained as a stable atmospheric gas until it got to very high altitudes in the stratosphere. In this region, ultraviolet radiation of sufficient energy (*h*ν)is available to break the very strong C-Cl bonds,

$$\mathrm{CCl_2F_2} + h\nu \rightarrow \cdot\mathrm{CClF_2} + \mathrm{Cl}\cdot \tag{10.4.1}$$

releasing Cl atoms. The dot represents a single unpaired electron remaining with the Cl atom when the bond in the molecule breaks. Species with such unpaired electrons are very reactive and are called **free radicals**. As discussed in Chapter 2 Section 2.13 and shown by reactions 2.13.1 and 2.13.2, in addition to molecular O_2 there are oxygen atoms and molecules of ozone, O_3, also formed by photochemical processes in the stratosphere. A chlorine atom produced by the photochemical dissociation of CCl_2F_2 as shown in Reaction 10.4.1 can react with a molecule of O_3 to produce O_2 and another reactive free radical species, ClO•. This species can react with free O atoms which are present along with the ozone to regenerate Cl atoms, which in turn can react with more O_3 molecules. These reactions are shown below:

$$\mathrm{Cl}\cdot + \mathrm{O_3} \rightarrow \mathrm{O_2} + \mathrm{ClO}\cdot \tag{10.4.2}$$

$$\mathrm{ClO}\cdot + \mathrm{O} \rightarrow \mathrm{O_2} + \mathrm{Cl}\cdot \tag{10.4.3}$$

These are chain reactions in which ClO• and Cl• are continually reacting and being regenerated, the net result of which is the conversion of O_3 and O in the atmosphere to O2. One Cl atom can bring about the destruction of as many as 10,000 ozone molecules! Ozone serves a vital protective function in the atmosphere as a filter for damaging ultraviolet radiation, so its destruction is a very serious problem that has resulted in the banning of chlorofluorocarbon manufacture.

Very small particles of the size of a micrometer or less called **aerosols** are important in atmospheric chemical processes. Photochemical reactions often result in the production of particles. Particle surfaces can act to catalyze (bring about) atmospheric chemical reactions. Some particles in the atmosphere consist of water droplets with various solutes dissolved in them. Solution chemical reactions can occur in these droplets. One such process is believed to be the conversion of gaseous atmospheric sulfur dioxide (SO_2) to droplets of dilute sulfuric acid (H_2SO_4), which contribute to acid rain. Some very small particles, such as sea salt crystals entrained into the atmosphere by wind-blown seawater spray droplets and formed by evaporation of water from the droplets, act as **condensation nuclei** around which raindrops form.

The Ionosphere

An important kind of photochemical reaction that occurs at altitudes generally above the stratosphere (50 km and higher) is the formation of ions by the action of ultraviolet and cosmic radiation energetic enough to remove electrons (e^-) from molecules as shown by the example below:

$$\mathrm{N_2} + h\nu \rightarrow \mathrm{N_2^+} + \mathrm{e^-} \tag{10.4.4}$$

The ions formed are very reactive, but air is so rarefied at the altitudes at which they form that they persist for some time before reverting to neutral species. This results in an atmospheric layer called the **ionosphere** in which ions are constantly being formed and neutralized. At night when the solar radiation responsible for ion formation is shielded by Earth, the predominant process is recombination of positive ions with electrons, a phenomenon that proceeds most rapidly in the lower, denser regions of the ionosphere. The result is a lifting of the ionosphere, a phenomenon first hypothesized in 1901 when Marconi, attempting to bridge the Atlantic ocean with shortwave radio discovered that radio waves could be propagated over long distances, especially at night, making long distance shortwave radio transmission possible. For a time in the 1900s until made obsolete by satellite and fiber optics, the ionosphere was a useful part of the atmosphere’s natural capital (see Section 10.12) by making possible long-distance shortwave radio broadcasts.

10.6: The Enormous Importance of Climate

The most important aspect of the atmosphere for humans and other living beings is **climate**. Climate consists of long-term trends in weather and varies a lot over Earth's surface. For example, the climate in desert regions of the world may be relatively hot and dry, but the weather in such regions may at times produce torrential rainfall or frigid temperatures. Of all the things that humans might do to irreversibly and catastrophically harm Mother Earth, the only home that they have or ever can have, the potential to change climate is the most serious. It is well established that climate has changed markedly in past times, most notably during several ice ages that each lasted for thousands of years. Volcanic eruptions noted in historical accounts have caused temporary cooling of the atmosphere and widespread hunger when summer growing seasons were cut short as a result. Tree-ring data indicate centuries-long droughts in parts of the world in the past, which resulted in the decline of some civilizations in the present-day U.S. Southwest, for example. Although these were natural events, recent weather data indicate changes in microclimate due to human activities. For example, some urban areas in Southeast Asia have become darker in recent decades due to particulate air pollution.

Of all the things that humans may be doing that could change climate, emissions of large quantities of gases that cause atmospheric warming are the most serious. Of these, carbon dioxide, CO_2, is the most important. Carbon dioxide is a normal constituent of the atmosphere, essential as a source of carbon for plant photosynthesis. Along with water vapor and other trace gases, atmospheric carbon dioxide absorbs outgoing infrared radiation from Earth, thus keeping the planet's surface temperature at a tolerable level. Levels of carbon dioxide gas in the atmosphere are now about 390 parts per million by volume. This represents an almost 50% increase overestimated pre-industrial concentrations of 260 ppm. Furthermore, as shown by the plot in Figure 10.4, global CO_2 levels are increasing by about 1 ppm per year, and ice core evidence indicates that these levels were only about 200 ppm at the peak of the last ice age around 18,000 years ago. So, humans are clearly increasing atmospheric carbon dioxide levels significantly, largely through the combustion of carbon-containing fossil fuels and as the result of destruction of forests. The importance of photosynthesis in determining atmospheric carbon dioxide is illustrated by the inset in Figure 10.4 showing an annual fluctuation of about 5 ppm CO_2 in the northern hemisphere attributed to photosynthesis. The minimum in this cycle occurs around September at the end of the summer growing season and the maximum occurs around April as photosynthesis is getting underway after winter.

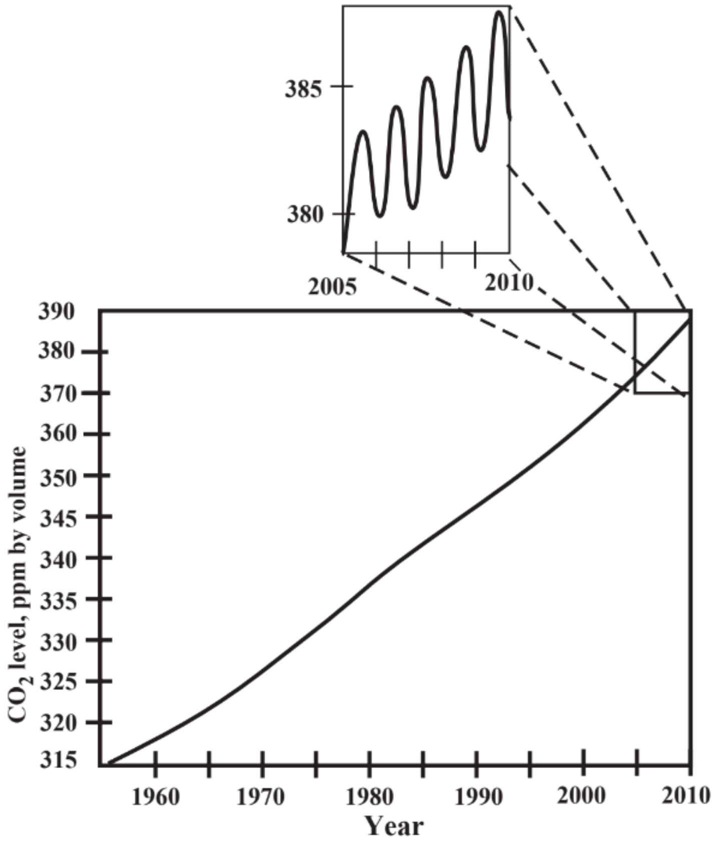


Figure 10.4. Concentrations of atmospheric CO_2 levels in recent decades. These levels are increasing by approximately 1 part per million by volume each year

The concern with increasing carbon dioxide in the atmosphere is that it will lead to — indeed *is* leading to — an excess of a good thing, warming of the global atmosphere. This is the now well known **greenhouse effect**, which may not become as dire as some experts predict, but which has a real possibility of becoming the worst environmental problem so far created by humans.

Is Earth warming? Sophisticated computer models indicate that it is backed by evidence from increasingly accurate temperature records over more than 100 years. These temperature records have been especially accurate over the last several decades because they have been read over all Earth's surface by satellite. Global temperatures analyzed by the Goddard Institute for Space Studies (GISS) in New York City show that the 1980s were the warmest decade on record globally since reasonably accurate global temperatures have been measured. The 1980s were followed by a warmer decade in the 1990s and the warmest decade of all from the beginning of 2000 to the end of 2009 (see Figure 10.5). The hottest year ever documented historically was 2005 with 1998, 2002, 2003, 2006, 2007, and 2009 all essentially tied for second.

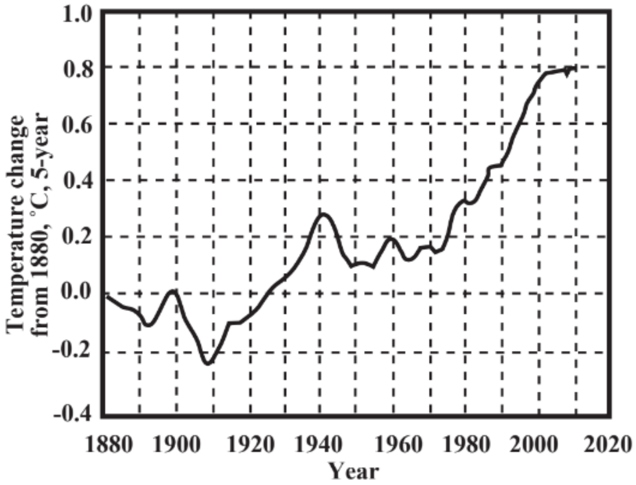


Figure 10.5. Global temperatures since 1880. Since about 1970 these measurements have been particularly accurate because they were taken by scanning throughout the globe by satellite

Gases other than carbon dioxide may be involved in greenhouse warming. These include chlorofluorocarbons and N_2O. The one most likely to cause a problem is methane, CH4, which has increased from estimated pre-industrial atmospheric levels of 0.70 ppm, to present values of l.8ppm. Although these values are much lower than those of carbon dioxide, each methane molecule is 20–30 times more effective in trapping heat than is each CO_2 molecule. A number of humana ctivities have contributed to the release of methane. Part of this is due to leakage of natural gas, which consists of methane, and from release as a byproduct of petroleum production. The 2010 blowout of the Deepwater Horizon well in the Gulf of Mexico released large quantities of methane that had been sequestered largely in combination with water as solid methane hydrates far below the ocean floor. These methane-containing structures belong to a class of materials called clathrates, an inherently unstable network of host molecules containing open cavities. In the case of methane hydrates the clathrates are clusters of approximately 46 H_2O molecules that enclose molecules of CH_4. Methane hydrates can form and be stable under pressure at temperatures significantly above the freezing point of water. Estimates are that more methane is contained in these structures globally than in all the deposits of natural gas. A major concern with global warming is that methane contained in methane hydrates held by permafrost will be released causing a feedback loop that will put even more methane into the atmosphere and result in even greater warming. Bacteria growing in the absence of oxygen in municipal refuse landfills, in rice paddies, and in the stomachs of ruminant animals (cows, sheep, moose) release enormous quantities of methane.

Although there could be some benefits of mild global warming, the net effect would almost certainly be bad, perhaps catastrophic. Climate models predict an average global temperature increase of 1.5–5°C. That does not sound like much, but it is about as much again as the temperature increase that occurred from the last ice age until now. Especially if the warming is toward the high side of the projected range, it would greatly affect climate and rainfall. The melting of the polar and Greenland ice caps along with expansion of warmer ocean water would cause sea levels to rise as much as 0.5–1.5 meters. Decreased rainfall and increased water evaporation would contribute to severe drought and water shortages that could make some currently popular areas of the world virtually uninhabitable.

Can Green Chemistry Help Deal With Global Warming?

Green chemistry and the related area of industrial ecology can help deal with the problem of global warming in two major respects. The first approach is to provide means to prevent global warming from taking place. The second approach is in coping with global warming, if it occurs.

The prevention of global warming is best accomplished by avoiding the release of potential greenhouse gases. As noted above, the most significant of these is carbon dioxide. One way to reduce the release of carbon dioxide is by using biomass as fuel or raw material for the manufacture of various products. Burning a biomass fuel does release carbon dioxide to the atmosphere, but an exactly equal amount of carbon dioxide was removed from the atmosphere in the photosynthetic process by which the biomass was made, so there is no net addition of CO_2. Unless or until biomass-derived materials used in feedstocks are burned or biodegraded, their use represents a net loss of carbon dioxide from the atmosphere.

Another potential use of green chemistry to prevent addition of carbon dioxide to the atmosphere is through **carbon sequestration** in which carbon dioxide is produced, but is bound in a form such that it is not released to the atmosphere. This approach has the greatest potential in applications where the carbon dioxide is produced in a concentrated form. In Chapter 16, reactions are shown by which carbon from coal is reacted with oxygen and water to produce elemental hydrogen and carbon dioxide. The net reaction for this production is the following:

$$2\,C + O_2 + 2\,H_2O \rightarrow 2\,CO_2 + 2\,H_2 \tag{10.6.1}$$

The hydrogen generated can be used as a pollution-free fuel in fuel cells or combustion engines. The carbon dioxide can be pumped into deep ocean waters, although this has the potential to lower ocean pH slightly, which would be detrimental to marine organisms. Another option is to pump the carbon dioxide deep underground. A side benefit of the latter approach is that in some areas carbon dioxide pumped underground can be used to recover additional crude oil from depleted oil-bearing formations.

An indirect green chemistry approach to the reduction of carbon dioxide emissions is to develop alternative methods of energy production. One thing that would be very beneficial is the development of more efficient photovoltaic cells. These devices have become marginally competitive for the generation of electricity, and even relatively small improvements in efficiency would enable their much wider use, replacing fossil fuel sources of electricity generation. Another device that would be extremely useful is a system for the direct photochemical dissociation of water to produce elemental hydrogen and oxygen, which could be used in fuel cells. An application of green biochemistry that would reduce carbon dioxide emissions is the development of plants with much higher efficiencies for photosynthesis. Plants now are only about 0.5%efficient in converting light energy to chemical energy. Raising this value to only 1% would make a vast difference in the economics of producing biomass as a substitute for fossil carbon.

Green chemistry can also be applied in the prevention of release of greenhouse gases other than carbon dioxide, especially ultrastable volatile compounds that have a high greenhouse gas potential. An excellent example of green chemistry has been the replacement of chlorofluorocarbons (Freons) with analogous compounds having at least one C-H bond, that are rather readily destroyed in the troposphere. Although this was done to prevent destruction of stratospheric ozone by chlorofluorocarbons, it has been useful to reduce greenhouse warming. Both kinds of compounds act as greenhouse gases, but those with at least one C-H bond last for much shorter times during which they are available to absorb infrared radiation. As discussed inSection 10.10, green chemistry can be applied to avoid generating extremely stable sulfurhexafluoride, SF_6, and completely fluorinated hydrocarbons, such as CF_4.

Another approach is to limit the emissions of methane, CH_4. Large quantities of methane are released by anoxic bacteria growing in flooded rice paddies. By developing strains of rice and means of cultivation that enable the crop to be grown on unflooded soil, this source of methane can be greatly reduced. Methane collection systems placed in municipal waste landfills can prevent the release of methane from this source and provide a source of methane fuel.

Green chemistry, biochemistry, and biology can be used to deal with global warming when it occurs. Crops, fertilizers, and pesticides can be developed that enable plants to grow under the drought conditions that would follow global warming. Another approach is the development of salt-tolerant crops that can be grown on soil irrigated with saline water, where fresh water supplies are limited.

10.7: Atmospheric Particle Pollutants

Although gases that cause global warming are arguably the most serious air pollutants, other air pollutants can cause serious problems with the atmospheric environment. These are discussed in the remainder of this chapter.

Because of their ability to reduce visibility and light, atmospheric particles are the most visible form of air pollution. Commonly called **particulates** in air pollution parlance, atmospheric *aerosols* are solids or liquids less than 100 micrometers (millionths of a meter,μm) in diameter, and commonly in a size range of 0.001 to 20μm. They may be inorganic or organic materials and may belong to the two general classes of **dispersion aerosols** formed by grinding solids, dispersing dusts, or atomizing liquids, and **condensation aerosols** produced by the condensation of gases or vapors, often formed as the result of atmospheric chemical processes. Common dispersion aerosols include water droplets from sea spray, solid particles of NaCl left over when water evaporates from sea spray droplets, cement dust, soil dust dispersed by wind, foundry dust, and pulverized coal. Carbon black, metal fumes, and combustion nuclei form as condensation aerosols from combustion or partial combustion. Liquid particle **mists** include raindrops, fog, cloud droplets, and droplets of sulfuric acid produced when atmospheric SO_2 is oxidized. Organisms produce an abundance of particles. For those afflicted with allergies, the most annoying such particles are plant pollen. Other particles of biological origin include viruses, bacteria, and spores of bacteria and fungi.

In the past and even now in some areas of the world, one of the more troublesome sources of atmospheric particles was **fly ash**, a byproduct residue from combustion of liquids or very finely divided coal. Often the most abundant component of fly ash is elemental carbon left over from incompletely burned fuel. Fly ash commonly includes oxides of aluminum, calcium, iron, and silicon, as well as some magnesium, sulfur, titanium, phosphorus, potassium, and sodium. With properly operating emission control devices, fly ash emissions are now well controlled.

One health concern with particles, especially those from combustion sources, is their ability to carry toxic metals. Of these, lead is of the greatest concern because it usually comes closest to being at a toxic level. Problems with particulate lead in the atmosphere have been greatly reduced by the elimination of tetraethyllead as a gasoline additive, an application that used to spew tons of lead into the atmosphere every day. Another heavy metal that causes considerable concern is mercury, which can enter the atmosphere bound to particles or as vapor-phase atomic mercury. Airborne mercury from coal combustion can become a serious water pollution problem leading to unhealthy accumulations of this toxic element in some fish. Other metals that can cause problems in particulate matter are beryllium, cadmium, chromium, vanadium, nickel, and arsenic (a metalloid).

Some areas of the world, including parts of the United States, have problems with radioactive particles resulting from underground sources of radioactive **radon**, a noble gas product of radium decay. The two major radon isotopes, 222Rn (half-life 3.8 days) and 220Rn (half-life 54.5 seconds)are alpha particle emitters that decay to radioactive 218Po and 216Po, respectively. These radionuclides are nongaseous and adhere readily to atmospheric particulate matter, which, along with gaseous radon, can cause significant indoor air pollution and potential health problems.

Pollutant particles in the atmosphere have both direct and indirect effects. The most obvious direct effects are reduction and distortion of visibility. The light scattering effects of particles in a size range of 0.1μm–1μm are especially pronounced due to interference phenomena resulting from the particles being about the same size as the wavelengths of visible light. Particles also have direct health effects when inhaled. This is especially true of very small particles that can be carried into the innermost parts (alveoli) of lungs. An indirect effect of particles is their ability to serve as reaction sites for atmospheric chemical reactions. They also act as nucleation bodies upon which water vapor condenses.

Limiting Particulate Emissions

The first widespread measures to limit air pollution were directed at control of particle emissions. These measures have become very effective so that the “smoke” that one sees emanating from smokestacks usually consists of droplets of water formed by condensation of steam.

The simplest method of particle control from stack gas and other gases released to the atmosphere consists of **sedimentation** in which particles entrained in stack gas are allowed to settle by gravity in relatively large chambers. Sedimentation is most effective for larger particles. **Inertial mechanisms** operate by spinning a gas in a round chamber such that particles impinge upon the container walls by centrifugal force. **Fabric filters** contained in **baghouses** act to filter particles from air or stack gas (Figure 10.6). The mechanism employed provides for periodic shaking of the fabric filters to collect particles held on their walls, thus restoring gas flow through the fabric. Numerous factors including moisture levels, particle abrasion, particle size, and acidity or alkalinity of the gas and particles must be considered in choosing filter fabrics. **Scrubbers** that spray water or solutions into stack gas are employed to literally wash particles out of gas. In some cases these are operated with a minimal amount of water, which evaporates, so that a solid material is collected. One of the most effective means of particle control consists of **electrostatic precipitators**. These devices use a very high voltage to impart a negative charge onto particles from a central electrode, and the particles are attracted to, and collect on the positively charged walls of the precipitator.

In keeping with the practice of sustainability the particulate matter, such as that collected by a fabric filter in a baghouse, may be used for various purposes. Typically, particulate matter from lead or zinc smelting operations is recycled back into the metal recovery process. Lime kiln dust is often used as agricultural lime. Some kinds of coal fly ash could be used as a source of aluminum if aluminum ore (bauxite) becomes scarce.

10.8: Pollutant Gaseous Oxides

Carbon Monoxide

Carbon dioxide, CO_2, which is an essential ingredient of the atmosphere, but a potential cause of global warming at elevated levels, was discussed in some detail in Section 10.6. Carbon monoxide, CO, is an air pollutant of some concern because of its direct toxicity to humans. Carbon monoxide is toxic because it binds to blood hemoglobin and prevents the hemoglobin from transporting oxygen from the lungs to other tissues. Global and regional levels of atmospheric carbon monoxide are too low to be of concern. However, local levels in areas with heavy automobile traffic can become high enough to pose a health hazard and on some congested urban streets have reached levels of 50–100 ppm. The use of exhaust pollution control devices on automobiles have lowered these levels significantly during the last 30 years. The numerous fatal cases of carbon monoxide poisoning that occur each year are almost always the result of improperly vented heating devices in indoor areas.

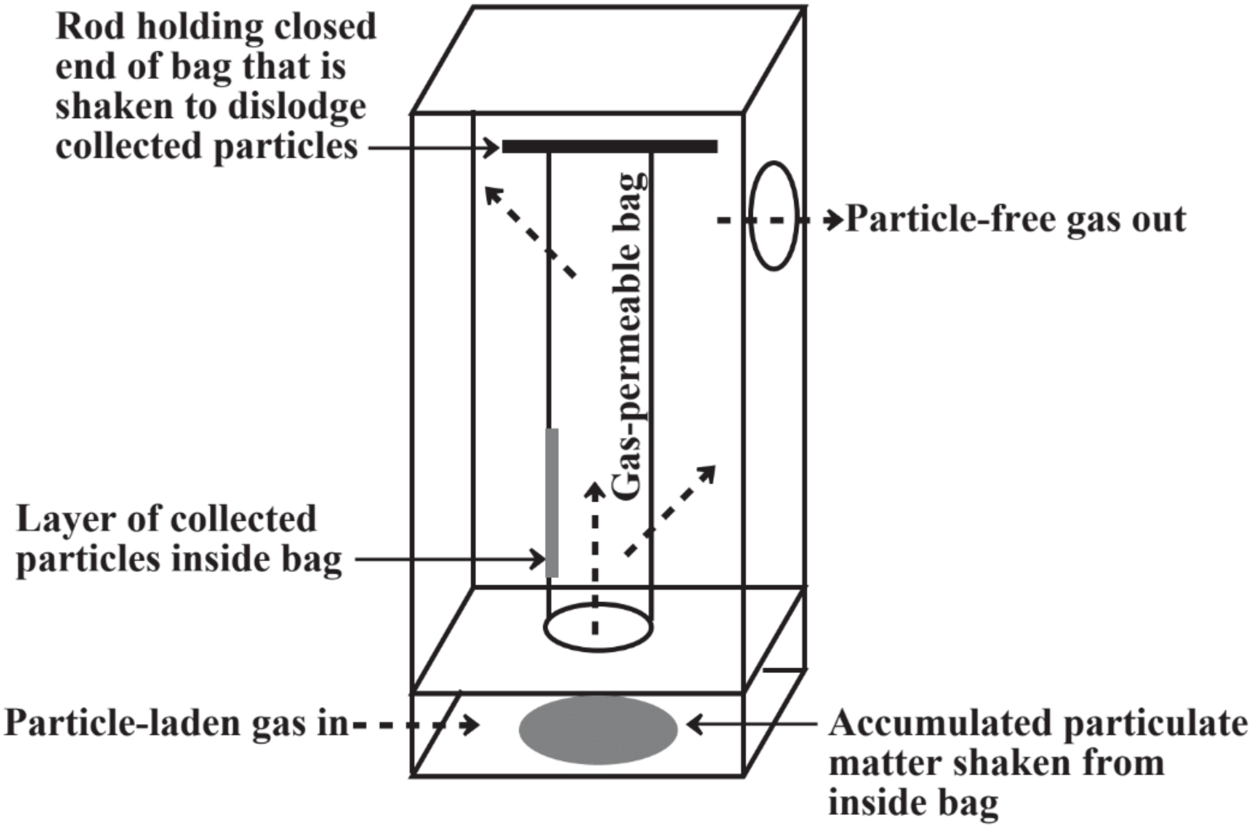


Figure 10.6. Illustration of a unit of a single bag in a baghouse for removal of particulate matter from a gas stream. The flow of gas is illustrated by the dashed lines. A bag is mounted on an opening in a plate such that particle-laden gas is forced up through the inside of the cylindrical bag and is filtered through the bag walls, then flows out as filtered gas. The particulate matter accumulates on the inside of the bag. Periodically, the gas flow through the bag is stopped and the rod suspending the closed upper end of the bag is shaken to dislodge particulate matter from the bag walls, which is collected at the bottom of the apparatus.

Carbon monoxide is produced by partial combustion of fuels, largely in the internal combustion engine. Carbon monoxide emissions can be reduced by careful control of combustion conditions. Running the exhaust along with pumped air over an exhaust catalyst can oxidize carbon monoxide to nontoxic carbon dioxide

$$2\,CO + O_2 \rightarrow 2\,CO_2 \tag{10.8.1}$$

Modern automobile engines use precise computerized control of engine operating parameters along with exhaust catalysts to control carbon monoxide emissions.

Sulfur Dioxide

Sulfur dioxide enters the atmosphere as the result of the following:

- Direct emissions from volcanoes

- Atmospheric oxidation of H_2S emitted to the atmosphere by bacteria and from geothermal sources (volcanoes, hot springs, geysers)
- Atmospheric oxidation of dimethyl sulfide, $(CH_3)_2S$, emitted to the atmosphere from marine organisms
- Pollutant sources from the combustion of organic sulfur and iron pyrite, FeS_2, in fossil fuels

The pollutant sources are of most concern because of their contribution to local and regional air pollution problems and because they are sources that humans can do something about.

The fate of sulfur dioxide in the atmosphere is oxidation and reaction with water to produce sulfuric acid. The overall process is complex and not completely understood, but it can be described by the reaction.

$$2\,SO_2 + O_2 + 2\,H_2O \rightarrow 2\,H_2SO_4 \tag{10.8.2}$$

This process is generally rather slow in the atmosphere, but it can be quite rapid under conditions of photochemical smog formation (see Section 10.11) in which highly reactive oxidizing species are present. It is very important because it is the main mechanism for forming acid rain, which can be directly harmful to vegetation, fish (especially fingerlings), and materials, such as building stone that can be attacked by acid. Sulfur dioxide forms aerosol droplets of sulfuric acid in the atmosphere. As a result, much of the Eastern United States is covered by a slight haze of sulfuric acid droplets during much of the year. In recent years, some volcanic eruptions have blasted enough sulfur dioxide into the atmosphere to produce a sufficient amount of sunlight-reflecting sulfuric acid aerosol to cause a noticeable cooling of the atmosphere.

In addition to indirect effects from the formation of acid rain, sulfur dioxide affects some plants directly, causing leaf necrosis (death of leaf tissue). Another symptom of sulfur dioxide phytotoxicity (toxicity to plants) is chlorosis, a bleaching or yellowing of green leaves.

The most straightforward means of reducing sulfur dioxide emissions is to avoid having sulfur in fuels. As discussed below, sulfur compounds are removed from natural gas and petroleum. Coal often has high levels of sulfur, and during recent years there has been a major shift to low sulfur coal in power plants. Much of the pyritic sulfur, FeS_2, can be washed from coal because it exists in a separate mineral phase that can be separated from the combustible organic matter in coal. However, about half of the sulfur in coal typically is bound to the coal as organic sulfur, and cannot be removed.

A number of coal-fired power plants have installed systems for removing sulfur dioxide resulting from the combustion of coal. One such approach uses **fluidized bed combustion** in which pulverized coal is blasted into a hot bed of calcium oxide, where the coal is burned, and sulfur dioxide is bound by the following reaction.

$$CaO + SO_2 \rightarrow CaSO_3 \tag{10.8.3}$$

Some of the $CaSO_3$ product is oxidized to $CaSO_4$. Another approach uses a slurry of calcium hydroxide (lime, $Ca(OH)_2$) to react with sulfur dioxide in stack gas.

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O \tag{10.8.4}$$

Although effective in removing sulfur dioxide, this process uses enormous quantities of limestone ($CaCO_3$) as a source of lime and produces huge quantities of byproduct.

Green Chemistry and Sulfur Dioxide

The problem of sulfur in fuel provides an excellent illustration of the potential for the application of green chemistry to the elimination of a pollution problem. Sulfur is a valuable raw material required in the manufacture of sulfuric acid, one of the largest volume chemicals made. Hydrogen sulfide, H_2S, occurs in large quantities in natural gas, such as that produced in the Canadian province of Alberta. This hydrogen sulfide must be removed from the natural gas. Rather than presenting a pollution problem, it is converted to elemental sulfur, then used to make sulfuric acid.

Another green chemistry approach to the reclamation of waste sulfur is practiced in Kalundborg, Denmark, the site of the world’s most clearly recognizable system of industrial ecology (see Chapter 14). The huge coal-fired power plant in Kalundborg uses lime scrubbing to remove sulfur dioxide from stack gas. The calcium sulfite product of this process is oxidized,

$$CaSO_3 + \tfrac{1}{2}O_2 + 2\,H_2O \rightarrow CaSo_4 \cdot 2\,H_2O \tag{10.8.5}$$

to generate gypsum, $CaSO_4 \cdot 2H_2O$. This mineral is then used to make wallboard, thus solving a pollution problem from the production of spent lime and a raw materials problem arising from the need for gypsum to make wallboard needed for building construction.

Nitrogen Oxides

Nitrous oxide (N_2O), colorless, odorless, nitric oxide (NO), and pungent-smelling, red-brown nitrogen dioxide (NO_2) occur in the atmosphere. Of these, nitrous oxide is generated by bacteria and its release is one of the ways in which chemically fixed nitrogen in the biosphere is returned to the atmosphere. It is not involved much with chemical processes in the troposphere, but undergoes photochemical dissociation in the stratosphere:

$$\mathrm{N_2O} + h\nu \rightarrow \mathrm{N_2} + \mathrm{O} \tag{10.8.6}$$

Both NO and NO_2, collectively designated as NO_x, are produced from natural sources, such as lightning and biological processes, and from pollutant sources. Pollutant concentrations of these gases can become too high locally and regionally, causing air pollution problems. A major pollutant source of these gases is the internal combustion engine in which conditions are such that molecular elemental nitrogen and oxygen react,

$$\mathrm{N_2} + \mathrm{O_2} \rightarrow 2\,\mathrm{NO} \tag{10.8.7}$$

to produce NO. Combustion of fuels that contain organically bound nitrogen, such as coal, also produces NO. Atmospheric chemical reactions convert some of the NO emitted to NO_2.

Exposed to electromagnetic radiation of wavelengths below 398 nm, nitrogen dioxide undergoes photodissociation,

$$\mathrm{NO_2} + h\nu \rightarrow \mathrm{NO} + \mathrm{O} \tag{10.8.8}$$

to produce highly reactive O atoms. The O atoms can participate in a series of chain reactions through which NO is converted back to NO_2, which can undergo photodissociation again to start the cycle over. Nitrogen dioxide is very reactive, undergoing photodissociation within a minute or two in direct sunlight.

Nitrogen dioxide, NO_2, is significantly more toxic than NO, although concentrations of NO_2 in the outdoor atmosphere rarely reach toxic levels. Accidental releases of NO_2 can be sufficient to cause toxic effects or even death. Brief exposures to 50–100 parts per million (ppm) of NO_2 in air inflames lung tissue for 6-8 weeks followed by recovery. Exposure to 500 ppm or more of NO_2 causes death within 2–10 days. Exposure to 100-500 ppm of NO_2 causes a lung condition with the ominous name of *bronchiolitis fibrosa obliterans* that is fatal within 3–5 weeks after exposure. Fatal incidents of NO_2 poisoning have resulted from accidental release of the gas used as an oxidant in rocket fuels and from burning of nitrogen-containing celluloid and nitrocellulose moving picture film (nitrocellulose has been used as an explosive and has long been banned in film because of catastrophic fires that killed numerous people). Plants exposed to nitrogen dioxide may suffer decreased photosynthesis, leaf spotting, and breakdown of plant tissue.

The release of NO from combustion sources can be reduced by limiting excess air so that there is not enough excess oxygen to produce NO according to Reaction 10.8.7. The production of NO is also reduced by relatively lower combustion temperatures. Exhaust catalytic converter reduce NO_x emissions from automobile exhausts. Scrubbing NO_x from furnace and power plant stack gases is difficult due to the low water solubilities of NO_x gases.

10.9: Acid Rain

Along with hydrogen chloride, HCl, emitted to the atmosphere by the combustion of chlorine-containing organic compounds, sulfur dioxide and nitrogen oxides react in the atmosphere to produce strongly acidic H_2SO_4 and HNO_3, respectively. Incorporated into rainwater, these acids fall to the ground as **acid rain**. A more general term, **acid deposition**, refers to the effects of atmospheric strong acids, acidic gases (SO_2), and acidic salts (NH_4NO_3 and NH_4HSO_4). Acid deposition is a major air pollution problem.

Figure 10.7 shows a typical distribution of acidic precipitation in the 48 contiguous U.S. states. This figure illustrates that acidic precipitation is a *regional* air pollution problem, not widespread enough to be a *global* problem, but spreading beyond *local* areas. (There have been some unfortunate cases where localized release of acid, usually as sulfur dioxide from metal ore smelting operations have affected local areas, often devastating vegetation within several kilometers of the source

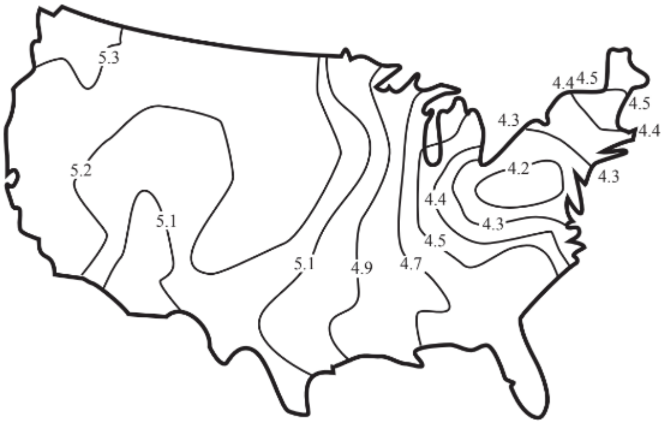


Figure 10.7. Lines showing precipitation with the same pH (isopleths) in the 48 contiguous United States. This is a hypothetical plot. The actual distribution of acidic precipitation varies constantly with time and climatic conditions, but is generally similar to the plot shown with lower values concentrating in the northeastern states.

Transport processes that move atmospheric acids and their precursor acid gases from their sources to downwind areas are very important in determining areas affected by acid rain. The northeastern U.S. and southeastern Canada are affected by acid originating from stack gas emissions carried by prevailing southwesterly winds from Missouri, Illinois, Kentucky and other regions to the southwest. Southern Norway, Sweden, and Finland receive acid precipitation originating farther south in Europe.

Numerous adverse effects have been reported as the result of acidic precipitation. These can be divided into the following major categories:

- Direct effects upon the atmosphere manifested by reduced and distorted visibility. These effects are due to the presence of sulfuric acid droplets and solutions or solid particles of acidic salts, such as NH_4HSO_4.

- Phytotoxicity (toxicity to plants) and destruction of sensitive forests. These effects can be direct, resulting from exposure of plant leaves and roots to acidic precipitation and to acid-forming gases, particularly SO_2 and NO_2. They can also be indirect, primarily by the liberation of phytotoxic Al^{3+} ion by the action of acidic rainfall on soil.

- Direct effects on humans and other animals. These are usually respiratory effects, and asthmatics are especially vulnerable.

- Effects upon plants and fish (especially fish fingerlings) in acidified lake water where the lake is not in contact with minerals, particularly $CaCO_3$, capable of neutralizing acid.

- Damage to materials. Stone (especially acid-soluble limestone and marble) and metal used in building can be corroded and etched by acidic precipitation. Electrical equipment, particularly relay contacts and springs can be corroded by acidic precipitation.

- Some measures can be taken to mitigate the effects of acid rain, although these are very limited once the pollutant has formed. Some success has been achieved with treating acidified lakes with pulverized limestone to neutralize acid. Corrosion-resistant materials can be used in applications where exposure to acid rain is likely. Protective coatings, such as corrosion-resisting paint primers on metals, can be applied to materials likely to be exposed to acidic precipitation. But the best protection is to prevent formation and release of SO_2 and NO_x gases leading to acid rain formation by measures described in the preceding section.

10.10: Miscellaneous Gases in the Atmosphere

There are several inorganic gases other than oxides that can be significant atmospheric he most common of these is ammonia, NH_3. In addition to industrial pollution, such as from heating coal to make coke for steel making, ammonia can be added to the atmosphere by bacterial sources, from sewage treatment, and from the decay of animal wastes. Accidental releases can occur from liquid anhydrous ammonia used as an agricultural nitrogen fertilizer.

Ammonia is strongly attracted to water, so it is normally present in the atmosphere in water droplets. It is the only significant gaseous base in the atmosphere, so that it reacts with atmospheric acids to produce corrosive ammonium salts as shown by the following reactions:

$$\mathrm{NH_3 + N_2SO_4 \rightarrow NH_4HSO_4} \tag{10.10.1}$$

$$\mathrm{NH_3 + HNO_3 \rightarrow NH_4NO_3} \tag{10.10.2}$$

Gaseous chlorine, fluorine, and volatile fluorides are uncommon air pollutants, but very serious where they occur. Elemental chlorine, Cl_2, is widely produced and distributed as a water disinfectant, bleach, and industrial chemical. It is very reactive and so toxic that it was the first poisonous gas used as a military poison in World War I. Most toxic exposures of chlorine occur as the result of transportation accidents leading to its release.

Hydrogen chloride, HCl, can get into the atmosphere from accidental releases of the gas, from reaction with atmospheric water of reactive chlorine-containing chemicals, of which one of the most common is $SiCl_4$,

$$\mathrm{SiCl_4 + 2\,H_2O \rightarrow 2\,SiO_2 + 4\,HCl} \tag{10.10.3}$$

and from the combustion of chlorine-containing polyvinylchloride (PVC) plastic. The strong affinity of HCl gas for water means that it exists as droplets of hydrochloric acid in the atmosphere. Atmospheric HCl is very irritating to mucous membrane tissue and damaging to corrodable materials.

Elemental fluorine (F_2) and hydrogen fluoride are both highly toxic. Fortunately, occurrences of these gases in the atmosphere are very rare. Gaseous silicon tetrafluoride, SiF_4, can be released during steel making and some metal smelting processes when fluorspar (CaF_2) reacts with sand (SiO_2)

$$\mathrm{2\,CaF_2 + 3\,SiO_2 \rightarrow 2\,CaSiO_3 + SiF_4} \tag{10.10.4}$$

Sulfur hexafluoride, SF_6, is an astoundingly unreactive gaseous compound used to blanket and degas molten aluminum and magnesium and in gas-insulated electrical equipment. It lasts essentially forever in the atmosphere. As noted in Section 10.6, the greatest concern with its release is that it is a powerful greenhouse warming gas with an effect per molecule about 24,000 times that of carbon dioxide.

Hydrogen sulfide, H_2S, enters the atmosphere from a number of natural sources including geothermal sources, the microbial decay of organic sulfur compounds and the microbial conversion of sulfate, SO_4^{2-}, to H_2S when sulfate acts as an oxidizing agent in the absence of O2. Wood pulping processes can release hydrogen sulfide. Hydrogen sulfide may occur as a contaminant of petroleum and natural gas, and these sources are the most common source of poisoning by H_2S, which has about the same toxicity as hydrogen cyanide. A tragic incident of hydrogen sulfide poisoning occurred in Poza Rica, Mexico, in 1950 as the result of a process to recover H_2S from natural gas. Incredibly, the hydrogen sulfide byproduct was burned in a flare to produce sulfur dioxide. The flare became extinguished at night so that toxic hydrogen sulfide spread throughout the vicinity, killing 22 people and hospitalizing over 300. A 2003 blowout in a natural gas field in southwestern China released hydrogen sulfide that killed almost 200 people in the surrounding area. As an emergency measure the escaping gas was set on fire producing sulfur dioxide, SO_2, still a toxic material, but much less deadly than hydrogen sulfide. Atmospheric H_2S is phytotoxic, destroying immature plant tissue and reducing plant growth. It also affects some kinds of materials, forming a black coating of copper sulfide, CuS, on copper roofing. This coating weathers to a rather attractive green layer (patina) of basic copper sulfate, $CuSO_4•3Cu(OH)_2$, which protects the copper from further attack. Hydrogen sulfide in the atmosphere becomes oxidized to SO_2. This process is especially rapid under oxidizing atmospheric conditions such as those in which photochemical smog is formed.

Carbonyl sulfide, COS, is another inorganic sulfur gas that can be detected in the atmosphere, though it is usually at very low levels. A related compound, carbon disulfide, CS_2, also occurs in the atmosphere

10.11: Photochemical Smog

One of the most common urban air pollution problems is the production of **photochemical smog**. This condition occurs in dry, stagnant air masses, usually stabilized by a temperature inversion (see Figure 8.1), that are subjected to intense sunlight. A smoggy atmosphere contains ozone, O_3, organic oxidants, nitrogen oxides, aldehydes, and other noxious species. In latter stages of smog formation visibility in the atmosphere is lowered by the presence of a haze of fine particles formed by the oxidation of organic compounds in smog.

The chemical ingredients of smog are nitrogen oxides and organic compounds, both released from the automobile, as well as from other sources. The driving energy force behind smog formation is electromagnetic radiation with a wavelength at around 400 nm or less, in the ultraviolet region, just shorter than the lower limit for visible light. Energy absorbed by a molecule from this radiation can result in the formation of active species, thus initiating *photochemical reactions.*

Although methane, CH_4, is one of the least active hydrocarbons in terms of forming smog, it will be used here to show the smog formation process because it is the simplest hydrocarbon molecule. Smog is produced in a series of chain reactions. The first of these occurs when a photon of electromagnetic radiation with a wavelength less than 398 nm is absorbed by a molecule of nitrogen dioxide.

$$\mathrm{NO_2} h\nu \rightarrow \mathrm{NO} + \mathrm{O} \tag{10.11.1}$$

to produce an oxygen atom, O. The oxygen atom is a very reactive species that can abstract a hydrogen atom from methane,

$$\mathrm{CH_4} + \mathrm{O} \rightarrow \mathrm{HO}\cdot + \mathrm{H_3C}\cdot \tag{10.11.2}$$

to produce a methyl radical, H3C•, and a **hydroxyl radical**, HO•. In these formulas, the dot shows a single unpaired electron. A chemical species with such a single electron is a **free radical**. The hydroxyl radical is especially important in the formation of smog and in a wide variety of other kinds of photochemical reactions. The methyl radical can react with an oxygen molecule,

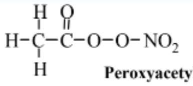
$$\mathrm{H_3C}\cdot + \mathrm{O_2} \rightarrow \mathrm{H_3COO}\cdot \tag{10.11.3}$$

to produce a methylperoxyl radical, H3COO•. This is a strongly oxidizing, reactive species. One of the very important reactions of peroxyl radicals is their reaction with NO, produced in the photochemical dissociation of NO_2 (see Reaction 8.10.1 above),

$$\mathrm{NO} + \mathrm{H_3COO}\cdot \rightarrow \mathrm{NO_2} + \mathrm{H_3COO}\cdot \tag{10.11.4}$$

To regenerate NO_2, which can undergo photodissociation, re-initiating the series of chain reactions by which smog is formed. Literally hundreds of other reactions can occur, leading eventually to oxidized organic matter that produces the small particulate matter characteristic of smog.

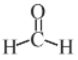
As the process of smog formation occurs, numerous noxious intermediates are generated. One of the main ones of these is ozone, O_3, and it is the single species most characteristic of smog. Whereas ozone is an essential species in the stratosphere, where it filters out undesirable ultraviolet radiation, it is a toxic species in the troposphere that is bad for both animals and plants. Another class of materials formed with smog consists of oxygen-rich organic compounds containing nitrogen of which peroxyacetyl nitrate, PAN,



$$\mathrm{H_3C{-}C(=O){-}O{-}O{-}NO_2}$$

Peroxyacetyl nitrate (PAN)

is the most common example. This compound and ones similar to it are potent oxidizers and highly irritating to eyes and mucous membranes of the respiratory tract. Also associated with smog are aldehydes, which are irritants to eyes and the respiratory tract. The simplest aldehyde, and one commonly found in smoggy atmospheres, is formaldehyde:



$$\mathrm{H{-}C(=O){-}H}$$

Formaldehyde

Harmful Effects of Smog

Smog adversely affects human health and comfort, plants, materials, and atmospheric quality. Each of these aspects is addressed briefly here. Ozone is the smog constituent that is generally regarded as being most harmful to humans, plants, and materials, although other oxidants and some of the noxious organic materials, such as aldehydes, are harmful as well. People exposed to 0.15 parts per million of ozone in air experience irritation to the respiratory mucous tissues accompanied by coughing, wheezing, and bronchial constriction. These effects may be especially pronounced for individuals undergoing vigorous exercise because of the large amounts of air that they inhale. On smoggy days, air pollution alerts may advise against exercise and outdoor activities. Because of these effects, the U.S. Environmental Protection Agency recommends an 8-hour standard limit for ozone of 0.075 ppm and is considering further lowering the standard. In a smoggy atmosphere, the adverse effects of ozone are aggravated by exposure to other oxidants and aldehydes.

Plants are harmed by exposure to nitrogen oxides, ozone, and peroxyacetyl nitrate (PAN, see above), all oxidants present in a smoggy atmosphere. PAN is the most harmful of these constituents, damaging younger plant leaves, especially. Ozone exposure causes formation of yellow spots on leaves, a condition called chlorotic stippling. Some plant species, including sword-leaf lettuce, black nightshade, quickweed, and double-fortune tomato, are extremely susceptible to damage by oxidant species in smog and are used as bioindicators of the presence of smog. Costs of crop and orchard damage by smog run into millions of dollars per year in areas prone to this kind of air pollution, such as southern California.

Materials that are adversely affected by smog are generally those that are attacked by oxidants. The best example of such a material is rubber, especially natural rubber, which is attacked by ozone. Indeed, the hardening and cracking of natural rubber has been used as a test for atmospheric ozone.

Visibility-reducing atmospheric aerosol particles are the most common manifestation of the harm done to atmospheric quality by smog. The smog-forming process occurs by the oxidation of organic materials in the atmosphere, and carbon-containing organic materials are the most common constituents of the aerosol particles in an atmosphere afflicted by smog. Conifer trees(pine and cypress) and citrus trees are major contributors to the organic hydrocarbons that are precursors to organic particle formation in smog.

Preventing Smog with Green Chemistry

Smog is basically a chemical problem, which would indicate that it should be amenable to chemical solutions. Indeed, the practice of green chemistry and the application of the principles of industrial ecology can help to reduce smog. This is due in large part to the fact that a basic premise of green chemistry is to avoid the generation and release of chemical species with the potential to harm the environment. The best way to prevent smog formation is to avoid the release of nitrogen oxides and organic vapors that enable smog to form. At an even more fundamental level, measures can be taken to avoid the use of technologies likely to release such substances, for example, by using alternatives to polluting automobiles for transportation.

The evolution of automotive pollution control devices to reduce smog provides an example of how green chemistry can be used to reduce pollution. The first measures taken to reduce hydrocarbon and nitrogen oxide emissions from automobiles were very much command-and-control and “end-of-pipe” measures. These primitive measures implemented in the early 1970s did reduce emissions, but with a steep penalty in fuel consumption and in driving performance of vehicles. However, over the last three decades, the internal combustion automobile engine has evolved into a highly sophisticated computer-controlled machine that generally performs well, emits few air pollutants, and is highly efficient. (And it would be much more efficient if those drivers who feel that they must drive “sport utility” behemoths would switch to vehicles of a more sensible size.) This change has required an integrated approach involving reformulation of gasoline. The first major change was elimination from gasoline of tetraethyllead, an organometallic compound that poisoned automotive exhaust catalysts (and certainly was not good for people). Gasoline was also reformulated to eliminate excessively volatile hydrocarbons and unsaturated hydrocarbons (those with double bonds between carbon atoms) that are especially reactive in forming photochemical smog.

An even more drastic approach to eliminating smog-forming emissions is the use of electric automobiles that do not burn gasoline. These vehicles certainly do not pollute as they are being driven, but they suffer from the probably unsolvable problem of a very limited range between charges and the need for relatively heavy batteries. However, hybrid automobiles using a small gasoline or diesel engine that provides electricity to drive electric motors propelling the automobile and to recharge relatively smaller batteries can largely remedy the emission and fuel economy problems with automobiles. The internal combustion engine on these vehicles runs only as it is needed to provide power and, in so doing, can run at a relatively uniform speed that provides maximum economy with minimum emissions.

Another approach that is being used on vehicles as large as buses that have convenient and frequent access to refueling stations is the use of fuel cells that can generate electricity directly from the catalytic combination of elemental hydrogen and oxygen, producing only harmless water as a product (see Chapter 16). There are also catalytic process that can generate hydrogen from liquid fuels, such as methanol, so that vehicles carrying such a fuel can be powered by electricity generated in fuel cells.

Green chemistry can be applied to devices and processes other than automobiles to reduce smog-forming emissions. This is especially true in the area of organic solvents used for parts cleaning and other industrial operations, vapors of which are often released to the atmosphere. The substitution of water with proper additives or even the use of supercritical carbon dioxide fluid can eliminate such emissions.

10.12: Natural Capital of the Atmosphere

As discussed in Section 1.4, Earth's natural capital is its ability to provide materials, protection, and conditions conducive to life including Earth's resources and its ecosystems. A large fraction of Earth's natural capital is in the atmosphere and includes materials, waste assimilative capacity and esthetics, largely determining the degree to which our surroundings are pleasant and conducive to our existence. The atmosphere's natural capital is discussed in this section.

A huge part of the atmosphere's natural capital is its ability to absorb and protect organisms from destructive ultraviolet and other short-wavelength cosmic and solar electromagnetic radiation which otherwise would make life on Earth impossible. The absorption of longer wavelength infrared radiation by which incoming solar energy is sent back into space leads to the second major protective function of the atmosphere, its ability to maintain surface temperature at a level at which life can thrive (see Figure 10.3).

The atmosphere is a source of essential raw materials, both for organisms and for industrial use and has major applications in the practice of green chemistry. Plants that provide the foundation of food chains within which all organisms thrive extract the carbon dioxide that they use to build biomass from the atmosphere. Animals and other organisms that perform oxic respiration obtain the molecular O_2 they require from the atmosphere. The refractory N_2 in the atmosphere is converted to biomass and protein nitrogen by bacteria growing in soil and water.

Humans also extract gases from the atmosphere for use in the anthrosphere. Adsorption, permeable membrane, and liquified air distillation processes are used to isolate nitrogen, oxygen, argon, and neon from air for use in the anthrosphere. Nitrogen extracted from air is first converted to ammonia, NH_3, then to industrial chemicals, fertilizers, and explosives. Boiling at a frigid-196°C, pure liquid nitrogen is the most widely used cryogenic liquid. Among its many uses are to preserve viable human embryos for embryo implantation to produce "test tube babies." As a generally unreactive gas, pure nitrogen is used as an inert atmosphere that prevents fires and other chemical reactions. Normally extracted from air along with pure nitrogen, pure oxygen has many industrial applications, such as in steel making, and is used for breathing by people with respiratory difficulties. Noble gas argon from the atmosphere is totally chemically inert and is used industrially, such as in specialized welding processes.

Green Oxygen and Nitrogen from the Air

Elemental oxygen and nitrogen are important commercial products extracted from air. Most commonly this is done by distilling cold liquid air, a process that can also produce noble gas neon, argon, and krypton, if desired. The initial step in air distillation is to compress air to about 7 times atmospheric pressure and cool it to remove water vapor and carbon dioxide. Further compression and cooling yields a liquid air product that can then be fractionally distilled to give relatively pure oxygen, nitrogen, and other gases. These can be stored as cold liquids or as the compressed gases.

Essentially pure oxygen has a number of applications, such as for breathing by people with pulmonary insufficiencies. Huge amounts are consumed in steel making. Pure nitrogen is used to provide inert atmospheres free of oxygen. Large quantities of liquid nitrogen are used in the science of **cryogenics** involving very low temperatures.

Emergency Oxygen

Emergency oxygen is required on aircraft that fly at high altitudes. The containers required to transport pure oxygen are too heavy to put on aircraft, so emergency oxygen is generated by a chemical process using a **chlorate candle**. This device contains sodium chlorate, $NaClO_3$, which decomposes when heated to generate oxygen gas:

$$2\,\mathrm{NaClO_3} \rightarrow 2\,\mathrm{NaCl} + 3\,\mathrm{O_2} \tag{10.12.1}$$

Some of the oxygen generated reacts with a fuel, commonly elemental iron, mixed with the sodium chlorate,

$$4\,\mathrm{Fe} + 3\,\mathrm{O_2} \rightarrow 2\,\mathrm{Fe_2O_3} \tag{10.12.2}$$

a heat-generating reaction that provides heat for the decomposition of the sodium chlorate. Chlorate candles can be stored for many years before being activated and still perform well. They are generally safe. However, chlorate candles improperly shipped in the baggage compartment of a ValuJet DC-9 aircraft caused an uncontrollable fire that brought the aircraft down in the Florida Everglades with the loss of all aboard in 1997.

As illustrated in Figure 8.1, the atmosphere is the conduit by which water is evaporated from oceans and carried over land where it falls as precipitation. This ability of the atmosphere is an important component of its natural capital and atmospheric conditions largely determine the quantity, quality, and distribution of water through the hydrologic cycle. Because of variations in atmospheric conditions, the distribution of rainfall is irregular, with excess in some locations and times and deficiencies in others. Hot drought conditions that cause great hardship and even starvation, especially in parts of Africa, are the result of climate conditions in the atmosphere. Sulfur dioxide and nitrogen oxides emitted to the atmosphere as air pollutants produce sulfuric acid and nitric acid, respectively, polluting the hydrosphere with strong acids, killing fish fingerlings and harming vegetation.

Its ability to assimilate and process materials is an important part of the atmosphere's natural capital and a crucial component of nature's natural cycles. Transpiration of water from plant leaves is an important route for conveying water from soil to the atmosphere. Oxic respiration by humans and other organisms discharges carbon dioxide to the atmosphere as do forest fires and anthrospheric combustion processes. Photosynthetically produced elemental oxygen enters the atmosphere. Pollen and small particles such as smoke or fumes produced by anthrospheric processes enter the atmosphere and are washed out with rain or deposited on Earth's surface. Hydrocarbons and nitrogen oxides from combustion are eventually purged from the atmosphere, often with the intermediate formation of oxidants, aldehydes, and particles characteristic of photochemical smog pollution.

The atmosphere's contribution to esthetics is a major facet of its natural capital. Clear, clean air free of visibility-obscuring particles, acidic gases, and ozone that hinders breathing and irritates eyes has genuine value including its contribution to good health. Whereas the water that humans use can be purified from muddy, even polluted sources, air used for breathing must usually be taken as it comes. Humid, foggy air contaminated by acidic constituents and particles is unpleasant and even unhealthy to breathe as is air heated and dried to uncomfortable levels by greenhouse gas emissions.

10.5: Energy and Mass Transfer in the Atmosphere

The flux of energy reaching Earth's atmosphere from the sun as sunlight is 1,340 watts/m2.This means that a square meter of area perpendicular to incoming sun rays above Earth'satmosphere is receiving solar energy at a rate sufficient to power 13 100-watt light bulbs plus a 40-watt bulb, enough to power an electric iron or a hair dryer set on high! This is an enormous amount of energy. As shown in Figure 10.3, some of the incoming energy reaches Earth's surface, some is absorbed in the atmosphere, warming it, and some is scattered back to space. The energy that comes in primarily as light at a maximum intensity of 500 nanometers in the visible region must go out, which it does as infrared radiation (with maximum intensity at about 10 micrometers(μm), primarily between 2μm and 40μm). Water molecules, carbon dioxide, methane, and other minor species in the atmosphere absorb some of the outbound infrared, which eventually is all radiated to space. This temporary absorption of infrared radiation warms the atmosphere — a greenhouse effect.

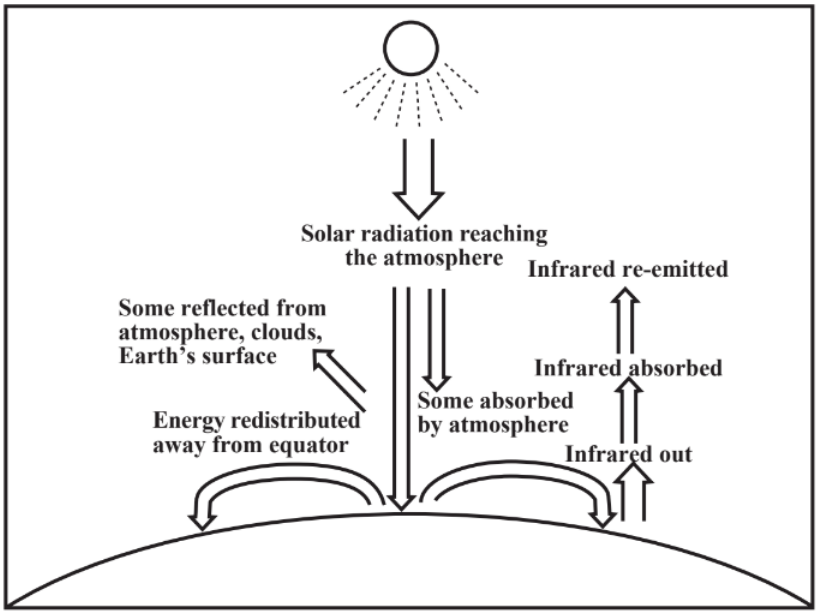


Figure 10.3. Some of the solar energy reaching the top of the atmosphere penetrates to Earth's surface, some is absorbed in the atmosphere, which warms it, and some is scattered by the atmosphere and from Earth's surface. Outgoing energy is in the infrared region. Some of it is temporarily absorbed by the atmosphere before being radiated to space, causing a warming (greenhouse effect). The equatorial regions receive the most energy, part of which is redistributed by warm air masses and latent heat in water vapor away from the equator.

The fraction of electromagnetic radiation from the sun that is reflected by Earth's surface varies with the nature of the surface. The percentage reflected is very important because it determines how effective incoming radiation is in warming the surface and it is expressed as **albedo**. Freshly plowed black topsoil has a very low albedo of only about 2.5%. In contrast, the albedo of a covering of fresh snow is about 90%. The anthrosphere affects albedo. One of the ways that this is done is in cultivating land, turning over relatively high albedo grass and covering it with exposed black soil that absorbs light energy very strongly. Another way is covering of large areas with asphalt paving, which reflects sunlight poorly.

The maintenance of Earth's heat balance to keep temperatures within limits conducive to life is very complex and not well understood. Geological records show that in times past, Earth was sometimes relatively warm and that at other times there were ice ages in which much of Earth'ssurface was covered by ice a kilometer or two thick. The differences in average Earth temperature between these extremes and the relatively temperate climate conditions that we now enjoy were only a matter of a few degrees. It is also known that massive volcanic eruptions and almost certainly hits by large asteroids have caused cooling of the atmosphere that has lasted for a year or more. As addressed later in this chapter, there is now concern that anthropogenic gas emissions, particularly of carbon dioxide from fossil fuel combustion, may be having a warming effect upon the atmosphere.

Earth receives solar energy most directly at the equator, so equatorial regions are warmer than regions farther north and south. A significant fraction of this energy moves away from the equator. This is largely done by **convection** in which heat is carried by masses of air. Such heat can be in the form of **sensible heat** from the kinetic energy of rapidly moving air molecules (the faster their average velocities, the higher the temperature). Heat can also be carried as **latent heat** in the form of water vapor. The **heat of**

vaporization of water is 2,259 joules per gram (J/g) meaning that 2,259 joules of heat energy are required to evaporate a gram of water without raising its temperature. This is a very high value, meaning that the evaporation of ocean water by solar energy falling on it in warmer regions absorbs an enormous amount of heat to form water vapor. This vapor may be carried elsewhere and condense to form rainfall. The heat energy released raises the temperature of the surrounding atmosphere.

Meteorology

The movement of air masses, cloud formation, and precipitation in the atmosphere are covered by the science of **meteorology**. Meteorologic phenomena have a strong effect upon atmospheric chemistry by processes such as the following:

- Movement of air pollutants from one place to another, such as the movement of air pollutant sulfur dioxide from the U.S. Ohio River Valley to New England and southern Canada, where it forms acid rain.
- Conditions under which stagnant pollutant air masses remain in place so that secondary pollutants, such as photochemical smog, can form.
- Precipitation, which can carry acidic compounds from the atmosphere to Earth's surface in the form of acid rain

Atmospheric chemical processes can influence meterological phenomena. The most obvious example of this is the formation of rain droplets around pollutant particles in the atmosphere.

Weather refers to relatively short term variations in the state of the atmosphere as expressed by temperature, cloud cover, precipitation, relative humidity, atmospheric pressure and wind. Weather is driven by redistribution of energy in the atmosphere. A particularly important aspect of this redistribution is the energy released when precipitation forms. This energy can be enormous because of the high heat of vaporization of water. As an example, heat energy from sunlight and from hot masses of air is converted to latent heat by the evaporation of ocean water off the west coast of Africa. Prevailing winds drive masses of air laden with water vapor westward across the ocean. Rainfall forms, releasing the energy from the latent heat of water and warming the air mass. The hot mass of air that results rises, creating a region of low pressure into which air flows in a circular manner. This can result in the formation of a whirling mass of air in the form of a hurricane that may strike Puerto Rico, Cuba, Florida, or other areas thousands of miles from the area where the water was originally evaporated from the ocean.

A very obvious manifestation of weather consists of very small droplets of liquid water composing **clouds**. These very small droplets may coalesce under the appropriate conditions to form raindrops large enough to fall from the atmosphere. Clouds may absorb infrared radiation from Earth's surface, warming the atmosphere, but they also reflect visible light, which has a cooling effect. Pollutant particles are instrumental in forming clouds. One of the more active kinds of cloud-forming pollutants are atmospheric strong acids, particularly H_2SO_4,

A lack of wind and air currents often occurs under conditions of **temperature inversion** in which warmer air masses overlay cooler ones (see Figure 10.1). As shown in this figure, topographical features, such as a mountain range that limits horizontal air movement, may make temperature inversion much more effective in trapping polluted masses of air. These conditions occur in the Los Angeles basin noted for photochemical smog formation.

Questions and Problems

1. Give two examples each of Earth’s natural capital in terms of (1) protective function and (2) raw materials.

2. In what respect is the composition of gases in the troposphere not uniform (which atmospheric constituent varies widely in time and location)?

3. Other than avoiding turbulence due to lower altitude weather, suggest an advantage for commercial aircraft to cruise at a relatively high altitude of around 10 km.

4. Look up the tropopause? Where is it located? What function has it served in keeping Earth in a livable state?

5. What chemical species in the stratosphere is essential for life on Earth?

6. What starts a photochemical reaction? What is it called when a series of photochemical reactions continues?

7. What is a free radical?

8. In what two important respects may very small particles participate in atmospheric chemical processes?

9. In what respect does the radiation by which Earth loses energy differ from that by which it gets energy from the sun?

10. What are two catastrophic events that could cause a sudden cooling of Earth’s atmosphere?

11. How is water vapor involved in moving energy through the atmosphere?

12. Distinguish among the terms meteorology, weather, and climate.

13. What do clouds consist of? What must happen before rain falls from clouds?

14. Why is there essentially no atmospheric chemistry involving elemental nitrogen gas in the atmosphere?

15. Cite an atmospheric chemical condition or phenomenon that shows that the O2 molecule iseasier to break apart than the N2molecule.

16. In what respect are elemental nitrogen and oxygen green elements?

17. Give a chemical reaction that produces oxygen that can be used for emergencies.

18. What are two major classes of atmospheric particles based upon how they are produced?

19. In the earlier days of coal utilization, fly ash was not a major problem. What has changed that has resulted in much greater production of fly ash? What modern mode of coal combustion significantly reduces the production of fly ash and acid gases from coal combustion?

20. Suggest why lead has become less of a problem as an atmospheric pollutant in recent years.

21. What is a radioactive element that can get into indoor spaces from underground sources?

22. What is an atmospheric phenomenon caused most prominently by particles 0.1μm–1μm in size? Why are very small particles especially dangerous to breathe?

23. List six means of controlling particle emissions.

24. What is the major health effect of carbon monoxide?

25. What is a serious air pollution phenomenon resulting from an atmospheric reaction of sulfur dioxide?

26. In what form may approximately half of the sulfur in coal be physically separated before combustion?

27. What is a method used to separate sulfur dioxide from furnace stack gas?

28. Name two ways in which green chemistry can be applied to reduce sulfur dioxide emissions.

29. What is an important health effect of nitrogen dioxide? Why is it particularly important in atmospheric chemistry?

30. In 2008/2009 problems arose in newer houses due to toxic drywall. What was the cause of this problem and how does it relate to material covered in this chapter?

31. What are five categories of adverse effects from acid precipitation?

32. Chemically, what is distinctive about ammonia in the atmosphere?

33. What is the historic evidence for the toxicity of elemental chlorine in the atmosphere?

34. What are some sources of atmospheric hydrogen sulfide? Is it a health concern?

35. In what respect is atmospheric carbon dioxide essential to life on Earth? Why may it end up being the “ultimate air pollutant?”

36. What are some of the more harmful effects projected if global warming occurs to a significant extent?

37. What can green chemistry do about global warming?

38. What is a greenhouse gas other than carbon dioxide that is produced by microorganisms?

39. What are the ingredients and conditions leading to the formation of photochemical smog?

40. What substances are found in a smoggy atmosphere?

41. What are some harmful effects of smog?

42. What are some of the ways that green chemistry can help prevent smog?

43. The temperature of a specific number of moles of gas occupying initially 23.0 L was changed from 75°C to -20°C at constant pressure. Recalling the significance of 273 in such calculations, what was the volume of the gas after the temperature change?

44. The pressure on a specific number of moles of gas occupying initially 13.0 L was changed from 1.15 atm to 0.900 atm at constant pressure. What was the volume of the gas after the temperature change?

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CHAPTER OVERVIEW

11: The Geosphere and a Green Earth

“The 2010 explosion, fire, and subsequent massive leakage of crude oil at the site of the Deepwater Horizon oil well in the Gulf of Mexico illustrates the hazards of probing deep into the geosphere without proper safeguards against the kinds of accidents that can occur at great depths where high temperatures and extreme pressures present unique challenges to technology.”

11.1: Probing Deep into the Geosphere - A Well Too Far?
11.2: The Nature of the Geosphere
11.3: The Geosphere as a Source of Natural Capital
11.4: Environmental Hazards of the Geosphere
11.5: Water on and in the Geosphere
11.6: Anthrospheric Influences on the Geosphere
11.7: The Geosphere as a Waste Repository
11.8: Have You Thanked a Clod Today?
11.9: Plant Nutrients and Fertilizers in Soil
11.10: Soil and Plants Related To Wastes and Pollutants
11.11: Soil Loss - Desertification and Deforestation
Literature Cited and Supplementary References
Questions and Problems

11.1: Probing Deep into the Geosphere - A Well Too Far?

In 2009 the British petroleum exploration and development company, BP, reached a record depth for an oil well of 10,685 meters (35055 feet, 6.6 miles) below the ocean floor in the Gulf of Mexico not counting the 1,220 meters of water above the wellhead. This well is part of the Tiber Prospect oil field estimated to contain between 4 billion and 6 billion barrels of crude oil equivalent (including natural gas). This well illustrates the ability that humans have acquired to probe far into the geosphere where conditions are extreme with pressures that may reach 1,200 times atmospheric pressure and temperatures may exceed 135°C. At these depths and under these conditions it is indeed a different world than the one encountered by more conventional petroleum exploration.

In early 2010 BP was in the process of completing another deep well in the Gulf of Mexico about 66 km off the coast of Louisiana in 1500 meters of water using the Deepwater Horizon semi-submersible mobile offshore drilling unit. This marvel of modern well drilling technology was a massive floating dynamically-positioned unit kept in place precisely by the computerized operation of propulsion units. At 9:45 p.m. on April 20, 2010, highly pressurized methane gas overcame the containment devices on the well, burst through the top of the drill column, and spread over the drill rig causing a massive explosion and huge fire. Although most of the personnel on the rig were rescued, 11 workers were killed and their bodies were never found. After 36 hours of uncontrollable fire, the Deepwater Horizon rig sunk on the morning of April 22, 2010. Despite efforts to contain the flow, oil pressurized by natural gas continued to pour from the wellhead, spreading across large areas of the Gulf of Mexico resulting in arguably the most catastrophic environmental disaster of our time. Financial costs of this disaster have been in the billions of dollars (in June 2010 BP set aside a $20 billion fund to pay claims resulting from the oil release) and damage to fisheries and coastal areas from the leaking petroleum have been immeasurable. The question can be raised whether this was “a well too deep,” a probing by humans too far into the depths of the geosphere, at least in consideration of the inadequate protective measures that had been taken?

11.2: The Nature of the Geosphere

Defined in Section 8.4 and illustrated in Figure 8.5, the **geosphere** consists of the rocks, minerals, soils, sediments, molten magma, and pressurized gases and liquids beneath Earth's surface. The Deepwater Horizon incident discussed above speaks to human efforts to extract from the geosphere the materials and energy that modern civilization demands and it illustrates the potential environmental hazards associated with exploiting the geosphere's resources. It speaks to the need for understanding the geosphere and treating it with the respect that it demands for the maintenance of the environment under living conditions.

Most of our food is grown on the geosphere and humans extract from it metals, fossil fuels, fertilizers for plants, and a variety of minerals used in construction and for other purposes. Over the years, huge quantities of waste products have been discarded to the geosphere, in some cases very carelessly in a manner that poses threats to humans and other organisms. A thin layer on top of the geosphere — in places only a few centimeters deep — composes topsoil which supports the plant life upon which humans and most other land-dwelling organisms depend for their food.

The geosphere interacts strongly with the other environmental spheres. Streams and rivers flow through channels in the geosphere, lakes and reservoirs occupy cavities on the surface of the geosphere, and groundwater occurs in aquifers underground that are part of the geosphere. Gases are exchanged between the geosphere and the atmosphere, light and infrared radiation transmitted through the atmosphere warm the surface of ground, and it in turn radiates back to the atmosphere the infrared radiation by which Earth loses the energy it absorbs from the sun.

The geosphere is tied to green chemistry in many important respects, including the following

- Plants that provide most food for humans and animals grow on the geosphere.
- Plants growing on the geosphere already provide, and have the potential to provide much more, biomass for use as renewable materials, such as wood, fiber, raw materials, and fuel.
- The geosphere is the source of nonrenewable minerals, ores, fossil fuels, and other materials used by modern industrialized societies.
- Modifications and alterations of the geosphere have profound effects upon the environment.
- Sources of fresh water are stored in lakes and rivers on the surface of the geosphere, move by means of streams, rivers, and canals on the geosphere, and occur in aquifers underground.
- The geosphere is the ultimate sink for disposal of a variety of wastes.

This chapter briefly addresses the nature of the geosphere, and resource utilization from the geosphere. Waste disposal on land or underground are considered in later chapters. Because of the special importance of soil and the plants that grow on it as sources of food and fiber, soil is discussed in some detail.

Physical Nature of the Geosphere

At the center of Earth is an iron-rich inner core, hot enough to be molten under normal pressures, but compressed to a solid by the enormous pressures at such great depths. Surrounding this core is an outer core consisting of molten rock called magma. Earth's solid outer layer consists of the mantle and the **crust**, a layer that is only 5-40 km thick. Only the upper layers of the crust are accessible to humans.

For the most part, the crust consists of **rocks**, which in turn are made up of **minerals** characterized by a definite chemical composition and crystal structure. Only about 25 of the approximately 2000 known minerals compose most rocks. Because most of the crust consists of chemically combined oxygen (49.5%) and silicon (25.7%), the most abundant minerals are **silicates** composed of various silicon oxides, examples of which are quartz, SiO_2, and potassium feldspar, $KAlSi_3O_8$. Other elements in Earth's crust are aluminum (7.4%, commonly occurring as Al_2O_3), iron (4.7% as Fe_3O_4 and other iron oxides), calcium (3.6% in limestone, $CaCO_3$, and dolomite, $CaCO_3•MgCO_3$), sodium (2.8%), potassium (2.6%), and magnesium (2.1%). That leaves only 1.6% of the crust to serve as a source of other important mineral substances, including metals other than iron and aluminum, phosphorus required for plant growth, and sulfur widely used in industrial applications.

The rocks that compose Earth's crust participate in the **rock cycle** shown in Figure 11.1. **Igneous rock** is rock that has solidified from molten rock called **magma** that has penetrated to near Earth's surface. Exposed to water, atmospheric oxygen, and various organisms, igneous rock becomes highly altered, reaching a state of greater physical and chemical equilibrium with the atmosphere. This is a process called **weathering**. Weathering products end up as soil and are carried by water to be deposited as sediments. Sediments that become buried and compressed become **secondary minerals**, among the most abundant of which are **clays**, consisting of silicon and aluminum oxides, produced by the weathering of minerals such as potassium feldspar, $KAlSi_3O_8$. A common clay is **kaolinite**, $Al_2Si_2O_5(OH)_4$.

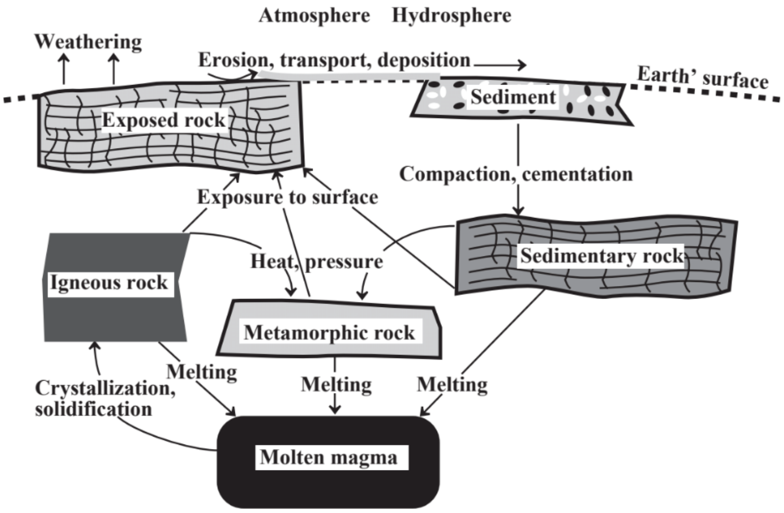


Figure 11.1. The rock cycle. Rock is produced when molten magma crystallizes and solidifies to produce igneous rock. Igneous rock is exposed to the atmosphere and hydrosphere at the surface where weathering and erosion produces sedimentary material that is deposited by the movement of water in sediments. The sediments become buried and subjected to pressure that result in compaction and cementation to produce sedimentary rock. Heat and pressure generate metamorphic rock. At sufficient depths rock of all kinds can be subjected to high temperatures to produce molten rock called magma. Magma that has crystallized and solidified is igneous rock. Igneous rock forced to the surface and exposed to water and air weathers and produces sedimentary material to start the rock cycle over.

Although the earth's crust is very thin compared to Earth's total diameter, there is an even much thinner, fragile and vitally important layer covering the crust —**soil**. Soil is the finely divided mixture of mineral and organic matter upon which plants grow, providing the food that humans and most other animals eat. Productive soil may be only a few centimeters thick, and rarely is more than a few meters in thickness. Soil is uniquely important and of crucial importance in sustainability. Humans are capable of inflicting great damage on soil causing it to become unproductive and in extreme cases resulting in widespread hunger and even starvation.

Geochemistry is the branch of chemistry that deals with rocks and minerals and the chemical interactions of the geosphere with other environmental spheres. The specialized branch of geochemistry relating to environmental influences and interactions of the geosphere is **environmental geochemistry**. Weathering by chemical processes is a particularly important aspect of geochemistry. Almost imperceptible under dry conditions, weathering proceeds at a much more rapid rate in the presence of water. The rate of weathering is also increased by the action of microorganisms, some of which secrete chemical species that attack rock and leach nutrients from it. Particularly important to weathering are **lichens**, which are algae and fungi living together synergistically. The algae utilize solar energy to convert atmospheric carbon dioxide to plant biomass and the fungi utilize the biomass and anchor the organisms to the rock surface and extract nutrients from it.

Human Influences

Human activities have a tremendous influence on the geosphere as evidenced by hills leveled, valleys filled in, and vast areas paved to make freeways, parking lots, and shopping centers. One such influence is on **surface albedo**, defined as the percentage of impinging solar energy reflected back from Earth's surface. The surface albedo of an asphalt paved surface is only about 8%. Amore alarming effect is desertification in which normally productive soil is converted to unproductive desert in areas where rainfall is marginal. This phenomenon is discussed in more detail in Section 11.10.

11.3: The Geosphere as a Source of Natural Capital

The geosphere is an immense source of natural capital, providing a living environment for most humans, minerals required by modern civilizations, and room for disposal of wastes. One of the greatest concerns with regard to sustainability is the acquisition of essential elements from the geosphere in ways that sustain to the maximum extent possible supplies of these irreplaceable resources. As technology advances priorities for specific geospheric resources change. In recent years, numerous uses have emerged for the **rare earth elements** consisting of the fifteen lanthanides (elements with atomic numbers 58 through 71 in the periodic table shown in Chapter 3) plus scandium and yttrium, transition elements with atomic numbers 21 and 39. The chemical properties of the lanthanides are generally quite similar making their separation difficult and the properties of scandium and yttrium are similar to those of the lanthanides, so they are commonly classified as rare earths.

The uses that have emerged for the rare earths are varied and for different ones include making metal alloys, superconductors, phosphors that glow various colors in light-emitting diodes(LEDs), electrodes, electrolytes, electronic filters, lasers, specialty (colored) glasses, X-ray tubes, mercury vapor lamps, computer memory, oxidizing agents, and reducing agents. Rare earth's are widely used in hybrid automobiles and in wind turbines. Each Toyota Prius hybrid automobile reportedly requires 1 kg of neodymium for its electric motor with terbium and dysprosium added in smaller quantities to preserve magnetic qualities and 10-15 kg of lanthanum for its electric motor.

Lithium has emerged as an important element because of the emergence of high-powered lithium storage batteries capable of storing and releasing large quantities of energy per unit mass of battery. These have largely been used in computers and other electronic devices, but will certainly find growing applications in electric and hybrid automobiles.

With the rather sudden development of new applications for rare earth elements and lithium, questions of supply have become important. China has had a near monopoly on rare earth elements and, with the advancement of high-tech industries in China which may consume available supply, other countries have become alarmed regarding availability. China is also a source of lithium, although Bolivia is the main supplier. Fortunately, rare earths are not very rare and the vast U.S. deposit in Mountain Pass, California, was the largest supplier until the facility was closed due to competition from China where labor costs are very low. Now the mine is being modernized in preparation for production to resume. Rare earth deposits also occur in Canada and even Vietnam.

In June 2010, U.S. military officials and geologists revealed that war-torn Afghanistan was a treasure trove of desired minerals including rare earths with a total value of all mineral resources estimated at around 1 trillion dollars. The most abundant and valuable of these is iron (estimated at $420 billion), copper ($274 billion), niobium ($81 billion), cobalt ($51 billion), gold ($25 billion), molybdenum ($24 billion), and rare earths ($7.4 billion). Other minerals of commercial value in Afghanistan likely include silver, potash, aluminum, graphite, fluorite, phosphorus, lead, zinc, mercury, strontium, sulfur, talc, magnesite, and kaolin clay. There are also believed to be lithium deposits in dry lake beds of Afghanistan's eastern province of Ghazni. The lithium deposits may in fact be equal to those of Bolivia, which currently produces most of the lithium used in battery manufacture. Development of these mineral sources has the potential to help move the economy of the troubled country of Afghanistan from dependence on the opium trade (and U.S. military expenditures) to an economy based upon mineral resources.

11.4: Environmental Hazards of the Geosphere

Having lain dormant for almost two centuries, the Eyjafjallajokull volcano, one of Iceland'slargest, began to ooze lava on March 20, 2010, visible as a red glow above the huge glacier covering the volcano. Initially, the eruption was nothing more than an interesting tourist attraction and the volcano appeared to revert to its normal state after a few days. However, on April 14 an enormous explosion sent volcanic ash as high as 11,000 meters followed by days in which the volcano spewed ash high into the atmosphere. This presented a significant problem for commercial aviation as the plume of volcanic ash spread eastward across the British Isles and northern and central Europe because volcanic ash can damage jet engines and even cause them to stop running. (In 1982 all four engines of a British Airways 747 stopped when it inadvertently flew into an ash cloud from Indonesia's Mount Galunggung and for several terrifying minutes what suddenly became the world's largest glider descended from 11,000 meters to 4100 meters before the engines restarted enabling an emergency landing in Jakarta.) The result of the Eyjafjallajokull eruption was that within two days most of Europe's major airports were closed canceling thousands of flights. Because of ripple effects across the world this incident became the worst peacetime travel disruption in history stranding millions of travelers, many with diminished financial resources from limited travel budgets. The result was a period of many days of travel chaos as flight bookings were rescheduled to eventually get travelers to their destinations. Airlines estimated financial losses of about $1.7 billion resulting from the cancellation of more than 100,000 flights.

The Iceland volcano eruption has been a reminder of the awesome, potentially destructive forces that reside in the geosphere and of the vulnerability of modern civilization to them. Along with earthquakes, volcanoes are geospheric phenomena that are beyond the power of humans to prevent or even accurately predict. Even in these cases, however, human activities can significantly influence the degree of damage done. As examples, structures constructed on poorly consolidated fill dirt are much more susceptible to earthquake damage than are those attached firmly to bedrock, and the construction of dwellings in areas known to be subject to periodic volcanic eruptions simply means that unstoppable lava flows and other volcanic effects will be much more damaging when they occur. Other, less spectacular, but very destructive geospheric phenomena can be greatly aggravated by human activities. Destructive and sometimes life-threatening landslides, for example, often result from human alteration of surface soil and vegetation.

Earthquakes

Earthquakes consist of violent horizontal and vertical movement of Earth's surface resulting from relative movements of tectonic plates. Plates move along fault lines. Huge masses of rock may be locked relative to each other for as long as centuries, then suddenly move along fault lines. This movement and the elastic rebound of rocks that occurs as a result causes the earth to shake, often violently and with catastrophic damage.

History provides many examples of astoundingly damaging earthquakes. Over 1 million lives(out of a much lower global population than now) were lost by an earthquake in Egypt and Syria in 1201 A.D. The Tangshan, China, earthquake of 1976 killed approximately 650,000. During the latter 1990s and early 2000s, a number of fatalities resulted from earthquakes in Turkey, Greece, Taiwan, Iran, India and China. The May 12, 2008, 7.9 magnitude Wenchuan earthquake in Sichuan Province, China, left 80,000 people dead or missing. Financial costs of earthquakes in highly developed areas are enormous; the 1989 Loma Prieta earthquake in California cost about 7 billion dollars. Phenomena caused by earthquakes can add to their destructiveness. In addition to their direct shaking effects, earthquakes can cause ground to rupture, subside, or rise. **Liquefaction** of poorly consolidated ground, especially where groundwater levels are shallow, occurs when soil particles disturbed by an earthquake separate and behave like a liquid, causing structures to sink and collapse. One of the more terrifying effects of earthquakes are giant ocean waves called **tsunamis** that can reach heights of as much as 30 meters. On December 26, 2004, a huge earthquake off the coast of Sumatra generated a tsunami up to 30 meters high, killing more than 150,000 people in countries around the Indian Ocean.

Earthquakes have defied all efforts to predict them, a fact that makes them all the more frightening. However, earthquake-prone areas, such as southern California, are well known, and loss of life and property can be minimized by taking appropriate measures. Buildings can be constructed to resist the effects of earthquakes using practices that have been known for sometime. For example, some buildings in Niigata, Japan, were constructed to be earthquake-resistant in the 1950s. When a destructive earthquake hit that city in 1964, some buildings tipped over on the liquified soil but remained structurally intact! (Current practice calls for the construction of more flexible structures designed to dissipate the energy imparted to them by an earthquake.) The construction of buildings, roadways, railroads, and other structures to withstand the destructive effects of earthquakes provides an excellent example of designing the anthrosphere in a manner that is as compatible as possible with the geosphere and the natural hazards it poses.

Although humans can do nothing to prevent earthquakes, there is some evidence that anthrospheric activities have helped cause them. Some seismologists have suggested that the pressure of water from newly constructed reservoirs in China provided lubrication that enabled earth movement. At least one experiment in injecting water into hot rock formations to produce steam for power had to be stopped because it caused a number of very small quakes detected by sensitive instruments.

Volcanoes

A volcano results due to the presence of liquid rock magma near the surface. In addition to liquid rock lava at temperatures ranging from 500˚C to 1400˚C that flows from volcanoes, these often very destructive phenomena are manifested by discharges of gases, steam, ash, and particles. Volcanic disasters have always plagued humankind. The 79 A.D. eruption of Mount Vesuvius in ancient Rome buried the city of Pompei in ash, preserving a snapshot of life in Rome at that time. The astoundingly massive eruption of Indonesia's Tambora volcano in Indonesia in 1815 was caused when water infiltrated the hot magma beneath the volcano resulting in an explosion equivalent to 100 million tons of TNT explosive and blasting an estimated 30 cubic kilometers of solid material into the atmosphere. The May 18, 1980, Mount St. Helens eruption in Washington State blew about 1 cubic kilometer of material into the atmosphere, killed 62 people, and caused about $1 billion in damage.

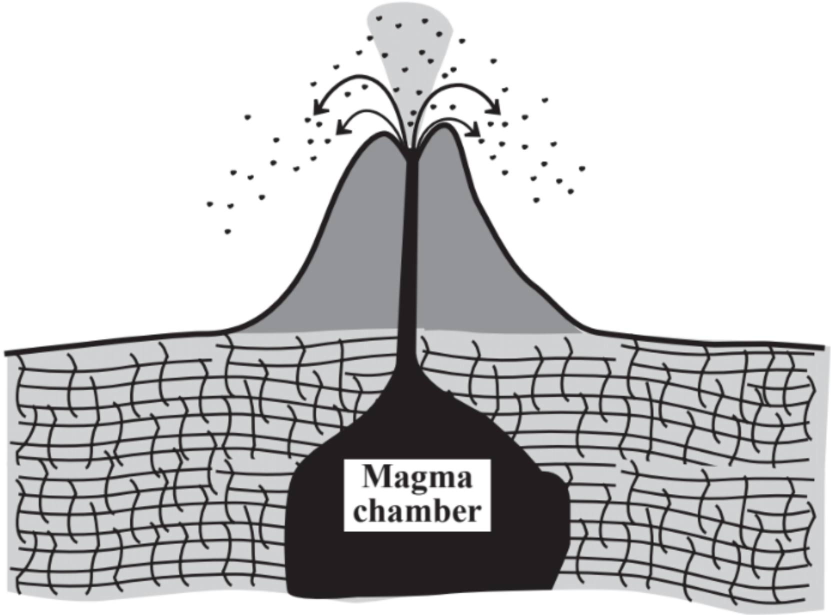


Figure 11.2. A volcano in a classic cone shape produced when molten lava and ash are ejected from a magma chamber underground.

In addition to their immediate effects upon surrounding areas, volcanoes can affect the atmosphere and climate. The Tambora volcano blasted enough particulate matter into the atmosphere to cause a very pronounced cooling effect. The following "year without a summer" caused global crop failures and starvation, and perceptible global cooling was observed for the next 10 years. Huge quantities of water vapor, dense carbon dioxide gas, carbon monoxide, hydrogen sulfide, sulfur dioxide, and hydrogen chloride may be emitted to the atmosphere in volcanic eruptions. People may suffocate in the carbon dioxide or be poisoned by the toxic carbon monoxide and hydrogen sulfide. Hydrogen chloride along with hydrogen sulfide and sulfur dioxide oxidized in the atmosphere to sulfuric acid can contribute to acidic rainfall. Volcanic emissions differ in their atmospheric chemical effects. The 1982 El Chichón eruption in Mexico generated little particulate mineral matter but vast amounts of sulfur oxides that were oxidized to sulfuric acid in the atmosphere. The tiny droplets of sulfuric acid suspended in the atmosphere effectively reflected enough sunlight to cause a perceptible cooling in climate.

Massive, atmospheric-damaging eruptions of volcanoes in recorded history have caused catastrophic crop failures. These will happen again. And since the world as a whole carries little food surplus from year to year, the certainty of food supply disruptions due to volcanic activity point to the desirability of storing substantial amounts of food for emergency use.

Surface Effects

Though less spectacular than major earthquakes or volcanic eruptions, surface earth movement causes enormous damage and significant loss of life. Furthermore, surface earth movement is often strongly influenced by human activities. Surface phenomena result from the interaction of forces that act to thrust earth upward countered by weathering and erosion processes(see Section 11.2) that tend to bring earth masses down. Both of these phenomena are influenced by the exposure of earth masses to water, oxygen, freeze-thaw cycles, alternate saturation with water and drying, organisms and human influences.

Landslides occur when finely divided (unconsolidated) earthen material slides down a slope.The results can be devastating. The 1970 earthquake-initiated landslide of dirt, mud, and rocks on the slopes of Mt. Huascaran in Peru may have killed 20,000 people. A 1963 landslide on slope surrounding a reservoir held by the Vaiont Dam in Italy suddenly filled the reservoir causing a huge wall of water to overflow the dam killing 2600 people and destroying everything in its path.

Along with weather and climate, human activities can influence the likelihood and destructiveness of landslides. Roads and structures constructed on sloping land can weaken the integrity of earthen material or add mass to it, increasing its tendency to slide. In some cases, strong root structures of trees and brush anchor sloping land in place. However, some plant roots destabilize and add mass to soil, increase the accumulation of water underground, and cause earth to slide. Fortunately, predicting a tendency for landslides to occur is relatively straightforward based upon the nature and slope of geological strata, climate conditions, and observations of evidence of a tendency toward landslides, such as movement of earth and evidence of cracked foundations in buildings built on slopes. In some cases remedial actions may be taken, but more important are the indications that structures should not be built on slide-susceptible slopes.

Less spectacular than landslides is **creep** characterized by a slow, gradual movement of earth. Creep is especially common in areas where the upper layers of earth undergo freeze/thaw cycles. A special challenge is **permafrost** which occurs in northern Scandinavia, Siberia, and Alaska. Permafrost refers to a condition in which ground at a certain depth never thaws, and thawing occurs only on a relatively thin surface layer. Structures built on permafrost may end up on a pool of water-saturated muck resting on a mixture of frozen ice and soil. One of the greater challenges posed by permafrost in recent times has been the construction of the Trans-Alaska pipeline in Alaska on a permafrost surface. Global warming is causing thawing of permafrost in Arctic regions such as parts of Siberia and is resulting in significant structural damage.

Expansive clays that alternately expand and contract when saturated with water, then become dried out, can cause enormous damage to structures, making the construction of basements virtually impossible in some areas. **Sinkholes** occur in areas where rock formations are dissolved by chemical action of water (particularly dissolved carbon dioxide acting on limestone). Earth can fall into a cavity generated by this phenomenon causing huge holes in the ground that can swallow several houses at a time.

11.5: Water on and in the Geosphere

The geosphere is the repository of virtually all the world's fresh water. As shown in Figure11.2, this water may be in underground aquifers as groundwater; on the surface as streams, rivers, lakes and impoundments; or as deposits of ice (glaciers) resting on Earth's surface. Water collected

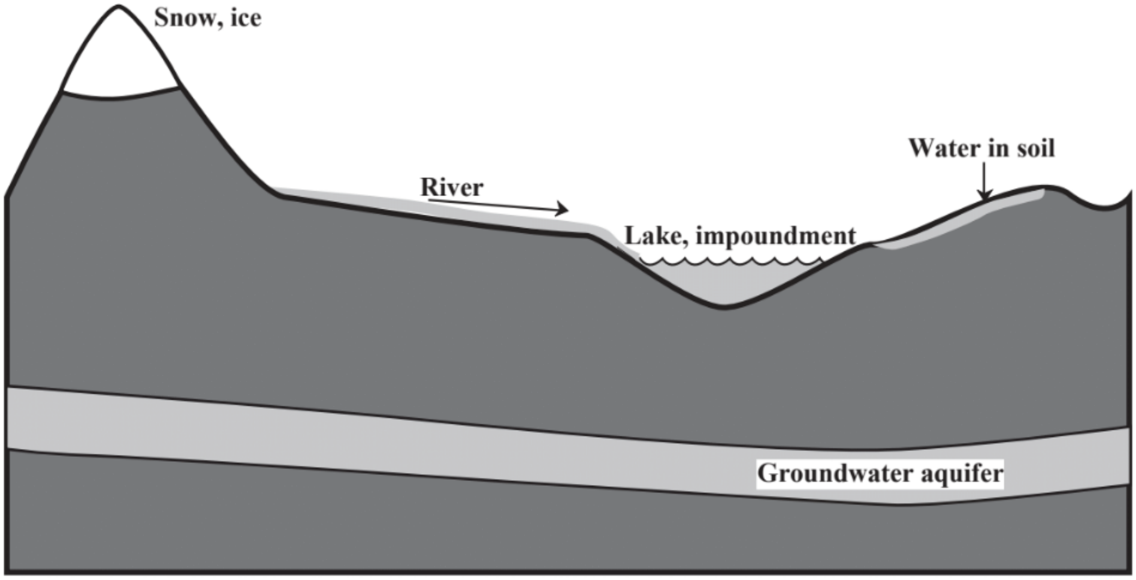


Figure 11.3. Major aspects of water on and in the geosphere

by the geosphere constitutes virtually all Earth's fresh water resources. This water is susceptible to pollution which in extreme cases can render the water sources virtually useless. One of the greater water pollution problems is when water in underground aquifers becomes contaminated with hazardous waste material improperly discarded in the geosphere.

Water commonly moves on the geosphere in **streams** or **rivers** consisting of channels through which water flows. Rivers collect water from drainage basins or watersheds. In order to protect water quality in rivers, pollution and pollution-causing agricultural practices in drainage basins must be avoided. Rivers continually erode the geosphere over which they flow and leave deposits of sediments. Over time, a river will erode earth away and create valleys. An undisturbed river continually cuts curving patterns known as **meanders** in a river valley. The flat area of a valley formed by erosion and sediment deposition in the valley and susceptible to periodic flooding is the river's floodplain.

Floods are the phenomena associated with river flow that are most likely to cause damage to human structures. Despite their destructiveness, floods are normal phenomena by which a river does much of its work of shaping the surface of the geosphere. However, by unwisely building in flood plains, humans have made themselves susceptible to the damaging effects of floods. This was illustrated most tragically by the deadly flood of the city of New Orleans following the 2005 Hurricane Katrina in which many of the areas flooded were built below sea level! Human activities on the geosphere surface can make the effects of floods much worse. For example, flash floods following intense rainfall in urban areas are made much worse by the removal of vegetation from watersheds and its replacement with paving. Concrete and asphalt surfaces do not slow down the flow of water like well-rooted plants do and such surfaces prevent the infiltration of water into the ground.

Attempts to control water flow and flooding provide interesting examples of how humans can interact with their natural environment. Control measures have concentrated on the downstream end on the rivers themselves by construction of levees to confine rivers to their banks, straightening and deepening river channels to increase the velocity and flow of the water in an effort to move it quickly downstream away from the potentially flooded area, and by building dams to contain floodwater until it can be safely released. Such measures can be deceptively successful, sometimes for many decades, until a massive flood overwhelms them. When a contained river carrying vast amounts of water flowing at a high velocity eventually breaks through the levees and dams designed to contain it, the resulting damage can be catastrophic.

An approach to flood control based upon the best practice of sustainability provides a means of minimizing flood damage. Such an approach tends to concentrate more on the upstream end, the watersheds from which water produced by rainfall flows into the river.

With the proper kind of vegetation cover, such as forests, and with terraces and small dams designed to temporarily slow the flow of water into the river from the watershed, extremes of high water (flood crests) can be greatly reduced. With regard to protection of dwellings and agricultural land in the river's floodplain, a fundamental question has to be asked whether houses should even be located in these areas and whether the land should be cultivated. In many cases, the answer is no, and the least costly alternative overall is to pay for removal of the structures and conversion of the land back to an uncultivated state, simply allowing the flooding that comes naturally to the river.

11.6: Anthrospheric Influences on the Geosphere

The urge to “dig in the dirt” and alter Earth surfaces seems to be innate in humans. During recent decades the potential of humans to alter the geosphere has been greatly increased by the development of massive earth-moving equipment. Flooding of rivers caused by human activities was discussed above. Other geospheric disturbances that can be detrimental include landslides on mounds of waste mine tailings, adverse effects resulting from exposure of minerals during mining (production of acid mine water from exposure of pyrite, FeS_2, in coal mining), and filling and destruction of wetlands upon which many forms of wildlife depend for breeding grounds.

Human effects upon the geosphere can be both direct and indirect. Construction of dams and reservoirs, flattening whole mountain tops to get to underground coal seams, and plowing natural prairies to grow crops are obvious direct effects. Indirect effects include pumping so much water from underground aquifers that the ground subsides, or exposing minerals to the atmosphere by strip mining so that the minerals undergo weathering to produce polluted acidic water. In extracting minerals from the earth, it is disturbed and rearranged in ways that can cause almost irreversible damage to the environment. A major objective of the practice of green chemistry and industrial ecology is to minimize these detrimental effects and, to the extent possible, eliminate them entirely.

Many of the effects of human activities on the geosphere have to do with the extraction of resources of various kinds from Earth’s crust. These may range from gravel simply scooped from pits on Earth’s surface to precious metals at such low concentrations that tons of ore must be processed to get a gram or less of the metal. The most straightforward means of obtaining materials from Earth’s crust is surface mining. This often involves removing unusable material in the form of the overburden of soil and rock that covers the desired resource. This may leave a pit that fills with water alongside a pile of the overburden. This kind of mining practice caused many environmental problems in the past. With the modern practice of surface mining, however, topsoil is first removed and stored, rock removed to get to the resource is either placed back in the pit or on contoured piles, and the topsoil placed over it for revegetation. In favorable cases, the result can be attractive lakes that support fish life and vegetated, gently sloping artificial hills.

Underground mining usually does not leave the visible scars that may be inflicted by surface mining. However, it can have profound environmental effects. Collapse of underground mines can cause surface subsidence. Water flowing through and from underground mines can pick up water pollutants. Most ores require a degree of beneficiation in which the usable portion of the ore is concentrated, leaving piles of tailings. These may collapse, and materials leached from them can pollute water. Examples of the latter include acidic water produced by the action of bacteria on iron pyrite, FeS_2, removed from coal and radium leached from the tailings remaining from uranium mining operations.

11.7: The Geosphere as a Waste Repository

As discussed above, mineral processing produces large quantities of waste solids. Other sources of waste solids include ash from coal combustion, municipal garbage, and solid wastes from various industrial processes. Ultimately, these wastes are placed on or in the geosphere. Such measures have an obvious potential for pollution.

One of the most common waste materials that ends up as part of the geosphere is **municipal refuse**, the “garbage” generated by human activities. This material is largely disposed in **sanitary landfills** made by placing the solid wastes on top of the ground or in depressions in the ground and covering it with soil to minimize effects such as windblown waste paper and plastic, emission of odorous materials to the atmosphere, and water pollution. Although “garbage dumps” used to be notably unsightly and polluting, modern practice of sanitary landfilling can result in areas that can be used as parkland, golf courses, or relatively attractive open space. The unconsolidated nature of decaying garbage and the soil used to cover it make municipal landfills generally unsuitable for building construction. Biological decay of degradable organic material ($\{CH_2O\}$) in the absence of oxygen generates methane gas by a process represented as

$$2\,(CH_2O) \rightarrow CO_2 + CH_4 \tag{11.7.1}$$

Methane is a powerful greenhouse gas in the atmosphere, much more effective per molecule at absorbing infrared radiation than is CO_2, so it is undesirable to release CH_4 to the atmosphere. However, modern sanitary landfills may be equipped with pipes and collection systems so that the methane can be collected and used as a fuel.

Whereas the release of gases, particularly methane, to the atmosphere is a potential air pollution problem with sanitary landfills, contaminated **leachate** consisting of water seeping through the landfilled wastes can pollute water, especially groundwater. This water may contain heavy metals, organic acids, odor-causing organics, and other undesirable pollutants. There are two general approaches to minimizing problems from contaminated landfill leachate. One of these is to construct the landfill in a manner that minimizes water infiltration, thus reducing the amount of leachate produced to lowest possible levels. To prevent the leachate from getting into groundwater, it is desirable to locate the landfill on a layer of poorly permeable clay. In some cases, the bottom of the landfill may be lined with impermeable synthetic polymer liners that prevent leachate from getting into groundwater. In cases where significant quantities of badly polluted leachate are generated, it is best to collect and treat the leachate, usually by biological treatment processes.

Minimization of the quantities of materials requiring sanitary landfill disposal using the best practice of industrial ecology and green chemistry is highly desirable. The best way to do that is by reducing quantities of materials at the source, simply using less material that ultimately will require disposal. Wherever possible, materials, such as packing materials, that ultimately get into landfills should be biodegradable. Recycling programs in which glass, plastic, paper, and food cans are removed from refuse prior to disposal are effective in reducing quantities of material requiring disposal in landfills. Burning of garbage with proper pollution control measures can reduce it to a low-volume ash that can be placed in a landfill. Although not practiced to a significant extent, anaerobic digestion of macerated wet refuse in an oxygen-free digester has the potential to produce methane for fuel use and greatly reduce the mass of the degradable wastes.

Sanitary landfills are not suitable for the disposal of hazardous substances. These materials must be placed in special **secure landfills**, which are designed to contain the wastes and leachate, thus preventing pollution of water, air, and the geosphere. One way in which this is accomplished is with impermeable synthetic membranes that prevent water from seeping into the fill and prevent leachate from draining into groundwater. These landfills are often equipped with water treatment systems to treat leachate before it is released from the system. Unfortunately, many hazardous chemicals **never** degrade and a “secure” chemical landfill leaves problems for future generations to handle. One of the major objectives of green chemistry is to prevent the generation of any hazardous materials that would require disposal on land. The best way to do that is to avoid making or using such materials. In cases where that is not possible and hazardous materials are generated, they should be treated in a way that renders them nonhazardous prior to disposal.

11.8: Have You Thanked a Clod Today?

A common bumper sticker is one that asks the question, “Have you thanked a green plant today?” this is an obvious reference to plants whose photosynthesis produces the food that we and most other animals depend upon for our existence. An even more fundamental question is whether we have thanked the soil — the clods of dirt — upon which green plants depend for their existence. Good, productive soil combined with a suitable climate and adequate water is the most valuable asset that a nation can have. Vast areas of the world lack this fundamental asset, and the people living in areas with poor soil often suffer poverty and malnutrition as a result. Furthermore, areas that once had adequate soil have seen it abused and degraded to the extent that it is no longer productive. One of the central challenges faced by the practice of green chemistry and industrial ecology is to retain and enhance the productive qualities of soil.

The remainder of this chapter addresses soil and those aspects of agriculture related specifically to soil. The biological aspects of agriculture and the production of **food and biomass are discussed in Chapter 12.**

What is Soil?

Soil is a term that actually describes a wide range of finely divided mineral matter containing various levels of organic matter and water that can sustain and nourish the root systems of plants growing on it. Soil is largely a product of the weathering of rock by physical, chemical, and biochemical processes that produces a medium amenable to the support of plant growth. A healthy soil contains water available to plants, has a somewhat loose structure with air spaces, and supports an active population of soil-dwelling organisms, including fungi and bacteria that degrade dead plant biomass and animals, such as earthworms. Although the solids in a typical soil are composed of about 95% inorganic matter, some soils contain up to 95% organic matter, and some sandy soils may have only about 1% organic matter.

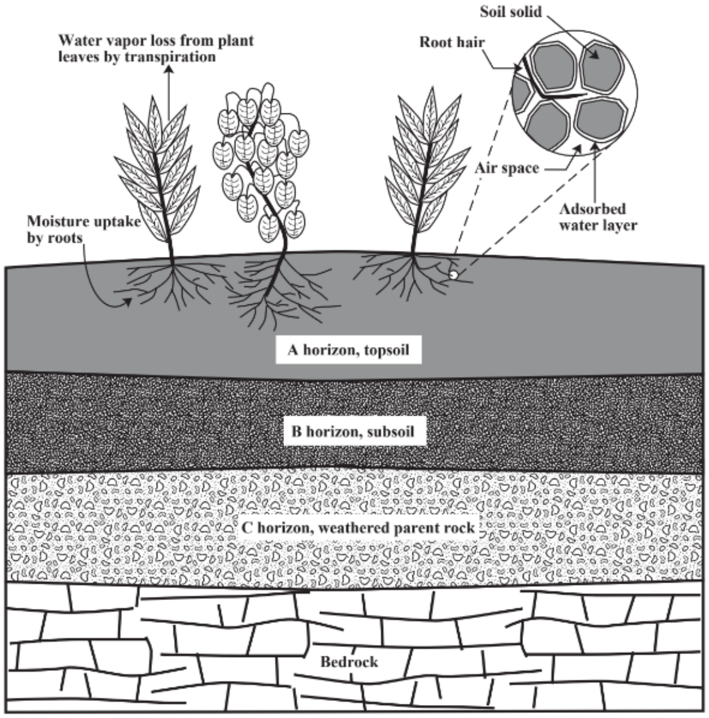


Figure 11.4. Major aspects of soil structure showing various soil horizons. The inset shows aspects of soil microstructure

Figure 11.4 shows the major aspects of the physical structure of soil. Soil is divided into layers called **horizons** formed by weathering of parent rock, chemical processes, biological processes, and the action of water including leaching of colloidal matter to lower horizons. The most important of these for plant growth is **topsoil**. Plant roots permeate the topsoil and take water and plant nutrients from it. Topsoil is the layer of maximum biological activity. The **rhizosphere** is the part of topsoil in which plant roots are especially active and in which the elevated levels of biomass are composed of plant roots and microorganisms associated with them. There are strong synergistic relationships between plant root systems and microorganisms in the rhizosphere. The surfaces of root hairs are commonly colonized by microorganisms, which thrive upon carbohydrates, amino acids, and root-growth-lubricant mucigel secreted from the roots.

Inorganic Solids in Soil

Reflecting the fact that the two most common elements in the earth's crust are oxygen and silicon (see Section 11.2), silicates are the most common mineral constituents of soil. These include finely divided quartz (SiO_2), orthoclase ($KAlSi_3O_8$), and albite ($NaAlSi_3O_8$). Other elements that are relatively abundant in Earth's crust are aluminum, iron, calcium, sodium, potassium, and magnesium; their abundance is reflected by various minerals such as epidote ($4CaO•3(AlFe)2O_3•6SiO_2•H_2O$), geothite ($FeO(OH)$), magnetite ($Fe_3O_4$), calcium and magnesium carbonates ($CaCO_3$, $CaCO_3•MgCO_3$), and oxides of manganese and titanium in soil. Soil parent rocks undergo weathering processes to produce finely divided colloidal particles, by far the most abundant of which are clays. These secondary minerals hold moisture and mineral nutrients, such as K^+ required for plant growth, that are accessible by plant roots and are repositories of plant nutrients. Inorganic soil colloids can absorb toxic substances in soil, thus reducing the toxicity of substances that would harm plants. It is obvious that the abundance and nature of inorganic colloidal material in soil are important factors in determining soil productivity.

Soil Organic Matter

The few percent of soil mass consisting of organic matter has a strong influence upon the physical, chemical, and biological characteristics of soil. Among its important effects in soil organic matter is effective in holding soil moisture and it holds and exchanges with plant roots some of the ions that are required as plant nutrients. Temperature, moisture, and climatic conditions significantly affect the kinds and levels of soil organic matter. Cold, wet conditions in which soil stays saturated with moisture preventing access of microorganisms to oxygen tend to prevent complete biodegradation of plant residues that compose soil organic matter allowing it to accumulate. This is clearly illustrated by accumulation of peat in Ireland and other locales with similar climatic conditions such that most of the solid soil is composed of organic matter. Tropical conditions, especially with alternate wet and dry seasons, can result in loss of soil organic matter. One reason that the soil supporting tropical rain forests degrades so quickly when the trees are removed is that the organic matter in the soil undergoes rapid biodegradation when the forest cover is removed,

The plant biomass residues that form soil organic matter undergo a biodegradation process by the action of soil bacteria and fungi in which the cellulose in the biomass is readily degraded leaving modified residues of the lignin material that binds the cellulose to the plant matter. This is the process of **humification** and the residue is **soil humus**, a black organic material of highly varied chemical structure. A fraction of soil humus is soluble in water (see the discussion of humic substances in water, Chapter 9, Section 9.3), especially when base is present in the water. Another fraction called **humin** does not dissolve and stays in the solid soil.

Though composing usually not more than a few percent of soil, soil humus has a very strong influence on the characteristics of soil. It has a strong affinity for water and holds much of the water in a typical soil. Primarily because of their carboxylic acid ($-CO_2H$) groups, soil humic molecules exchange H^+ ion and act to buffer the pH of water in soil (the soil solution). Humic substances bind metal ions and other ionic plant nutrients. Soil humus also binds and immobilizes organic materials, such as herbicides applied to soil.

Water in Soil and The Soil Solution

Water in soil is required for plants. This water is taken up by plant root hairs, transferred through the plant, and evaporated from the leaves, a process called **transpiration**. The quantities of water involved are enormous; for example, the water transpired to produce a kilogram of dry hay can amount to several hundred kg. Most of the water in normal soils is not present as visible liquid, but is absorbed to various degrees upon the soil solids. In fact, a condition in which all the spaces in soil are filled with water — waterlogging — slows the growth of most plants. The water that is available in soil is called the **soil solution** and contains a number of dissolved materials, including plant nutrients. It plays an essential role in transferring substances, such as dissolved metal cations, between roots and the soil solid. Cations commonly present in the soil solution include H^+, Ca^{2+}, Mg^{2+}, Na^+, and K^+ along with very low levels of Fe^{2+}, Mn^{2+}, and Al^{3+}. Commonanions present are HCO_3^-, CO_3^{2-}, HSO_4^-, SO_4^{2-}, Cl^-, and F^-.

11.9: Plant Nutrients and Fertilizers in Soil

Plant biomass is composed largely of carbon, hydrogen, and oxygen, which plants extract from water and atmospheric carbon dioxide. Other nutrients that plants require in relatively large quantities are calcium, magnesium, and sulfur, which are usually in sufficient abundance in soil, and nitrogen, phosphorus, and potassium, which are commonly added to soil as fertilizers.

Soil acidity in the form of H+ ion builds up as plant roots exchange H+ for other cationic nutrients in soil. When acidity reaches excessive levels, the soil is no longer productive. Acidity can be neutralized by the addition of lime ($CaCO_3$), which neutralizes acidity according to the following reaction:

\ce{Soil (H^{+})_2 + CaCO3 \rightarrow Soil) Ca^{2+} + CO2 + H2O}

This process also adds calcium to soil.

Essential plant nutrient nitrogen is very much involved with nature's nitrogen cycle, which is significantly modified by human activities. Major aspects of this cycle are the following:

- At 79% N_2, Earth's atmosphere constitutes an inexhaustible nitrogen resource, although, because of the extreme stability of the N_2 molecule, it is difficult to extract nitrogen from air in a chemically combined form.
- *Rhizobium* bacteria growing on the roots of leguminous plants, such as clover and soybeans, convert atmospheric nitrogen to nitrogen chemically bound in biomolecules. This nitrogen is converted to ammonium ion, NH_4^+, when plant residues and animal feces, urine, and carcasses undergo microbial decay.
- Lightning and combustion processes convert atmospheric nitrogen to nitrogen oxides, and ammonia manufacturing plants produce NH_3 from atmospheric elemental nitrogen and elemental hydrogen produced by natural gas.
- Soil microbial processes oxidize ammoniacal nitrogen (NH_4^+) to nitrate ion, NO_3^-, the form of nitrogen most readily used by plants. Microbial processes also produce gaseous N_2 and NO_2 which are released to the atmosphere, a process called denitrification that completes the nitrogen cycle.

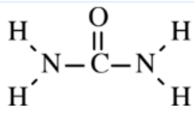
Natural processes usually do not produce sufficient nitrogen to allow maximum plant growth, so that artificial means are used to extract nitrogen in a chemically combined form from the atmosphere. This is done by the Haber process combining elemental N_2 and H_2 over a catalyst at very high pressures of about 1000 times atmospheric pressure and an elevated temperature of 500°C. The reaction is

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3 \tag{11.9.1}$$

producing ammonia that is 82% chemically bound N. This anhydrous ammonia can be applied directly below the soil surface where its tremendous attraction to soil moisture binds it to the soil. It can also be applied as a 30% solution of NH_3 in water, and is sometimes added directly to irrigation water. Ammonia, which is held in soil as ammonium ion, NH_4^+, is not well assimilated directly by most plants. But it is slowly oxidized by the action of soil bacteria using atmospheric O_2 oxidant to nitrate ion, NO_3^-, which is used directly by plants.

A solid form of nitrogen fertilizer can be made by reacting ammonia with oxygen over a platinum catalyst to make nitric acid, HNO_3, and reacting the acid with basic ammonia to make ammonium nitrate, NH_4NO_3. This molten material is solidified into small pellets that can be applied to soil as fertilizer. Ammonium nitrate mixed with fuel oil is used for blasting to quarry rock, and it was the explosive used in the bombing of the Oklahoma City Federal Building in 1995. A safer alternative to ammonium nitrate as a solid nitrogen fertilizer is urea, which is made by a process that, overall, involves the reaction of carbon dioxide and ammonia:

$$CO_2 + 2\,NH_3 \rightarrow CO(NH_2)_2 + H_2O \tag{11.9.2}$$



Urea

Phosphorus is an essential plant nutrient required for cellular DNA and other biomolecules. Itis utilized by plants as $H_2PO_4^-$ and HPO_4^{2-} ions. Phosphate minerals that can be used to manufacture phosphorus-containing fertilizers occur in a number of places throughout the world. In the United States, Florida has especially abundant phosphate resources, largely as fluorapatite, $Ca_5(PO_4)_3F$, as well as hydroxyapatite, $Ca_5(PO_4)_3OH$. These phosphate minerals are too insoluble to serve directly as fertilizers and are treated with phosphoric acid and sulfuric acid to make superphosphates that are much more soluble and available to plants:

$$2\,\mathrm{Ca_5(PO_4)_3F(s)} + 14\,\mathrm{H_3PO_4} + 10\,\mathrm{H_2O} \rightarrow 2\,\mathrm{HF(g)} + 10\,\mathrm{Ca(H_2PO_4)_2 \cdot H_2O} \tag{11.9.3}$$

$$2\,\mathrm{Ca_5(PO_4)_3F(s)} + 7\,\mathrm{H_2SO_4} + 3\,\mathrm{H_2O} \rightarrow 2\,\mathrm{HF(g)} + 3\,\mathrm{Ca(H_2PO_4)_2 \cdot H_2O} + 7\,\mathrm{CaSO_4} \tag{11.9.4}$$

Potassium as the potassium ion, K^+, is required by plants to regulate water balance, activate some enzymes, and enable some transformations of carbohydrates. Potassium is one of the most abundant elements in the earth's crust, of which it makes up 2.6%; however, much of this potassium is not easily available to plants. For example, some silicate minerals such as leucite, $K_2O•Al_2O_3•4SiO_2$, contain strongly bound potassium. Exchangeable potassium held by clay minerals is relatively more available to plants. Potassium for fertilizer is simply mined from the ground as salts, particularly KCl, or pumped from beneath the ground as potassium-rich brines. Large potassium deposits occur in the Canadian province of Saskatchewan.

Plants require several **micronutrients**, largely elements that occur only at trace levels, for their growth. These include boron, chlorine, copper, iron, manganese, molybdenum (for N-fixation), and zinc. Some of these are toxic at levels above those required for optimum plant growth. Most of the micronutrients are required for adequate function of essential enzymes. Photosynthetic processes use manganese, iron, chlorine, and zinc. Since the micronutrients are required at such low levels, soil normally provides sufficient amounts.

11.10: Soil and Plants Related To Wastes and Pollutants

Soil is a repository of large quantities of wastes and pollutants, and plants act as filters to remove significant quantities of pollutants from the atmosphere. Sulfates and nitrates from the atmosphere, including acid-rain-causing H_2SO_4 and HNO_3 deposit largely on the land and the plants growing on it. Gaseous atmospheric SO_2, NO, and NO_2 are absorbed by soil and oxidized to sulfates and nitrates. Soil bacteria and fungi are known to convert atmospheric CO to CO_2. When leaded gasoline was widely used, soil along highways became contaminated with lead, and lead mines and smelters were significant sources of this toxic element. Organic materials, such as those involved in photochemical smog formation, are removed by contact with plants and are especially attracted by the waxy organic-like surfaces of the needles of pine trees.

A number of materials that can be considered as pollutants are deliberately added to soil. The most obvious of these consists of insecticides and herbicides added to soil for pest and weed control. Chemicals from hazardous waste disposal sites can get onto soil or below the soil surface by leaching from landfill or drainage from waste lagoons. Some kinds of wastes, especially petroleum hydrocarbons, are disposed on soil where adsorption and microbial processes immobilize and degrade the wastes. Soil can be effective for the treatment of sewage. Leakage from underground storage tanks of organic liquids, such as gasoline and diesel fuel, have created major soil contamination problems.

Soils in parts of New York State have been contaminated with polychlorinated biphenyls (PCBs) discarded from the manufacture of industrial capacitors. Analyses of PCBs in United Kingdom soils archived for several decades have shown levels of these pollutants that parallel their production. Starting with very low levels around 1940 before PCBs were manufactured in large quantities, concentrations of PCBs increased markedly, peaking around 1970, when PCB manufacture was ceased. More recent soil samples have shown PCB concentrations near the pre-1940 levels. It is believed that these results reflect evaporation of PCBs and their condensation onto soil. They are consistent with observations of high PCB levels in remote Arctic and sub-Arctic regions believed to be due to the condensation of these compounds from the atmosphere onto soil in very cold regions.

The degradation and eventual fates of the enormous quantities of herbicides and other pesticides applied to soil are very important in understanding the environmental effects of these substances. Many factors are involved in determining pesticide fate. One of the main ones of these is the degree of adsorption of pesticides to soil, strongly influenced by the nature and organic content of the soil surface as well as the solubility, volatility, charge, polarity, and molecular structure and size of the pesticides. Strongly adsorbed molecules are less likely to be released and thus harm organisms, but they are less biodegradable in the adsorbed form. The leaching of adsorbed pesticides into water is important in determining their water pollution potential. The effects and potential toxicities of pesticides to soil bacteria, fungi, and other organisms have to be considered. It must be kept in mind that pesticides may be converted to more toxic products by microbial action.

11.11: Soil Loss - Desertification and Deforestation

Soil erosion refers to the loss and relocation of topsoil by water and wind action. About a third of U.S. topsoil has been lost to erosion since cultivation began on the continent and at present about a third of U.S. cropland is eroding at a rate sufficient to lower productivity. About 10% of U.S. land is eroding at an unacceptable rate in excess of 14 tons of toposil per acre annually. Soil erosion is largely a product of cultivation. Except in cases of extreme slopes, very high winds, and torrential rains, uncultivated soils undergo little erosion. Erosion was recognized as a problem in the central United States within a few years after forests and prairie grasslands were first plowed to plant crops, particularly in the latter 1800s. The recognition that precious topsoil was being lost at an unsustainable rate lead to soil conservation measures going back to 1900, or even earlier. In that sense, soil conservation was the first environmental movement, predating efforts to alleviate water and air pollution by many decades.

Water erosion is responsible for greater loss of soil than is wind erosion. Whereas wind erosion tends to move soil around and deposit it in areas where it can still be used for growing crops, water erosion normally moves greater quantities of soil and carries them into streams and rivers and ultimately to the oceans. The overall pattern of soil erosion in the Central Continental United States is shown in Figure 11.5. This figure shows that erosion is especially bad in agricultural areas draining into the Missouri and Mississippi Rivers; millions of tons of soil are carried by these rivers into the Gulf of Mexico each year. These are areas of relatively high rainfall, which can sometimes come as very intense rainstorms, especially during the spring. A high proportion of the farmlands in these areas are devoted to row crops, which are crops such as corn, soybeans, and sorghum grains planted in rows with bare soil in between. This mode of cultivation leaves soil that is especially susceptible to water erosion.

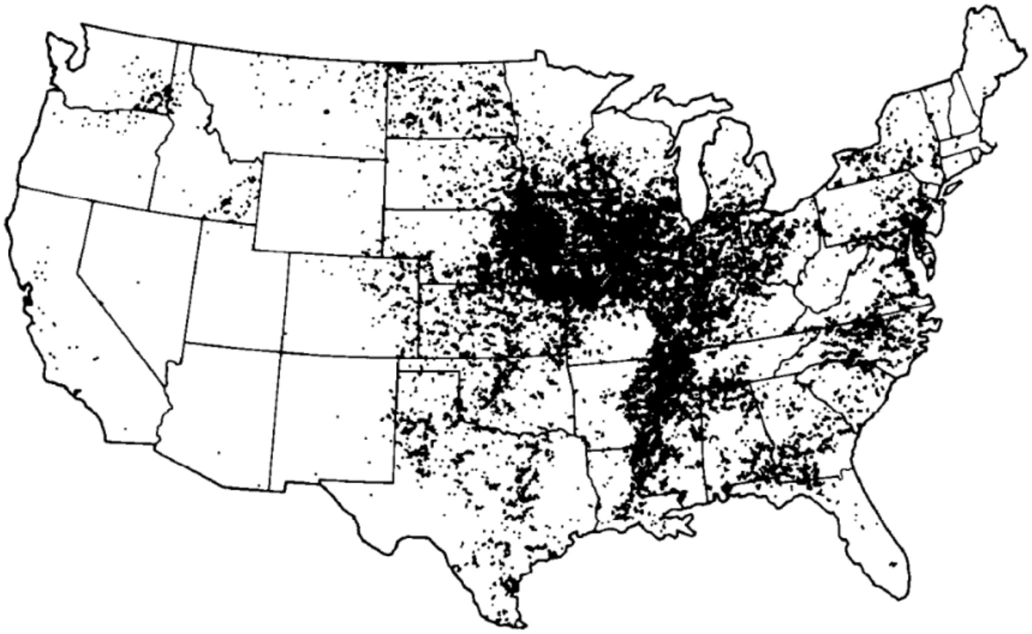


Figure 11.5 Pattern of soil erosion (dark areas) in the major agricultural states of the central continental U.S. It is seen that erosion is particularly severe in the highly cultivated Missouri and Mississippi River watersheds.

The ultimate result of soil erosion and other unsustainable agricultural practices in relatively dry areas is **desertification**. This condition occurs when permanent plant cover is lost from soil so that it loses its capacity to retain moisture, dries out, and loses fertility so that plants no longer grow on it. Among the interrelated factors involved in desertification are wind erosion, water erosion (which occurs during sporadic cloudbursts even in arid areas), development of adverse climate conditions, depletion of underground water aquifers, lack of water for irrigation, accumulation of salt in water supplies, loss of soil organic matter, and deterioration of soil physical and chemical properties. Eventually the land becomes unable to support agriculture, grazing, or even significant human populations. Desertification is one of the most troublesome results of global warming caused by greenhouse gases. It is actually a very old problem and is a serious concern in many parts of the world, such as the Mideast, the southern boundary of Africa’sSahara, and regions of the southwestern U. S. Formerly productive areas of the Middle East and North Africa, “lands of milk and honey” described in biblical terms, have turned into desert, largely due to human agricultural activities. The growth of domestic grazing animals on these areas — especially goats, which tend to pull vegetation up by its roots — has been a particularly strong contributor to desertification. Much of the productive capacity of arid grasslands in the western and southwestern United States has been drastically diminished by overgrazing.

Fortunately, human ingenuity and technological tools can be used to prevent or reverse desertification. For example, water, which upon occasion falls as torrential rain upon normally dry desert lands, can be collected and used to recharge underground water aquifers. Advanced cultivation and irrigation techniques can be used to establish perennial plant cover on erosion-prone desert soils. Potentially, plants can be genetically engineered to grow under severe conditions of temperature, drought, and salinity. Environmentally friendly mining practices can be employed to obtain minerals, and land surfaces damaged by harmful strip mining practices can be restored.

The loss of forest growth to cultivated land —**deforestation**— has occurred extensively in the United States. However, much of the colonial U.S., particularly in New England, which was deforested for cultivation of crops, is now undergoing largely spontaneous reforestation as unprofitable farmlands are abandoned and trees become established again. Deforestation is a particularly severe problem in tropical regions. Rich tropical forests contain most known plant and animal species many of which are becoming extinct as the forests are destroyed. Once destroyed, tropical forests are almost impossible to restore. This is because tropical forest soil has been leached of nutrients by the high annual rainfalls in tropical regions. When forest cover is removed, the soil erodes rapidly, loses the plant roots and other biomass that tends to hold it together, loses nutrients, and becomes unable to sustain either useful crops or the kinds of forests formerly supported.

The key to preventing soil loss from erosion as well as preventing desertification from taking place lies in a group of practices that agriculturists term **soil conservation**. A number of different approaches are used to retain soil and enhance its quality. Some of these are old, long-established techniques such as construction of terraces and planting crops on the contour of the land (see Figure 11.6). Crop rotation and occasional planting of fields to cover crops, such as clover, are also old practices. A relatively new practice involves minimum cultivation and planting crops through the residue of crops from the previous year. This practice, now commonly called **conservation tillage**, is very effective in reducing erosion because of the soil cover of previous crops and the roots that are left in place. Conservation tillage does make use of herbicides to kill competing weeds until the desired crop is established enough to shade out competing plants, but only minimum quantities of herbicides are applied. There is some concern that fungi (molds) will thrive in old crop residues and cause problems with new crops.

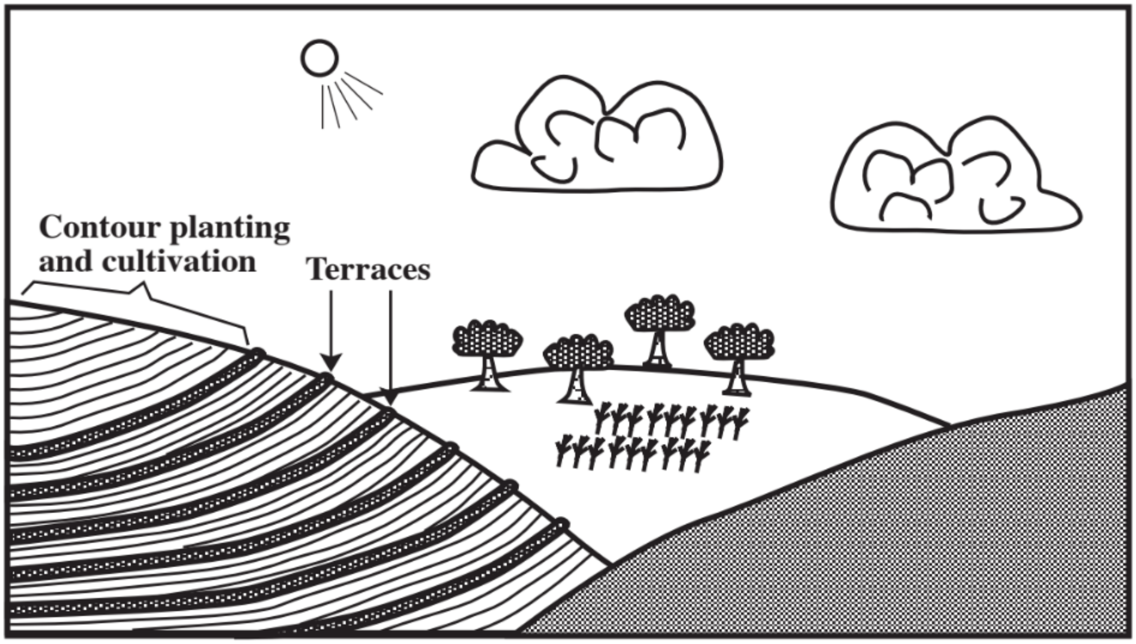


Figure 11.6. Construction of terraces on the contour of land and planting crops on the contour are practices that have been very effective in reducing soil erosion

The ultimate in no-till agriculture is the use of perennial plants that do not have to be planted each year. Trees in orchards and grape vines in vinyards are such plants. The roots of perennial plants are very effective in holding soil in place. Efforts to develop perennial plants that produce grain have not been successful to date. This is because a successful grain-producing plant is one that dedicates its metabolic processes to the production of large quantities of seed that can be used for grain, whereas perennial plants put their energy into the development of large, bulbous root structures that store food for the next growing system. It is possible that sometime in the future genetic engineering may be applied to the development of perennial plants capable of producing high grain yields.

Among the most successful plants at stopping erosion are trees. These plants grow for many years and some tree varieties will grow back from their root structures when the wood is harvested. Wood and wood products are probably the most widely used renewable resources. Hybrid tree varieties have been developed that are outstanding producers of biomass.

Wood is a renewable resource used for many purposes. In construction, wood substitutes for steel, aluminum, and cement. All of these materials are produced by very energy-intensive processes, so substitution of wood, where applicable, conserves large amounts of energy. Wood is about 50% cellulose, a carbohydrate polymer that is used directly to make paper. Although humans and many other animals cannot use cellulose directly for fuel, it can be broken down chemically or biochemically to glucose sugar. This material serves as a food source for yeasts (a form of fungi) that generate ethanol, an alcohol that can be used as fuel and to make other chemicals. In the process, the yeasts produce protein that can be fed to animals.

Biochar for Soil Conservation and Enrichment

A relatively recent development in enhancing soil quality is the use of biochar as a soil amendment. **Biochar** is made by the pyrolysis of organic matter such as crop residues. It is a natural constituent of soil as the result of forest and prairie fires, but is now produced artificially for addition to soil.[1] The two major advantages of biochar are its high affinity for nutrients by adsorption and its extremely high persistence; unlike humic material it never degrades. Furthermore, the production of biochar has the net effect of permanently sequestering atmospheric carbon dioxide fixed by photosynthesis thus helping to alleviate global warming.

Water and Soil Conservation

Conservation of soil and conservation of water go together very closely. Soil is normally the first part of the geosphere that water contacts, and contaminated soil yields contaminated water. Most fresh water falls initially on soil, and the condition of the soil largely determines the fate of the water and how much is retained in a usable condition. Soil in a condition that retains water allows rainwater to infiltrate into groundwater. If water drains too rapidly from soil, the soil erodes and the water runoff is badly contaminated with soil sediments. Measures taken to conserve soil usually conserve water as well. Terraces, contour cultivation, constructed waterways, and water-retaining ponds (Figure 11.6) prevent water from washing soil away, but also retain water and help prevent flash floods. Some of these measures, especially terracing, involve modification of the contour of the soil. Bands of trees can be planted on the contour to retain both soil and water. Reforestation of land unsuitable for growing crops and avoiding practices, such as overgrazing, that tend to lead to desertification conserve water as well as land.

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Questions and Problems

Access to and use of the internet is assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be "right."

1. Suggest the main contributions made by the geosphere to the biosphere.

2. Distinguish between rocks and minerals.

3. How does igneous rock turn into secondary minerals?

4. What is the branch of chemistry that deals with rocks and minerals and their chemical characteristics and interactions?

5. Suggest ways in which improved materials, some made by green chemical processes, can reduce the effects of earthquakes.

6. In what respect do volcanoes have the potential to drastically affect global climate? Is there any evidence for such an effect?

7. How may human activities lead to landslides?

8. What are the formations called that contain water under ground? What is a major threat to groundwater in such formations?

9. What is FeS_2? Why is its exposure of this material from mining a potential problem?

10. Give an example of an air pollutant and of a water pollutant that may be generated by sanitary landfills.

11.How is soil divided? Which is the top one of these divisions?

12. What is humification, and what does it have to do with soil?

13. What is water in soil called? Give the name of the process by which this water enters the atmosphere by way of plants.

14. In what respects is conservation tillage consistent with the practice of green chemistry?

15. Name a gaseous form and two solid forms of fixed nitrogen used as fertilizer.

16. Explain what is meant by desertification.

17. What is the good news in the U. S. regarding deforestation?

18. What is the potential use of perennial plants in grain production and how does it tie in with soil conservation?

19. What are the processes occurring in soil that operate to reduce the harmful effects of pollutants?

20.Of the following, the one that is **not** a manifestation of desertification is (explain): (A) Declining groundwater tables, (B) salinization of topsoil and water, (C) increased organic matter in soil, (D) reduction of surface waters, (E) unnaturally high soil erosion.

21.Why do silicates and oxides predominate among earth's minerals?

22. Explain how the following are related: weathering, igneous rock, sedimentary rock, soil.

23.What is the distinction between weathering and erosion? Suggest ways in which air pollution may contribute to both phenomena.

23.In what respect is biochar a material that gets into soil by natural processes? Where would soils with significant levels of naturally-occurring biochar likely be found?

24.In what sense may volcanoes contribute to air pollution? What possible effects may this have on climate?

25.Large areas of central Kansas have vast deposits of halite. What is halite? What does this observation say about the geologic history of the area?

26. One way in which coal and other fossil fuels may be used without contributing to higher levels of greenhouse gas carbon dioxide in the atmosphere is through carbon sequestration by pumping carbon dioxide into mineral strata. Explain with a chemical reaction how formations of limestone (calcium carbonate) might be used for this purpose. Suggest how this might cause problems on the surface.

27. In what respects do humus and biochar perform similar functions in soil? What are the main differences between these two kinds of materials.

28. Explain how bamboo might be used for restoring degraded soil. How does bamboo prevent erosion?

CHAPTER OVERVIEW

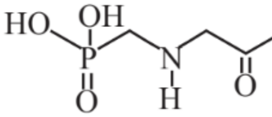
12: The Biosphere and the Role of Green Chemistry in Feeding a Hungry World

“From the 1990s, genetically engineered crops resistant to glyphosate herbicide that can be sprayed directly for weed control resulted in a revolution in the production of corn, soybeans, and cotton. Unfortunately, weeds are now emerging that are resistant to glyphosate. Pigweed has been an especially bad actor that can grow 7 or 8 centimeters in a day, reach heights of 2 meters, and with stalks so thick and strong that they can damage harvesting machinery.”

12.1: Pigweed’s Revenge
12.2: The Biosphere
12.3: Cells - Basic Units of Life
12.4: Metabolism and Control in Organisms
12.5: Reproduction and Inherited Traits
12.6: Stability and Equilibrium of the Biosphere
12.7: DNA and the Human Genome
12.8: Genetic Engineering
12.9: Biological Interaction with Environmental Chemicals
12.10: Biodegradation
12.11: Production of Food and Fiber by the Biosphere - Agriculture
12.12: Agricultural Applications of Genetically Modified Organisms
12.13: The Anthrosphere in Support of the Biosphere
12.14: Livestock and their Wastes
Questions and Problems
Supplementary References

12.1: Pigweed’s Revenge

Glyphosate, marketed by Monsanto under the brand name Roundup, has been an ideal herbicide that is effective against a broad spectrum of weeds, with low toxicity to animals, and readily degraded in the environment. In the 1990s Monsanto began selling “Roundup ready” seeds of corn, soybeans, and cotton genetically engineered to resist the herbicidal action of glyphosate. These crops could be sprayed directly with glyphosate, killing competing weeds and leaving the crops untouched. This enabled a revolution in agriculture eliminating the need to till the crops and facilitating the adoption of environmentally friendly conservation (no till) crop production, saving large amounts of fuel formerly consumed in tillage. By 2010 in the U.S. about 90% of the soybeans and 70% of corn and cotton were glyphosate-resistant varieties.



Glyphosate

Unfortunately, not long after the introduction of Roundup ready seeds, glyphosate-resistant weeds began appearing including horseweed, giant ragweed, and several of a number of species in the genus *Amaranthus* (pigweed) that by 2010 had afflicted 7-10 million acres of the approximately 170 million acres of corn, soybeans, and cotton planted in the U.S.. Pigweed has been an especially bad actor that can grow 7 or 8 centimeters in a day, reach heights of 2 meters, and with stalks so thick and strong that they can damage harvesting machinery. The first glyphosate-resistant weeds appeared in California in year 2000. In 2003 in the U.S. such weeds had been observed in 10 states, in 2006 14 states and in 2009 20 states. By 2010 there were known to be 10 glyphosate-resistant weed species infesting 7-8 million acres of soybeans, cotton, and corn in 22 states.

Dealing with glyphosate-resistant weeds is a major challenge to the agricultural industry. In response to this problem crop varieties resistant to other herbicides including glufosonate, Dicamba, Sygenta’s Calliston, and 2,4-D are being developed.

It is interesting to note that some of the amaranth species that include pigweed have the potential to serve as a major food source with leaves that can be consumed as leafy green vegetables and seeds that can be made into a protein-rich flour. Now sold in some health food stores, amaranth has been a staple food in some native cultures in Peru and Mexico.

12.2: The Biosphere

The **biosphere** consists of all living organisms and the materials and structures produced by living organisms. There is a very close connection between the biosphere and green chemistry including the following:

- Living organisms produce a wide range of materials that are used by humans for a variety of purposes.
- Large quantities of substances including pesticides and fertilizers are generated in the anthrosphere for use to control pests and enhance the growth and health of organisms in the biosphere.
- Reduction of the use and generation of toxic substances in the anthrosphere is designed to prevent harm to humans and other organisms in the biosphere.
- Environmental conditions largely determined by anthrospheric activities strongly affect organisms in the biosphere

Individual organisms in the biosphere and organisms interacting in ecosystems can teach humans a lot about how to apply green chemistry. One important respect in which this is done is by the mild conditions under which organisms carry out complex chemical syntheses. Living organisms can function only within narrow temperature ranges that are close to those that humans find comfortable. (Even the 90-100° C temperatures under which thermophilic bacteria function in hot springs and similar locations are not very far from room conditions.) Therefore, the enzyme-catalyzed reactions that organisms carry out occur under much milder conditions than the often high-temperature, high-pressure conditions of conventional chemical synthesis. Furthermore, organisms cannot tolerate highly toxic substances that are often used in chemical synthesis, the elimination of which is a primary objective of the practice of green chemistry.

Another lesson that living organisms provide for an efficiently operating anthrosphere is in the relationships between organisms with each other and with their environment in biological ecosystems. The wide variety of such ecosystems that have evolved over hundreds of millions of years of evolution have had to be sustainable to survive, completely recycling materials and preserving and enhancing their environment. This is in contrast to the way in which anthrospheric systems have evolved, especially during the last two centuries of the industrial revolution. In general, humans and their industrial systems have exploited nonrenewable resources and have polluted water, air, and land in a manner that simply cannot be sustained. Humans have a lot to learn from the biosphere regarding how to operate the anthrosphere sustainably (see the discussion of industrial ecology in Chapter 13) in which various enterprises compose sustainable industrial ecosystems analogous to ecosystems in the biosphere.

Biology

Biology is the science of life and the organisms that comprise life. So what is life? Biologists define living organisms as those that share (1) constitution by particular classes of life molecules,(2) hierarchical organization, (3) capability to carry out metabolic processes, (4) ability to reproduce, (5) development, and (6) heredity

The kinds of molecules that comprise living organisms were discussed in Chapter 7. Recall that these are *proteins* composed of polymers of nitrogen-containing amino acids, *carbohydrates* consisting of small molecules and polymers with an approximate simple formula of CH_2O, *lipids* defined by their property of solubility in organic solvents, and *nucleic acids* that are long polymers of sugars, nitrogen-containing bases, and phosphate. Two of these kinds of materials are often bonded together as hybrid molecules. Along with water and some kinds of salts they make up the matter in living organisms. Literally thousands of kinds of structural and functional characteristics are possible with the four kinds of molecules mentioned above. For example, proteins comprise muscle tissue and make up the enzyme molecules that act as catalysts to enable biochemical reactions to occur. A simple carbohydrate, glucose, $C_6H_{12}O_6$, is the primary organic product generated by plant photosynthesis and is present in animal bloodstreams. Large numbers of glucose molecules bonded together make up polymeric cellulose that is the structural material in plants. Lipids make up the crucial membranes that enclose living cells. And nucleic acids compose the genetic material that regulate cell function and reproduction.

Hierarchical organization applies to living organisms from the level of atoms all the way to the biosphere as a whole. Proteins, carbohydrates, lipids, and nucleic acids in living organisms are organized into distinct microscopic bodies contained in cells and called **organelles**. Cells are bodies of several micrometers (μm) in size that are the basic building blocks of organisms in that they are the smallest bodies of organisms that can exist independently (even cells of humans can be grown in cell cultures outside the body, given the appropriate nutrients and conditions). In higher organisms cells with similar functions comprise **tissues** and tissues in turn make up **organs**, which may be organized into whole systems of organs. An **organism** is a collection of organs and organ systems. Organisms from the same species assembled in a group comprise a **population** and a cluster of populations existing in the same place makes up a **community**. Numerous communities living in a particular environmental area, interacting with each other and with their environment, make up an **ecosystem**. Finally, all Earth's ecosystems comprise the entire **biosphere.**

The process of **metabolism** is what occurs when organisms mediate chemical (biochemical)processes to get energy, make raw materials required for tissues in organisms or modify raw materials for this purpose, and reproduce. Although there are thousands of different metabolic reactions, two stand out. The first of these is *photosynthesis* shown in Reaction 12.3.1 in which plants use light energy to convert inorganic CO_2 and H_2O to glucose sugar, $C_6H_{12}O_6$. The second major type of metabolic reaction is the mirror image of photosynthesis, **cellular respiration** in which glucose is oxidized to CO_2 and H_2O, yielding energy that is used by the organism. An interesting aspect of the conversion and utilization of energy in metabolism is that all organisms use the high-energy chemical species **adenosine triphosphate**, **ATP**, (structural formula shown in Chapter 7, Section 7.8) to transfer, convert, and store energy.

All organisms undergo **reproduction** to produce offspring to continue the species. In addition to continuing a species, reproduction enables evolution to occur that results in new species.

Development is the process that occurs as an organism progresses from a fertilized egg to a juvenile and on to adulthood. Development occurs in higher forms of life (obvious in human babies) and even single-celled bacteria that reproduce by cell division undergo development as the cells grow and produce additional organelles prior to further division.

Heredity refers to the process by which traits characteristic of a species of organism are passed on to later generations. Heredity occurs through the action of DNA. Heredity is the mechanism by which organisms have undergone evolution and adaptation to their environment.

Organisms that comprise living beings in the biosphere range in size and complexity from individual bacterial cells less than a micrometer in dimensions up to giant whales and human beings capable of thought and reasoning and may be divided into several kingdoms. **Archaebacteria** and **Eubacteria** are generally single-celled organisms without distinct, defined nuclei. **Protists** are generally single-celled organisms that have cell nuclei and may exhibit rather intricate structures. The three other kingdoms are **Plantae**(plants), **Animalia** (animals), and **Fungi** typified by molds and mushrooms.

Organisms are classified according to their food and energy sources and their utilization of oxygen. **Autotrophs** synthesize their food and biomass from simple inorganic substances, usually using solar energy to perform **photosynthesis**. **Chemautotrophs** mediate inorganic chemical reactions for their energy. **Heterotrophs**, including humans, derive their energy and biomass from the metabolism of organic matter, usually biomass from plants. **Oxic** (aerobic) organisms require oxygen, whereas **anoxic** (anaerobic) organisms use alternate sources of oxidants. **Facultative** organisms can use oxygen or other oxidants depending upon conditions.

The biosphere is greatly influenced by the other environmental spheres. In an environment where temperatures are moderate, sunshine abundant, and nutrients readily available, the biosphere consists of diverse groups of organisms interacting and codependent within thriving ecosystems. Under extreme conditions, there may be only a few organisms composing the localized biosphere, specialized for existence at extreme temperatures, high acidities, high levels of pollutants, or other conditions that make life impossible for most organisms.

Just as the biosphere is strongly influenced by the environment in which the organisms are found, it has a strong influence upon its surroundings. Organisms act to break down inhospitable rock to form soil that supports a variety of plants. The oxygen in the atmosphere, upon which we all depend for our existence, was put there by photosynthesis performed by bacteria capable of photosynthesis. The nature of the anthrosphere that humans have constructed is influenced by the biosphere; examples include dwellings constructed of wood, and shelters and clothing used by Plains Native Americans made from bison hides.

12.3: Cells - Basic Units of Life

As a fundamental unit of the biosphere, it is appropriate to choose living **cells**, which were discussed in Chapter 7, Section 7.2, as entities in which biochemical processes occur. A single cell visible only under a microscope may perform all the functions required for an organism to process nutrients and energy and to reproduce. Or cells may be highly specialized entities, such as human liver, brain, and red blood cells.

Cell structure has an important influence on determining the nature of the biomaterials generated by biochemical processes in the cells. Muscle cells consist largely of strong structural proteins capable of contracting and movement. Bone cells secrete a protein mixture that then mineralizes with calcium and phosphate to produce solid bone. The walls of cells in plants are largely composed of strong cellulose, which makes up the sturdy structure of wood.

As noted in Section 7.2, there are two general classes of cells. **Prokaryotic cells** are those that make up bacteria and simple single-celled organisms that composed all of life on Earth for the first approximately 2 billion years of life on the planet. These cells are only about 1–2 micrometers in size, have only limited external appendages, and have relatively less (though still complex)internal structures. **Eukaryotic cells** compose all organisms other than bacteria, are typically 10µm or more in size, often have external appendages, and generally show well differentiated internal structures with numerous distinct parts. These cells appeared only about 1.5 billion years ago in the estimated 3.5 billion years that life has existed on Earth. Figure 12.1 represents prokaryotic cells and plant and animal eukaryotic cells.

Three features largely distinguish plant eukaryotic cells from animal cells in that the plant cells have a cell wall, a large central vacuole, and chloroplasts. The cell wall gives the plant cell strength and rigidity. The vacuole takes up most of the cell volume and allows contact with gases. The chloroplasts are sites in which chlorophyll uses light energy ($h\nu$) to synthesize carbohydrates as shown by the following reaction for the photosynthetic generation of glucose sugar:

$$6\,\mathrm{CO_2} + 6\,\mathrm{H_2O} + (\mathrm{light energy}, h\nu) \rightarrow \mathrm{C_6H_{12}O_6}(\mathrm{glucose}) + 6\,\mathrm{O_2} \tag{12.3.1}$$

Shown by the above reaction, **photosynthesis** was responsible for the greatest changes that the biosphere has ever caused in the atmosphere and geosphere. This occurred with the evolution of **cyanobacteria** (once thought to be algae and called “blue-green algae”) about 3 billion years ago, the first organisms capable of carrying out photosynthesis and producing oxygen, which for them was a waste product. This raised the oxygen content of the atmosphere from virtually zero to the current value of 21% (by volume of dry air). The result was conversion of the atmosphere to an oxidizing medium. Vast deposits of solid iron minerals now used for iron ore were formed when atmospheric oxygen reacted with dissolved Fe in the oceans to produce solid iron oxide.

$$4\,\mathrm{Fe^{2+}} + \mathrm{O_2} + 4\,\mathrm{H_2O} \rightarrow 2\,\mathrm{Fe_2O_3} + 8\,\mathrm{H^+} \tag{12.3.2}$$

Part of the oxygen generated by photosynthesis dissolved in water, where it was available for the development of organisms that used oxygen to metabolize organic matter. Whereas Earth’s surface had been a most inhospitable place for the existence of life, the oxygen released by photosynthesis enabled the formation of the ultraviolet-radiation-filtering layer of ozone (O_3) in the stratosphere that made life possible outside the protective confines of water. Thus life became possible on Earth’s land surface, soil was formed, aided by the weathering action of organisms including cyanobacteria that grew on rock surfaces, plants growing in soil became well established, and animals developed. The huge changes made possible by the action of single-celled cyanobacteria carrying out photosynthesis are obvious.

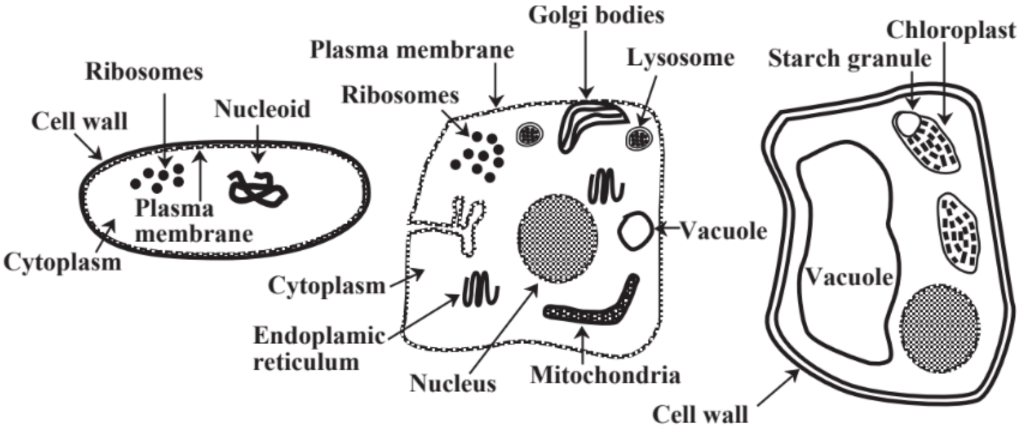


Figure 12.1 Representations of prokaryotic cells (left), eukaryotic animal cells (center), and eukaryotic plant cells (right). Eukaryotic cells are very complex and not all of the many organelles are shown

Prokaryotic cells characteristic of bacteria are enclosed by strong **cell walls** composed largely of carbohydrates that hold the cells together. The plasma membrane controls passage of materials into and out of the cell and is the site of photosynthesis in photosynthetic bacteria. Gelatinous **cytoplasm** composed largely of protein and water fills the cell. There is not a defined nucleus, but the cell has a mass of genetic material (DNA) that composes a **nucleoid**. The DNA directs cell metabolism and reproduction. Proteins are made in the cell in **ribosomes** that are distributed around the cell interior. Ribosomes and other bodies in the prokaryotic cell are not enclosed by separate defined membranes as is the case with more complex eukaryotic cells.

Major Features of Eukaryotic Cells

Animal and plant cells shown in Figure 12.1 represent the two major kinds of **eukaryotic cells** that compose all organisms other than bacteria and cyanobacteria. The major features of eukaryotic cells include the following:

- **Cell membrane**, which encloses the cell and determines what enters and leaves the cell interior. The cell membrane has varying **permeability** for various substances so that one of its crucial functions is regulation of the passage of ions, nutrients, lipid-soluble ("fat-soluble") substances, metabolic products, toxicants, and toxicant metabolites into and out of the cell interior thus protecting the contents of the cell from undesirable outside influences. One of the adverse effects of some toxicants is damage to the cell membrane causing the cell to function improperly.
- **Cell nucleus**, which controls cell function and the genetic material required for reproduction. **Deoxyribonucleic** acid (**DNA**) discussed in Section 7.6 is the key substance in the nucleus. Damage to DNA by foreign substances may cause mutations, cancer, birth defects, defective immune system function, and other toxiceffects.
- **Cytoplasm** composed of a water-soluble proteinaceous filler called **cytosol** fills the interior of the cell not occupied by the nucleus or other bodies. Bodies of **cellular organelles**, such as mitochondria or chloroplasts are suspended in the cytoplasm.
- **Mitochondria** mediate energy conversion and utilization where carbohydrates, proteins, and fats are broken down to yield carbon dioxide, water, and energy, which is then used by the cell. The best example of this is the oxidation of the sugar glucose, $C_6H_{12}O_6$ in a process called **cellular respiration** (see Reaction 12.4.1).
- **Ribosomes** are involved in protein synthesis.
- **Endoplasmic reticulum** is the site of enzymatic metabolism of some toxicants.
- **Lysosome**, a type of organelle that contains potent substances capable of hydrolyzing and breaking down food material that enters the cell through a **food vacuole**.
- **Golgi bodies** are flattened bodies of material in some types of cells that serve to hold and release substances produced by the cells.
- **Cell walls** of provide stiffness and strength in cell walls composed primarily of cellulose (see Section 7.3 and Figure 7.3).
- **Vacuoles** inside plant cells often contain materials dissolved in water.
- **Chloroplasts** in plant cells that are the sites of photosynthesis, the chemical process which uses energy from sunlight to convert carbon dioxide and water to organic matter which is stored in the chloroplasts as **starch grains**.

12.4: Metabolism and Control in Organisms

As discussed in Section 7.8 in respect to the processing of biochemicals, living organisms continually process materials and energy, a process called **metabolism**. *Photosynthesis*, which is mentioned above, is the metabolic process that provides the base of the food chain for most organisms. Animals break down complex food materials to smaller molecules through the process of **digestion**. **Respiration** occurs as nutrients are metabolized to yield energy:

$$\mathrm{C_6H_{12}O_6(glucose) + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O + energy} \tag{12.4.1}$$

Organisms assemble small molecules to produce biomolecules, such as proteins, by a **synthesis** process.

In addition to viewing metabolism as a phenomenon within an individual organism, it can be viewed as occurring within groups of organisms living in an ecosystem. Consider, for example, the metabolism of nitrogen within an ecosystem. Elemental nitrogen from the atmosphere may be fixed as organic nitrogen by bacteria living symbiotically on the roots of leguminous plants, then converted to nitrate when the nitrogen-containing biomass decays. The nitrate may be taken up by other plants and incorporated into protein. The protein may be ingested by animals and the nitrogen excreted as urea in their urine to undergo biological decay and return to the atmosphere as elemental nitrogen. Carbon from carbon dioxide in the atmosphere may be incorporated into biomass by plant photosynthesis, then eventually returned to the atmosphere as carbon dioxide as the biomass is used as a food source by animals.

Enzymes in Metabolism

In Chapter 5, Section 5.5, *catalysts* were defined as materials that enable a reaction to occur without themselves being consumed. Living organisms have catalysts that are very important in metabolism. These catalysts are special proteins that enable biochemical reactions to take place called **enzymes**. Enzymes speed up metabolic reactions by as much as almost a billion-fold. In addition to making reactions go much more rapidly, enzymes are often highly specific in the reactions that they catalyze. The reason for the specificity of enzymes is that they have very specific structures that fit with the substances upon which they act.

Enzymes were discussed in Chapter 7, Section 7.7, and their action illustrated in Figure 7.9 with respect to their processing of biochemicals. The first step in the function of enzymes is the reversible formation of an enzyme/substrate complex that forms because of the complementary shapes of the enzyme (more specifically the active site on the enzyme) and the substrate. The second step is the formation of products accompanied by release of the unchanged enzyme molecule. A very common enzymatic process called **hydrolysis** involves splitting a molecule accompanied by the addition of water with an H atom going to one of the products and an OH group to the other. Other types of enzyme-catalyzed reactions occur, including the joining of two molecules, modifications of organic functional groups on substrate molecules, and rearranging the structures of molecules.

The names of enzymes, usually ending in "*-ase*" often reflect their functions and may also indicate where they operate. An example is *gastric proteinase*, a name that indicates the enzyme acts in the stomach (*gastric*) and hydrolyzes proteins (*proteinase*). The enzyme released by the pancreas that hydrolyzes fats is called *pancreatic lipase.*

A number of factors can affect enzyme action. One important factor is temperature. Organisms without temperature-regulating mechanisms have enzymes that increase in activity as temperature increases up to the point where the heat damages the enzyme, after which the activity declines precipitously with increasing temperature. Enzymes in mammals function optimally at body temperature (37°C for humans) and are permanently destroyed by about 60°C. There is particular interest in enzymes that function in bacteria that live in hot springs and other thermal areas where the water is at or near boiling. These enzymes may turn out to be very useful in commercial biosynthesis operations where the higher temperature enables reactions to occur faster. Acid concentration also affects enzymes, such as those that function well in the acidic environment of the stomach, but stop working when discharged into the slightly basic environment of the small intestine (were this not the case, they would tend to digest the intestine walls).

A significant concern with potentially toxic substances is their adverse effects upon enzymes. As an example, organophosphate compounds, such as insecticidal parathion and military poison sarin "nerve gas" bind with acetylcholinesterase required for nerve function, causing it not to act and stopping proper nerve action. Some substances cause the intricately wound protein structures of enzymes to come apart, a process called denaturation, which stops enzyme action. The active sites of enzymes at which substrates are recognized have a high population of -SH groups. Heavy metals, such as lead and cadmium, have a strong affinity for−SH groups and may bind at enzyme active sites thus destroying the function of the enzymes.

Enzymes are of significant concern in the practice of green chemistry. One obvious relationship is that between enzymes and chemicals that are toxic to them. In carrying out green chemical processes, such chemicals should be avoided wherever possible.

Another obvious relationship has to do with the use of biological processes to perform chemical operations, which are usually done under much milder and environmentally friendly conditions biologically than chemically. Biochemical processes are all carried out by enzymes. For example, several enzymes, starting with hexokinase, are involved in the multistepped biochemical fermentation synthesis of ethyl alcohol from carbohydrate glucose. With recombinant DNA technology (see Section 12.8) it is now possible to invest bacteria with enzyme systems from other organisms designed to carry out desired biochemical processes. Bacteria are much more amenable to handling and usually much more efficient than the organisms from which the genes for the desired enzyme systems are taken. Another approach is to use isolated enzymes immobilized on a solid support to carry out biochemical processes without the direct involvement of an organism.

Nutrients

The raw materials that organisms require for their metabolism are **nutrients**. Those required in larger quantities include oxygen, hydrogen, carbon, nitrogen, phosphorus, sulfur, potassium, calcium, and magnesium and are called **macronutrients**. Plants and other autotrophic organisms use these nutrients in the form of simple inorganic species, such as H_2O and CO_2, which they obtain from soil, water, and the atmosphere. Heterotrophic organisms obtain much of the macronutrients that they need as carbohydrates, proteins and lipids (see Chapter 7) from organic food material.

An important consideration in plant nutrition is the provision of **fertilizers** consisting of sources of nutrient nitrogen, phosphorus, and potassium. A large segment of the chemical manufacturing industry is involved with fixing nitrogen from the atmosphere as ammonia, NH_3, and converting it to nitrate (NO_3^-), urea (CON_2H_4), or other compounds that are applied to the soil as nitrogen fertilizer. Phosphorus is mined as mineral phosphate that is converted to biologically available phosphate ($H_2PO_4^-$ and HPO_4^{2-} ions) by treatment with sulfuric or phosphoric acid. Potassium is mined as potassium salts and applied directly as fertilizer. The ongoing depletion of sources of phosphorus and potassium fertilizer is a sustainability issue of significant concern.

Organisms also require very low levels of a number of **micronutrients**, which are usually used by essential enzymes that enable metabolic reactions to occur. For plants, essential micronutrients include the elements boron, chlorine, copper, iron, manganese, sodium, vanadium, and zinc. The bacteria that fix atmospheric nitrogen required by plants require trace levels of molybdenum. Animals require in their diet elemental micronutrients including iron and selenium as well as micronutrient vitamins consisting of small organic molecules.

Control in Organisms

Organisms must be carefully regulated and controlled in order to function properly. A major function of these regulatory functions is the maintenance of the organism’s homeostasis, its crucial internal environment. The most obvious means of control in animals is through the **nervous system** in which messages are conducted very rapidly to various parts of the animal as **nerve impulses**. More advanced animals have a brain and spinal cord that function as a **central nervous system** (CNS). This sophisticated system receives, processes, and sends nerve impulses that regulate the behavior and function of the animal. Effects on the nervous system are always a concern with toxic substances. For example, exposure to organic solvents that dissolve some of the protective lipids around nerve fibers can lead to a condition in which limbs do not function properly called **peripheral neuropathy**. Therefore, a major objective of green chemistry is to limit the use of and human exposure to such solvents.

Both animals and plants employ **molecular messengers** that move from one part of the organism to another to carry messages by which regulation occurs. Messages sent by these means are much slower than those conveyed by nerve impulses. Molecular messengers are often **hormones** discussed as lipids in Section 7.5. Hormones are carried by a fluid medium in the organism, such as the bloodstream, to cells where they bind to **receptor proteins** causing some sort of desired response. For example, the process may cause the cell to synthesize a protein to counteract an imbalance in homeostasis. Some hormones called **pheromones** carry messages from one organism to another. They commonly serve as sex attractants. Some biological means of pest control use sex pheromones to cause sexual confusion in pesticidal insects, thus preventing their reproduction. Figure 12.2 shows a common plant hormone and a common animal hormone.

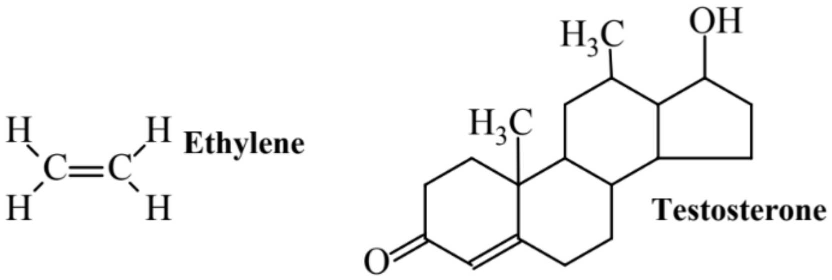


Figure 12.2. A simple molecule that acts as a plant hormone to promote maturation processes (ethylene) and a common animal hormone, testosterone, the male sex hormone. See Chapter 6, Section 6.3, for the meaning of line formulas, such as those shown for testosterone.

In animals, regulatory hormones are commonly released by **endocrine glands** shown for humans in Chapter 7, Figure 7.6. Endocrine glands in humans include the anterior pituitary gland that releases human growth hormone, the parathyroid gland that releases a hormone to stimulate uptake of calcium into the blood from bones and the digestive tract, and the pancreas that release insulin to stimulate glucose uptake from blood. These hormones are carried to target cells in fluids external to the cells. A significant concern with toxic substances is their potential to interfere with the function of endocrine glands. Another concern is that some toxic substances may mimic the action of hormones. For example, evidence exists to suggest that premature sexual development in some young female children can be caused by ingestion of synthetic chemicals that mimic the action of the female sex hormone estrogen.

12.5: Reproduction and Inherited Traits

As noted in the preceding section, one of the major activities of organisms is metabolism by which organisms process materials and energy. The other major activity of all organisms is reproduction. Most organisms are capable of reproducing a large excess of their species because throughout time predators and hostile conditions have required large numbers of juveniles to ensure survival of enough members to continue the species. Unrestrained reproduction, especially by humans, poses a strong threat of overpopulation that will outstrip Earth’s resources and is a major concern related to reproduction and the environment. A second major concern is the potential effect of environmental chemicals upon reproduction and the threat of such chemicals to cause birth defects. Therefore, chemicals that may affect reproduction are given strong consideration in the practice of green chemistry.

Primitive single-celled organisms, particularly bacteria, undergo **asexual** reproduction in which a cell simply splits to form two cells. Humans and most other multicelled organisms undergo **sexual reproduction** requiring that male sperm cells fertilize female egg cells to produce cells capable of dividing and producing new individuals.

Reproduction is directed by **genes** which occur in molecules of deoxyribonucleic acid, DNA, discussed in Chapter 7, Section 7.6. The DNA of an individual, which in sexual reproduction has contributions from both parents, determines the physical, biochemical, and behavioral traits of the organism. The DNA can be altered resulting in changes called **mutations**. A minuscule fraction of mutations are desirable and convey advantages to an individual that are passed along as heritable characteristics in offspring. This is the process of *natural selection* that has resulted in literally millions of different species of organisms.

Some chemicals are capable of producing mutations. Control of production and exposure to these **mutagens** is a major thrust of green chemistry. This is particularly so because substances that cause mutations are generally regarded as being capable of causing cancer as well and substances that give positive tests for mutagenicity are suspect carcinogens.

12.6: Stability and Equilibrium of the Biosphere

In order for an organism to survive and thrive, it must reach a state of stability and equilibrium with its environment. The term given to such a state is **homeostasis** (“same status”). In maintaining homeostasis, an organism must interact with its surroundings and other organisms in its surroundings and must balance flows and processing of matter (including nutrients) and energy. On an individual basis, organisms do a remarkably good job of keeping their internal levels of water, materials such as calcium in blood, and temperature within a range conducive to their well being. Mammals have developed extraordinary capabilities of homeostasis; a healthy individual maintains its internal temperature within a few tenths of a degree. The concept of homeostasis applies to entire groups of organisms living together in ecosystems and, ultimately, to the entire biosphere. Therefore, a major objective of environmental science, including the practice of green chemistry, is to maintain and enhance conditions of homeostasis in the biosphere.

Ecology describes the interaction of organisms with their surroundings and each other. An important consideration in ecology is the manner in which organisms process matter and energy. An **ecosystem** describes a segment of the environment and the organisms in it with all of the interactions and relationships that implies. An ecosystem has means of capturing energy, almost always by plants or algae that perform photosynthesis. Light, temperature, moisture, and nutrient supplies are critical aspects of an ecosystem. Ecosystems recycle essential nutrient carbon, oxygen, nitrogen, phosphorus, sulfur, and trace elements. An important part of any ecosystem is the **food chain**, or more complicated **food webs**, in which food generated by photosynthesis is utilized by different organisms at different levels. An important aspect of the food chain in respect to persistent, poorly degradable organic chemicals that are soluble in lipid (fat) tissue occurs through the sequence of animals eaten in the food chain (small creatures in water are fed upon by small fish that are eaten by large fish that are eaten by large birds). Thus, aquatic pollutants become more concentrated in lipid tissue at the top of the food chain, a process called biomagnification (see Section 12.9). An objective of the practice of green chemistry is to avoid the generation and use of chemicals capable of biomagnification in the environment.

The surroundings over a relatively large geographic area in which a group of organisms live constitute a **biome**. There are a number of different kinds of biomes. Regions near the equator may support **tropical rain forest** biomes that stay warm all of the year and in which nutrients remain largely in the organisms (rain forest soil is often notably poor in nutrients, which are mostly held in forest biomass). Temperate regions may support **temperate deciduous forests** in which the trees grow new leaves for a warm, wet summer season and shed them for cold winters. Temperate regions may also have **grassland biomes** in which grass grows from a tough mass of dense roots called **sod**. **Tundra** are treeless arctic regions in which during summer only a layer of wet soil thaws above a permanently frozen foundation of permafrost. Global warming is causing some profound changes in tundra biomes.

Different kinds of biomes pose a variety of environmental challenges. Some of these have come about from the conversion of biomes to cropland. Grasslands in which the sod has been broken to support wheat and other crops have proven susceptible to wind erosion, which gave rise to the catastrophic Dust Bowl that caused such great hardship on the U. S. Great Plains during the 1930s. Climate changes resulting from global warming could change the distribution of biomes, giving rise to much larger areas of hot deserts that humans might have to learn how to utilize.

Biomes in Unexpected Places

The conventional thinking in the past was that biomes would occur only in those areas where sunlight enabled conversion of inorganic carbon to biomass that could sustain a food web. It came as a surprise to marine scientists in 1977 that thousands of meters below the surface of the Pacific ocean, far too deep for light to penetrate and without significant amounts of fallout from biomass generated in surface waters, biomes existed that teemed with tubeworms, clams, and mussels. It is now known that this abundance of life is nourished by microorganisms that thrive in hot volcanic springs and that get their energy through chemosynthesis by mediating reactions of hydrogen sulfide and other substances often toxic to more familiar organisms.

A new kind of habitat was found in 1954 with the discovery of organisms, including tubeworms over two meters long that may be centuries old, that thrive on petroleum seepage on relatively cold ocean floors. These colonies, which may contain hundreds of different species, are especially abundant on the seabed of the Gulf of Mexico, where Spanish accounts from the 1500s noted oil slicks from natural petroleum leakage.

Response of Life Systems to Stress

Organisms and the ecosystems in which they exist are subject to a number of threats that can result in loss of populations and even total destruction of the system. Natural threats include drought, flooding, fire, landslide, and volcanic eruption. Humans threaten life systems with cultivation, deforestation, mining, and severe pollution. The ability of a community of organisms to resist alteration and damage from such threats, sometimes called **inertia**, depends upon several factors and provides important lessons for the survival of the human community in the face of environmental threats. One of the basic factors involved in providing resistance of a community to damage is its overall rate of photosynthesis, its **productivity**. Another important factor is **diversity** of species so that if one species is destroyed or seriously depleted, another species may take its place. **Constancy** of numbers of various organisms is desirable; wide variations in populations can be very disruptive to a biological community. Finally, **resilience** is the ability of populations to recover from large losses.

The ability of a biological system to maintain high levels of the desirable factors listed above is commonly determined by factors other than the organisms present. This is clearly true of productivity, which is a function of available moisture, suitable climate, and nutrient-rich soil. Since all organisms depend upon the availability of good food sources, diversity, constancy, and resilience tend to follow high productivity.

Relationships Among Organisms

In a healthy, diverse ecosystem, there are numerous, often complex relationships among the organisms involved. Species of organisms strongly influence each other. And organisms may greatly alter the physical portion of the system in which they live. An example of such an influence is the tough, soil-anchoring sod that develops in grassland biomes.

In most ecosystems there is a **dominant plant species** that provides a large fraction of the biomass anchoring the food chain in the ecosystem. This might be a species of grass, such as the bluestem grass that thrives in the Kansas Flint Hills grasslands. Herbivores feed upon the dominant plant species and other plants and, in turn, are eaten by carnivores. At the end of the food cycle are organisms that degrade biomass and convert it to nutrients that can nourish growth of additional plants. These organisms include earthworms that live in soil and bacteria and fungi that degrade biological material.

In a healthy ecosystem different species compete for space, light, nutrients, and moisture. In an undisturbed ecosystem the **principle of competitive exclusion** applies in which two or more potential competitors exist in ways that minimize competition for nutrients, space, and other factors required for growth. Much of agricultural chemistry is devoted to trying to regulate the competition of weeds with crop plants. Large quantities of herbicides are applied to cropland each year to kill competing weeds. In this never-ending contest, green chemistry has an important role in areas such as the synthesis of herbicides that have maximum impact on target pests with minimum impact on the environment.

Within ecosystems there are large numbers of **symbiotic relationships** between organisms which exist together to their mutual advantage. The classic case of such a relationship is that of lichen consisting of algae and fungi growing together. The fungi anchor the system to a rock surface and produce substances that slowly degrade the rock and extract nutrients from it. The algae are photosynthetic, so they produce the biomass required by the system, which is utilized in part by the fungi. Another important symbiotic relationship is that in which nitrogen-fixing bacteria grow in nodules on leguminous plant roots. The bacteria receive nutrients from the plants in exchange for chemically fixed nitrogen required for plant nutrition.

12.7: DNA and the Human Genome

In Chapter 7, Section 7.6, *deoxyribonucleic acid, DNA*, was discussed and it was noted that this macromolecule stores and passes on genetic information that organisms need to reproduce and synthesize proteins. Recall that DNA is composed of repeating units called *nucleotides* each consisting of a molecule of the sugar 2-deoxy-β-D-ribofuranose, a phosphate ion, and one of the four nitrogen-containing bases, adenine, cytosine, guanine, and, thymine (conventionally represented by the letters A, C, G, and T, respectively). DNA is one of two *nucleic acids*, the other one of which is *ribonucleic acid, RNA*. Like DNA, RNA consists of repeating nucleotides but the sugar in RNA is β-D-ribofuranose and it contains uracil instead of thymine in its bases. The structural formulas of segments of DNA and RNA are shown in Figure 7.7.

The structure of DNA is a key aspect of its function, and its elucidation by Watson and Crickin 1953 was a scientific insight that set off a revolution in biology that is going on to this day. The huge DNA molecules consist of two strands counter wound with each other and held together by hydrogen bonds; a representation of this structure is shown in Figure 7.8. In this structure, the hydrogen bonds connecting complementary bases on the two strands are represented by dashed lines. Because of their structures that make hydrogen bonding possible, adenine on one strand is always hydrogen bonded to thymine on the opposite strand and guanine to cytosine. During cell division the two strands of DNA unwind and each generates a complementary strand for the DNA of each new cell.

In organisms with eukaryotic cells, DNA is divided into units associated with protein molecules called **chromosomes**. The number of these varies with the organism; humans have 23pairs of chromosomes, a total of 46. The strands of DNA in chromosomes, in turn, are divided into sequences of nucleotides, each distinguished by the nitrogen-containing base in it. These sequences of nucleotides give directions for the synthesis of a specific kind of protein or polypeptide. (Proteins are the biological molecules that make up much of the structure of cells and that perform most of the key functions of living organisms. Polypeptide is a general term for polymers of amino acids; proteins are the relatively long-chain polypeptides.) These specific groups of nucleotides, each of which has a specific function, are called **genes**. When a particular protein is made, DNA produces a nucleic acid segment designated *m*RNA, which goes out into the cell and causes the protein to be formed through a process called **transcription** and **translation** (the gene is said to be **expressed**).

As the units that give the directions for protein synthesis, genes are obviously of the utmost importance in living organisms. As discussed in Section 12.8, genes can now be transferred between different kinds of organisms and will direct the synthesis of the protein for which they are designed in the recipient organism. It is now known that a number of human diseases are the result of defective genes, and there is a genetic tendency toward getting other kinds of diseases. For example, certain gene characteristics are involved in susceptibility to breast cancer.

Because of the known relationship of gene characteristics to disease, the decision was made in the mid-1980s to map all the genes in the human body. This collective body of genes is called the **human genome** and the project to map it is called the Human Genome Project. The original impetus for this project in the U. S. arose because of interest in the damage to human DNA by radiation, such as that from nuclear weapons. But, from the beginning, it was recognized that the project had enormous commercial potential, especially in the pharmaceutical industry, and could be very valuable in human health.

The announcement in 2001 that mapping of the human genome was complete promised great progress in biology, especially in medicine. Genes function by directing the synthesis of specific proteins and the action of most pharmaceuticals is to alter the activities of proteins, the drug’s target. In some cases proteins are made more active and in others their activity is diminished. Knowledge of the human genome enables a better understanding of protein activity and should facilitate the development of more specific drugs, something that has developed only slowly. For example, the gene responsible for cystic fibrosis was discovered in 1989 by examination of family histories of the disease and only in 2010 were two drugs designed to combat that disease in clinical trials.

Genome Sequencing and Green Chemistry

The Human Genome Project and related genome sequencing of other organisms have a number of implications for green chemistry. One of the key goals of green chemistry is to use chemicals that have maximum effectiveness for their stated purpose with minimum side effects. This certainly applies to pharmaceuticals in which a knowledge of the human genome may enable development of drugs that do exactly what they are supposed to do without affecting non target systems. This means that drugs can be made very efficiently with little waste material.

Some of the most important effects of DNA sequencing as it relates to green chemistry has to do with a wide variety of organisms other than humans. With an exact knowledge of DNA and the genes that it contains, it is possible to deal with organisms on a highly scientific basis in areas such as pest control and the biosynthesis of raw materials. An accurate map of the genetic makeup of insects, for example, should result in the synthesis of precisely targeted insecticides which kill target pests without affecting other organisms. Such insecticides should be effective at very low doses, thus minimizing the amount of insecticide that has to be synthesized and applied, consistent with the goals of green chemistry.

An exact knowledge of the genomes of organisms is extremely helpful in the practice of genetic engineering in which genes are transferred between species to enable production of desired proteins and to give organisms desirable characteristics, such as pest resistance. A number of medically useful proteins and polypeptides are now produced by genetically engineered microorganisms, most commonly genetically modified *Escherichia coli* bacteria. Perhaps the greatest success with this technology has been the biosynthesis of human insulin, a lack of which causes diabetes in humans. Two genes are required to make this relatively short polypeptide which consists of only 51 amino acids. Other medically useful substances produced by genetically engineered organisms include human growth hormone, tissue plasmogen activator that dissolves blood clots formed in heart attacks and strokes, and various vaccine proteins to inoculate against diseases such as meningitis, hepatitis B, and influenza. Genetic engineering is discussed in more detail in Section 12.8.

12.8: Genetic Engineering

Recombinant DNA and Genetic Engineering

Ever since humans started raising crops for food and fiber (and later animals) they have modified the genetic makeup of the organisms that they use. This is particularly evident in the cultivation of domestic corn which is physically not at all like its wild ancestors. Until now, breeding has been a slow process. Starting with domestication of wild species, selection and controlled breeding have been used to provide desired properties, such as higher yield, heat and drought tolerance, cold resistance, and resistance to microbial or insect pests. For some domesticated species these changes have occurred over thousands of years. During the 1900s, increased understanding of genetics greatly accelerated the process of breeding different varieties. The development of high-yielding varieties of wheat and rice during the "green revolution" of the 1950s has prevented (or at least postponed) starvation of millions of people. A technology that enabled a quantum leap in productivity of domestic crops was the development of **hydrids** from crossing of two distinct lines of the same crop, dating in a practical sense from the mid-1900s.

Traditional breeding normally takes a long time and depends largely upon random mutations to generate desirable characteristics. One of its greatest limitations has been that it is essentially confined to the same species, whereas more often that not, desired characteristics occur in species other than those being bred. Since about the 1970s, however, humans have developed the ability to alter DNA so that organisms synthesize proteins and perform other metabolic feats that would otherwise be impossible. Such alteration of DNA is commonly known as **genetic engineering** and **recombinant DNA** technology. Organisms produced by recombinant DNA techniques that contain DNA from other organisms are called **transgenic organisms**. With recombinant DNA technology, segments of DNA that contain information for the specific syntheses of particular proteins are transferred between organisms. Most often the recipient organisms are bacteria, which can be reproduced (cloned) over many orders of magnitude from a cell that has acquired the desired qualities. Therefore, to synthesize a particular substance such as human insulin or growth hormone, the required genetic information can be transferred from a human source to bacterial cells, which then produce the substance as part of their metabolic processes.

The mechanics of recombinant DNA gene manipulation is a complex and sophisticated operation. The first step involves lyzing (opening up) a cell that has the genetic material needed and removal of this material from the cell. Through enzyme action the sought-after genes are cut from the donor DNA chain. These are next spliced into small DNA molecules. These molecules, called **cloning vehicles**, are capable of penetrating the host cell and becoming incorporated into its genetic material. The modified host cell is then reproduced many times and carries out the desired biosynthesis.

Recombinant DNA technology is a rapidly growing area that is having profound effects, especially in agriculture and medicine. It is being used increasingly to produce crops with unique characteristics, to synthesize pharmaceuticals, and to make a variety of useful raw materials as renewable feedstocks. Recombinant DNA technology has a lot of potential in the development of green chemistry and sustainability, such as in the sustainable production of chemical feedstocks and products of various kinds. An example is synthesis of polylactic acid using lactic acid produced enzymatically with corn and polymerized by standard chemical processes. In the environmental area genetic engineering offers the potential for the production of bacteria engineered to safely destroy troublesome wastes and to produce biological substitutes for environmentally damaging synthetic pesticide.

Early concerns about the potential of genetic engineering to produce "monster organisms" or new and horrible diseases have been largely allayed, although not entirely so, and resistance to the application of recombinant DNA technology is strong in some quarters, particularly in Europe. However, caution is still required with this technology. One example of a problem has been the emergence of weeds resistant to the widely used herbicide glyphosate as discussed at the beginning of this chapter.

Once plants containing desired transgenes have been produced, an exhaustive evaluation process occurs. This process has several objectives. The most obvious of these is an evaluation of the transplanted gene's activity to see if it produces adequate quantities of the protein for which it is designed. Another important characteristic is whether or not the gene is passed on reliably to the plant's progeny through successive generations. It is also important to determine whether the modified plant grows and yields well and if the quality of its products are high.

Only a few strains of plants are amenable to the insertion of transgenes, and normally their direct descendants do not have desired productivity or other characteristics required for a commercial crop. Therefore, transgenic crops are crossbred with high-yielding varieties. The objective is to develop a cross that retains the transgene while having desired characteristics of a commercially viable crop. The improved variety is subjected to exhaustive performance tests in greenhouses and fields for several years and in a number of locations. Finally, large numbers of genetically identical plants are grown to produce seed for commercial use.

Many kinds of genetically modified plants have been developed and more are being marketed commercially every year. These are discussed in more detail in Chapter 14.

12.9: Biological Interaction with Environmental Chemicals

Organisms in the environment interact significantly with xenobiotic materials (those foreign to living systems) in their surroundings. The uptake of such materials by organisms is discussed in this section. The biodegradation of xenobiotic substances, primarily through the action of bacteria, is discussed in Section 12.10.

Bioaccumulation is the term given to the uptake and concentration of xenobiotic materials by living organisms. The materials may be present in water in streams or bodies of water, sediments in bodies of water, drinking water, soil, food, or even the atmosphere. Bioaccumulation can lead to **biomagnification** in which xenobiotic substances become successively more concentrated in the tissues of organisms higher in the food chain. This usually occurs with poorly degradable, lipid-soluble organic compounds. Suppose, for example, that such a compound contacts lake water, accumulates in solid detritus in the water, sinks to the sediment, is eaten by small burrowing creatures in the sediment, which are eaten by small fish. The small fish may be eaten by larger fish, which in turn are consumed as food by birds. At each step, the xenobiotic substance may become more concentrated in the organism and may reach harmful concentrations in the birds at the top of the food chain. This is basically what happened with DDT, which almost caused the extinction of eagles and hawks.

Fish that bioaccumulate poorly degradable, lipid-soluble organic compounds from water will lose them back to water if they are placed in an unpolluted environment. The process by which this occurs is called **depuration**. The time required to lose half of the bioaccumulated xenobiotic material is called the **half-life** of the substance.

The most straightforward case of bioaccumulation is **bioconcentration**, which occurs when a substance dissolved in water enters the body of a fish or other aquatic organism by passive processes (basically, just “dissolves” in the organism), and is carried to bodies of lipid in the organism in the blood flow. The model of bioconcentration assumes that the organism taking up the compound does not metabolize the compound, a good assumption for refractory organic compounds such as DDT or PCBs. It also assumes that uptake is by nondietary routes, including diffusion through the skin and especially through the gills of fish. The model of bioconcentration applies especially to substances that have low water solubilities (though high enough to make the compound available for uptake) and high lipid solubilities. This model of bioconcentration assumes a dynamic equilibrium between the xenobiotic substance dissolved in water and the same substance dissolved in lipid tissue. It is called the **hydrophobicity model** because of the hydrophobic (“water-hating”) nature of the substance being taken up.

The degree of bioconcentration depends upon a number of factors. The most important of these are the relative water and lipid solubility of the compound. The size and shape of the xenobiotic molecule also seem to be factors, as is temperature. In addition, bioconcentration depends upon the species of fish and their age, size, and lipid contents. Bioconcentration may be expressed by **bioconcentration factors** defined as

$$\text{Bioconcentration factor} = \frac{\text{Concentration of xenobiotic in lipid}}{\text{Concentration of xenobiotic in water}} \tag{12.9.1}$$

The bioconcentration factor can also be regarded as the ratio of the solubility of the compound in lipid to its solubility in water. Typical bioconcentration factors for PCBs and hexachlorobenzene in sunfish, trout, and minnows range from somewhat more than 1,000 to around 50,000, reflecting the high lipid solubility of these compounds.

12.10: Biodegradation

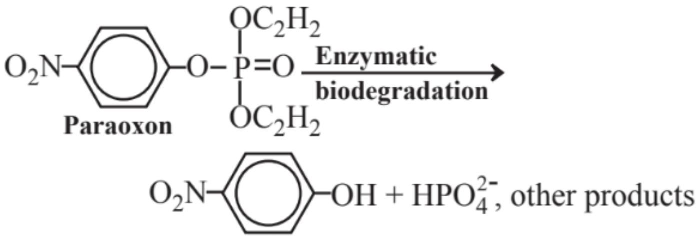
Bacteria, fungi, and protozoa in the environment play an important role in biodegrading both natural materials and synthetic substances. These processes occur predominantly in water, in sediments in bodies of water, and in soil. Biodegradation is the process by which biomass from deceased organisms is broken down to simple inorganic constituents, thus completing the cycle in which biomass is produced from atmospheric carbon dioxide and from water by photosynthesis.

The biodegradation of substances in the environment by the action of enzymes in microorganisms can be divided metabolically into two categories. The first of these is the utilization by microorganisms of organic matter that can be metabolized for energy and as material to synthesize additional biomass. This is the route taken by microorganims degrading biomass from other organisms, and to a lesser extent in the biodegradation of some xenobiotic materials.The second way in which microorganisms metabolize environmental chemicals is through **cometabolism** in which the organism's enzymes act upon the substances as a "side-line" of their normal metabolic processes. The substances that are cometabolized are called secondary substrates because they are not the main compounds for which the enzymatic processes are designed.

A commonly cited example of cometabolism occurs with the action of *Phanerochaete chrysosporium* on organochlorine compounds, including PCBs and dioxins. Commonly known as the white rot fungus, this organism has an enzyme system that normally breaks down lignin, the degradation-resistant "glue" that holds cellulose together in wood and woody plants. Under certain stressed conditions, however, the enzyme will act to cometabolize synthetic organochlorine compounds and was once widely promoted as a means of remediating hazardous waste sites contaminated with such compounds.

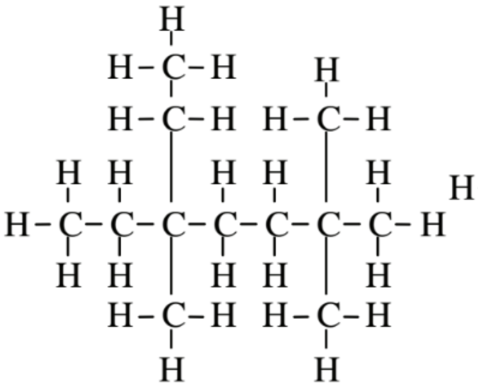
The degree of biodegradation varies over a wide range. In the simplest case, the change to the substrate molecule is relatively minor, such as addition, deletion, or modification of a functional group. Complete biodegradation to simple inorganic species—CO_2 for carbon, NH_4^+ or NO_3^- for nitrogen, HPO_4^{2-} for phosphorus, SO_4^{2-} for sulfur—is the process of **mineralization**, which is crucial in completing elemental cycles in the environment.

An important step in biodegradation is the modification of a substance to reduce its toxicity. This process is called **detoxication** (or often detoxification). An example of detoxication is given in Reaction 12.10.1 below for the conversion of insecticidal paraoxon, a potent nerve poison, to *p*-nitrophenol, which is only about 0.005× as toxic. In some cases, however, action of microorganisms in the environment may produce a much more toxic material. An example of this is the generation of highly toxic, mobile methylmercury species, $Hg(CH_3)_2$ and $HgCH_3^+$ from insoluble, relatively harmless inorganic mercury species.

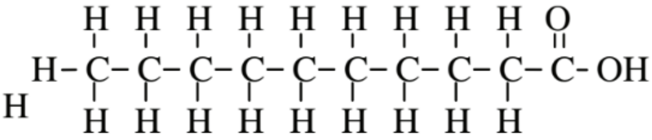


(12.10.1)

A number of factors are involved in determining the effectiveness and rate of biodegradation.The compound in question has to be biodegradable. Biodegradability is influenced by both physical properties, such as water solubility, and chemical characteristics including the presence of functional groups amenable to microbial attack. As illustrated by the example, below,

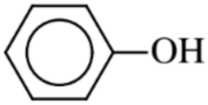


Highly branched, poorly biodegradable compound



Highly biodegradable compound with a straight hydrocarbon chain and a functional group amenable to biological attack

branched-chain hydrocarbons are very resistant to biodegradation whereas straight-chain hydrocarbons, especially those with a suitable functional group, are readily metabolized by microorganisms. It should be noted that even very poorly biodegradable compounds can often be degraded under suitable conditions. As an example, phenol,



Phenol

is a biocidal compound that kills bacteria and was once the most commonly used disinfectant. However, in dilute solution and under the appropriate conditions, phenol can be destroyed by bacteria. An important aspect of biodegradation of resistant compounds is to use microorganisms acclimated to the particular kind of compounds. Populations of acclimated microorganisms are commonly found in locations where the kinds of compounds to be treated have been spilled, such as in petroleum spills on soil.

Biodegradability of compounds is an important consideration in green chemistry. This is especially true of “consumable” materials that are dissipated to the environment. One of the most common examples of the use of a biodegradable material as a consumable material is the substitution in household detergents of biodegradable LAS surfactant, which has a readily biodegradable straight hydrocarbon chain as part of its molecular structure, in place of ABS surfactant, which has a poorly biodegradable branched chain.

12.11: Production of Food and Fiber by the Biosphere - Agriculture

The most important use of soil and the biosphere for humans is **agriculture**, the production of food and fiber by growing crops and livestock. Agriculture is very closely tied with the practice of green chemistry in many ways. Agricultural chemicals, including fertilizers, herbicides, and insecticides are produced and applied to crops and land in enormous quantities. Annual production of millions of kilograms of these chemicals demands the proper practice of green chemistry and engineering. The judicious use of relatively small quantities of herbicides enables planting of crops in soil covered with residues of the previous year's crops with little or no cultivation of soil. This practice of low-tillage agriculture, now called conservation tillage (see Section 11.11), is in keeping with the best practice of green chemistry and industrial ecology. Organic biomass produced by plants can be used as a renewable source of raw material and fuel. Some plants are now being genetically engineered to produce specific chemicals.

The practice of agriculture is absolutely essential for the survival of humankind. In order to continue to feed growing world populations while maintaining and even enhancing the ability of soil to produce food, it is necessary that the practice of agriculture be as green as possible. In the past and still today, this has often not been true. Cultivation of soil by humans has displaced native plants, destroyed wildlife habitat, contaminated soil with pesticides, filled rivers and bodies of water with sediments, and otherwise perturbed and damaged the environment. Agricultural practices arguably represent the greatest incursion of the anthrosphere into the other environmental spheres. On the positive side, growth of domestic crops temporarily removes greenhouse gas carbon dioxide from the atmosphere and provides organic raw materials and biomass fuel without any net addition of carbon dioxide to the atmosphere.

The basis of agriculture is the development of domestic plants from their wild ancestors. (The same can be said of animals, but only a handful of animal species have been domesticated, although each consists of many different breeds.) Our prehistoric ancestors learned to select plants with desired characteristics for the production of food and fiber, developing new species that often require the careful efforts of expert botanists to relate them to their wild ancestors. Only around 1900 were the scientific principles of heredity applied to plant breeding, eventually with excellent results. Using scientific methods, agriculturists accomplished a "green revolution" in the 1950s and 1960s that resulted in varieties of rice and wheat, especially, that had vastly increased yields. The techniques used included selective breeding, hybridization, cross-pollination, and back-crossing to develop grain varieties which, combined with chemical fertilizers and pesticides, lead to much higher crop yields. India, a country on the verge of starvation in the 1940s, increased its grain output by 50%. Developments such as higher yielding and faster maturing dwarf varieties of rice enabled better nutrition for an increasing world population, at least postponing the inevitable problems that will result from population growth. By breeding plants resistant to cold, drought, and insects, overall crop productivity has been further increased. Increased nutritional values for grain have been achieved, such as the development of corn varieties that have higher levels of lysine amino acid.

One of the major advances in plant breeding has been the development of **hybrids** produced by crossing **true-breeding** strains of plants. So-called "hybrid vigor" is well known, and many hybrids have vastly greater yields than their parent strains. Corn, a remarkably productive photosynthesizer, has proven most amenable to the production of hybrids, in part because of the separation of male flowers which grow on the tops of plants from female flowers attached to the budding corn ears. By planting rows of corn that alternate between two different strains and cutting the tassels from the tops of the plants that are to produce the corn seed, hybrid corn varieties are readily produced. More recently, techniques have been developed for growing hybrids of other kinds of plants.

There are, of course, many factors other than the genetic strains of plants that are involved in high crop productivity. The effects of weather have been mitigated by the development of crop varieties that resist heat, cold, and drought. The provision of water by artificial irrigation has greatly increased crop productivity and is essential for crop productivity in some regions, such as the vegetable-growing areas of California. Irrigation practices continue to become more efficient with the replacement of wasteful spray irrigators by systems that apply water directly to soil, or even directly to plant roots. Computerized control of irrigation can make it much more efficient. Environmentally, widespread use of herbicides has had some excellent benefits, along with some harmful effects, by enabling greater crop productivity with less tillage of land.

12.12: Agricultural Applications of Genetically Modified Organisms

As discussed in Section 7.6 of Chapter 7, genes composed of deoxyribonucleic acid, DNA, located in the nuclei of cells direct cell reproduction and synthesis of proteins and generally direct the organism activities. Plant scientists are now able to modify DNA by processes called *recombinant DNA technology*. (This technology is also being applied to a lesser extent to animals.) Recombinant DNA technology normally involves taking a single characteristic from one organism— the ability to produce a bacterially synthesized insecticide, for example — and splicing it into another organism. By so doing, for example, corn and cotton have been genetically engineered to produce their own insecticide. Plants produced by this method are called **transgenic** plants. During the 1970s, the ability to manipulate DNA through genetic engineering became a reality, and during the 1990s, it became the basis of a major industry. This technology promises some exciting developments in agriculture and, indeed, is leading to a "second green revolution." Direct manipulation of DNA can greatly accelerate the process of plant breeding to give plants that aremuch more productive, resistant to disease, and tolerant to adverse conditions. In the future, entirely new kinds of plants may even be engineered.

Plants are particularly amenable to recombinant DNA manipulation. In part this is because huge numbers of plant cells can be grown in appropriate media and mutants can be selected from billions of cells that have desired properties, such as virus resistance. Individual plant cells are capable of generating whole plants, so cells with desired qualities can be selected and allowed to grow into plants which may have the qualities desired. Ideally, this accomplishes in weeks what conventional plant breeding techniques would require decades to do.

Transgenic crops have many detractors, and demonstrations have broken out and test plots of crops destroyed by people opposed to what they call "Frankenfoods." Opposition has been especially strong in Europe, and the European Commission, the executive body of the European Union, has disallowed a number of transgenic crops. Despite these concerns, transgenic crops are growing in importance and they have become widely utilized in highly populated countries, particularly China, where they are seen as a means of feeding very large populations.

The Major Transgenic Crops and their Characteristics

The two characteristics most commonly developed in transgenic crops is tolerance for herbicides that kill competing weeds and resistance to pests, especially insects, but including microbial pests (viruses) as well. In the earlier years of transgenic crop plantings most of the crops had traits for only one of these characteristics, but in more recent years so-called stacked varieties with two or more characteristics have become more common and now comprise the fastest growing sector of transgenic crops. As of 2008, the land areas planted to transgenic crops in the eight leading countries were the following (millions of hectares in parentheses): United States (62.5), Argentina (21.0), Brazil (15.8), India (7.6), Canada (7.6), China (3.8), Paraguay (2.7), and South Africa (1.8 million hectares). The most common biotech crops are the following (hectares planted in 2008 in parentheses): Soybeans (65.8), maize (corn, 37.5), cotton (15.5), and canola (5.9). Herbicide tolerance has been the predominant biotech trait with 79 million hectares (of a global total of 125 million hectares), next were stacked traits (27 million hectares), then insect resistance (19 million hectares).

In 2010 Monsanto and Dow Agrosciences introduced stacked transgenic corn with 8 traits including resistance to insects above and below the soil as well as tolerance of some common herbicides. It is claimed that this variety will reduce the refuge area for corn planting from 20% to 5%. (The refuge is a fraction of the area of a crop that is planted to non-transgenic crops to generate enough insecticide-susceptible insects to dilute the resistant ones that eventually develop in the transgenic areas. The rationale for this approach is that insects growing in refuge areas without any incentive to develop resistance will crossbreed with resistant strains, preventing them from becoming dominant.) In addition to pest resistance and tolerance to herbicides, future stacked transgenic crops are expected to have characteristics such as drought resistance, high omega-3 lipid production in soybeans and elevated levels of pro-Vitamin A in Golden Rice.

The disruption of natural ecosystems by cultivation of land and planting agricultural crops provides an excellent opportunity for opportunistic plants — weeds — to grow in competition with the desired crops. To combat weeds, farmers use large quantities of a variety of herbicides. The heavy use of herbicides poses a set of challenging problems. In many cases, to be effective without causing undue environmental damage, herbicides must be applied in specified ways and at particular times. Collateral damage to crop plants, environmental harm, and poor biodegradation leading to accumulation of herbicide residues and contamination of water supplies are all problems with herbicides. A number of these problems can be diminished by planting transgenic crops that are resistant to particular herbicides discussed above. The most common such plants are those resistant to Monsanto's Roundup herbicide (glyphosate, structural formula shown in Section 12.1).

This widely used compound is a broad-spectrum herbicide, meaning that it kills most plants that it contacts. One of its advantages from an environmental standpoint is that it rapidly breaks down to harmless products in soil, minimizing its environmental impact and problems with residue carry-over. By using "Roundup Ready" crops, of which by far the most common are transgenic soybeans, the herbicide can be applied directly to the crop, killing competing weeds. Application when the crop plants are relatively small, but after weeds have had a chance to start growing, kills weeds and enables the crop to get a head start. After the crop has developed significant size, it deters the growth of competing weeds by shade that deprives the weeds of sunlight.

Aside from weeds, the other major class of pests that afflict crops consists of a variety of insects. Two of the most harmful of these are the European corn borer and the cotton bollworm, which cost millions of dollars in damage and control measures each year and can even threaten an entire year's crop production. Even before transgenic crops were available, *Bacillus thuringiensis* (Bt) was used to control insects. This soil-dwelling bacterium produces a protein called delta-endotoxin. Ingested by insects, delta-endotoxin partially digests the intestinal walls of insects causing ion imbalance, paralyzing the system, and eventually killing the insects. Fortunately, the toxin does not affect mammals or birds. Bt has been a popular insecticide because as a natural product it degrades readily and has gained the acceptance often accorded to "natural" materials(many of which are deadly).

Genetic engineering techniques have enabled transplanting genes into field crops that produce Bt. This is an ideal circumstance in that the crop being protected is generating its own insecticide, and the insecticide is not spread over a wide area. There are several varieties of insecticidal Bt, each produced by a unique gene. Several insecticidal pests are well controlled by transgenic Bt. In addition to the European corn borer mentioned above, these include the Southwestern corn borer and corn earworm. Cotton varieties that produce Bt are resistant to cotton bollworm. Bt-producing tobacco resists the tobacco budworm. Potato varieties have been developed that produce Bt to kill the Colorado potato beetle, although this crop has been limited because of concerns regarding Bt in the potato product consumed directly by humans. Although human digestive systems are not affected adversely by Bt, there is concern over its being an allergen because of its proteinaceous nature.

Virus resistance in transgenic crops has concentrated on papaya. This tropical fruit is an excellent source of Vitamins A and C and is an important nutritional plant in tropical regions. The papaya ringspot virus is a devastating pest for papaya, and transgenic varieties resistant to this virus are now grown in Hawaii. One concern with virus-resistant transgenic crops is the possibility of transfer of genes responsible for the resistance to wild relatives of the plants that are regarded as weeds, but are now kept in check by the viruses. For example, it is possible that virus-resistant genes in transgenic squash may transfer to competing gourds, which would crowd out the squash grown for food.

Future Crops

The early years of transgenic crops can be rather well summarized by soybeans, corn, and cotton resistant to herbicides and insects. In retrospect, these crops will almost certainly seem rather crude and unsophisticated. In part, this lack of sophistication is due to the fact that the genes producing the desired qualities are largely expressed by all tissues of the plants and throughout their growth cycle, giving rise to problems such as the Bt-contaminated corn pollen that may threaten Monarch butterflies or Bt-containing potatoes that may not be suitable for human consumption. It is anticipated that increasingly sophisticated techniques will overcome these kinds of problems and will lead to much improved crop varieties in the future.

There are many potential green chemistry aspects from genetic engineering of agricultural crops. One promising possibility is to increase the efficiency of photosynthesis, which is only a few tenths of a percent in most plants. Doubling this efficiency should be possible with recombinant DNA techniques, which might significantly increase the production of food and biomass by plants. For example, with some of the more productive plant species, such as fast-growing hybrid poplar trees and sugarcane, biomass is competitive with fossil fuels as an energy source. A genetically engineered increase in photosynthesis efficiency could enable biomass to economically replace expensive petroleum and natural gas for fuel and raw material. A second possibility with genetic engineering is the development of the ability to support nitrogen-fixing bacteria on plant roots in plants that cannot do so now. If corn, rice, wheat, and cotton could be developed with this capability it could save enormous amounts of energy and natural gas (a source of elemental hydrogen) now consumed to make ammonia synthetically.

A wide range of other transgenic crops are under development. One widely publicized crop is"golden rice" which incorporates β-carotene in the grain, which is therefore yellow, rather than the normal white color of rice. The human body processesβ-carotene to Vitamin A, the lack of which impairs vision and increases susceptibility to maladies including respiratory diseases, measles, and diarrhea. Since rice is the main diet staple in many Asian countries, the widespread distribution of golden rice could substantially improve health. As an example of the intricacies of transgenic crops, two of the genes used to breed golden rice were taken from daffodil and one from a bacterium! Some investigators contend that humans cannot consume enough of this rice to provide a significant amount of Vitamin A.

As of 2010, transgenic alfalfa and sugar beets resistant to glyphosate herbicide were being promoted for agricultural use. Alfalfa is a nutritious forage crop for animal feed, a legume that grows synergistically with nitrogen-fixing *Rhizobium* bacteria growing in nodules attached to its roots. In 2010 the U.S. Supreme Court overturned a lower court decision that had prevented widespread distribution of these crops because of the possibility that their glyphosate-resistant qualities might spread to other plants and violate restrictions on foods designated as “organic” and that some countries have put in place against all transgenic food.

Work continues on improved transgenic oilseed crops. The one getting the most attention is canola, the source of canola oil. Efforts are underway to modify the distribution of oils in canola to improve the nutritional value of the oil. Another possibility is increased Vitamin E content in transgenic canola. Sunflower, another source of vegetable oils, is the subject of research designed to produce improved transgenic varieties. Herbicide tolerance and resistance to white mold are among the properties that are being developed in transgenic sunflowers.

Decaffeinated coffee and tea have become important beverages. Unfortunately, the processes that remove caffeine from coffee beans and tea leaves also remove flavor, and some such processes use organic solvents that may leave undesirable residues. The genes that produce caffeine in coffee and tea leaves have now been identified, and it is possible that they may be removed or turned off in the plants to produce coffee beans and tea leaves that give full-flavored products without the caffeine. Additional efforts are underway to genetically engineer coffee trees in which all the beans ripen at once, thereby eliminating the multiple harvests that are now required because of the beans ripening at different times.

Although turf grass for lawns would not be regarded as an essential crop, enormous amounts of water and fertilizers are consumed in maintaining lawns and grass on golf courses and other locations. Healthy grass certainly contributes to the “green” esthetics of a community. Furthermore, herbicides, insecticides, and fungicides applied to turf grass leave residues that can be environmentally harmful. So the development of improved transgenic varieties of grass and other groundcover crops can be quite useful. There are many desirable properties that can benefit grass. Included are tolerances for adverse conditions of water and temperature, especially resistance to heat and drought. Disease and insect resistance are desirable. Reduced growth rates can mean less mowing, saving energy. For grass used on waterways constructed to drain excess rain runoff from terraced areas (see Figure 11.6) a tough, erosion-resistant sod composed of masses of grass roots is very desirable. Research is underway to breed transgenic varieties of grass with some of these properties. Also, grass is being genetically engineered for immunity to the effects of Roundup herbicide (see above), which is environmentally more benign than some of the herbicides such as 2,4-D currently used on grass.

An interesting possibility for transgenic foods is to produce foods that contain vaccines against disease. This is possible because genes produce proteins that resemble the proteins in infectious agents, causing the body to produce antibodies to such agents. Diseases for which such vaccines may be possible include cholera, hepatitis B, and various kinds of diarrhea. The leading candidate as a carrier for such vaccines is the banana. This is because children generally like bananas and this fruit is readily grown in some of the tropical regions where the need for vaccines is the greatest.

12.13: The Anthrosphere in Support of the Biosphere

Although humans are commonly blamed — usually with ample justification — for adverse effects upon the biosphere, human activities and modern technology have a high potential for benefitting the biosphere. This is especially true now that there is such an explosion in the understanding of biological sciences. The realization that the biosphere can contribute immeasurably to the benefit of humankind through such things as the provision of renewable feedstocks as raw materials provides a strong incentive to use technology to the benefit of the biosphere.

The most direct interface between the biosphere and technology occurs in agriculture. The production of biomass per unit area of land has increased in a spectacular fashion in recent decades with the use of fertilizers, herbicides, insecticides, and sophisticated means of cultivation and harvesting. Now the application of recombinant DNA technology (see Section 12.12) to agriculture promises even greater advances. In the past, the ways in which techniques for improved agricultural productivity were applied were largely divorced from considerations of the natural ways in which plants and animals grow on land. Fortunately, there is a growing realization of the important information that nature can provide in maintaining agricultural productivity. For example, in the prevention of water erosion, terraces constructed on land are designed to funnel excess water runoff onto grassed waterways. By planting these waterways to native grasses, a tough, erosion-resistant sod can be established that stands up under the punishment of occasional deluges of runoff water while surviving intermittent severe droughts. On a larger scale, in place of cultivating drought-prone prairie land to grow grain to feed to cattle, a better approach may be to reseed these lands to tough native grasses and allow bison to feed upon the grass as a source of meat (less fat and more healthy than beef from cattle).

The restoration and development of “natural” areas has become an important endeavor commonly termed **restoration ecology**. This often is advised with farmland that is too marginal to support profitable agricultural operations. The example of restoring native grasslands was mentioned above. Much of the rocky, hilly, unproductive farmland in New England is now reverting to forests. In such restoration efforts, modern construction machinery with the capacity to move enormous quantities of dirt have proven useful. One example in which such machinery is used is in leveling large areas for the construction of wetlands. Rivers that were once straightened to facilitate water flow — with catastrophic results in the form of flooding and erosion — are now being restored with the bends and meanders that characterize a healthy river. As discussed in Chapter 8, Section 8.2, following the catastrophic 500-year floods on the Missouri and Mississippi Rivers in 1993, large areas of cropland in the river bottoms were purchased by the Federal Government, river dikes designed to prevent flooding were breached, and the land was allowed to revert to a wild state. Land disrupted by strip mining has been smoothed over to reduce erosion, topsoil applied, and trees planted to produce natural areas and wildlife habitat.

A significant amount of restoration ecology has been devoted to restoring game animals, some of which had been driven virtually to extinction by over-hunting and habitat destruction. Animals that have come back in significant numbers include wild turkeys, wood ducks, snowy egrets, and American bison. Some of these efforts have been almost too successful. Once endangered Canadian geese have greatly increased in numbers and now populate many suburban areas where they often show their displeasure with sharing their new habitats with humans by hissing, flapping their wings aggressively, and even pinching exposed flesh with their sturdy beaks. In many areas deer now destroy crops and are a traffic hazard. Sophisticated captive breeding techniques are now used to reproduce endangered species of animals, and animal cloning may reach a point at which these efforts are routine.

In the area of green chemistry, sophisticated chemical analysis techniques can now be used to find and eliminate the sources of chemical hazards to wildlife. The classic example of this occurred in the 1960s when it was found that insecticidal DDT, biomagnified through the food chain, was preventing reproduction of endangered eagles and hawks at the top of the chain. In 1970 a newly developed technique for the determination of mercury showed that large fish were contaminated by this heavy metal released from sediments by bacterial methylation. Analysis of lipid tissue in humans, caribou, and polar bears now indicate a global distillation mechanism by which persistent organic compounds evaporate into the atmosphere in warmer regions of Earth and condense in the polar regions, leading to significant contamination of food supplies. One of the major objectives of green chemistry is the elimination of the generation and use of such materials.

As the projected effects of global warming become more pronounced during the next century, technology will be employed to a greater extent to deal with these effects upon the biosphere. Increasingly sophisticated genetic engineering techniques will be used to develop plant varieties that can withstand the heat and drought resulting from global warming. Another possibility is the development of plants that can grow in saltwater. Using renewable solar and wind energy, vast water desalination projects will be developed to provide fresh water to irrigate high-value crops where the costs can be justified.

12.14: Livestock and their Wastes

Areas where agriculture is practiced intensively with heavily fertilized crops and large populations of livestock can cause serious water pollution problems. This is true of the watershed of Chesapeake Bay, the largest U.S. estuary with a watershed that includes areas of New York, Pennsylvania, Delaware, Maryland, Virginia, and West Virginia. One of the agricultural areas that discharges runoff to the bay is Lancaster County, Pennsylvania, that is the location of more than 5000 farms with some of the most productive soil in the world. More than half of these farms are owned by Amish, a religious sect that does not use electricity, automobiles, and other modern conveniences. These farms are livestock-intensive with heavy production of dairy products. Unlike most modern farms that use tractors and other farm equipment powered by diesel and gasoline engines, the Amish rely upon horses and mules for cultivation. The result of these factors is that each year Lancaster County produces about 9 million kilograms of manure plus large quantities urine, more than any of the other counties in the region. Both of these materials are rich in nitrogen, phosphorus, and potassium that have resulted in drainage into Chesapeake Baycontributing to heavy growths of algae leading to eutrophication. As a result of algal nutrient pollution Chesapeake Bay has had a dead zone that has been the subject of remediation efforts since the 1970s. In addition to runoff pollution, problems have been reported of pollution of farm wells in the county contaminated with *Escherichia coli* bacteria, which are indicators of animal feces pollution and some wells have shown elevated levels of nitrate ion that can come from the biodegradation of nitrogenous biomaterials. (Nitrate is generally harmless to adult humans but in human infants and ruminant animals including cattle can cause methemoglobinemia, a condition in which the iron(II) in blood hemoglobin is oxidized to iron(III) producing methemoglobin, which does not transport blood in the bloodstream.)

Attempts are underway to reduce the water pollution from livestock in Lancaster and other livestock-intensive counties by measures including minimal tillage agriculture, cover crops, reduction and containment of barnyard runoff, forested buffers along streams, and manure pits to collect wastes from concentrated livestock feeding operations. Farms such as those in Lancaster County actually provide a great opportunity to practice sustainable, green agriculture. Horses and mules used for cultivation require no petroleum, the animal wastes provide abundant fertilizer, and anoxic biodegradation of animal wastes can generate large quantities of methane gas, a fuel for engines and household heating that is probably acceptable to religious sects who reject modern, especially electrically-powered, devices. A farm operated with such sustainable practices could serve as a largely self-sufficient industrial ecosystem (an alternative term that does not include“industrial” would probably be more acceptable to the operators).

Questions and Problems

1. Fill in the blanks in the following statement: Living organisms carry out chemical processes in ________, which are bodies of the order of a __________ in size.

2. Name several constituents of living cells. What are two constituents typical of plant cells?

3. What are hormones? Where are they produced?

4. To what general class of kinds of biomolecules do enzymes belong? What is their function?

5. How are enzymes named?

6. How does temperature relate to enzyme action, particularly as it pertains to enzymes acting in the body?

7. What is recombinant DNA? Why is it produced?

8. What is metabolism? How is respiration related to metabolism?

9. What can natural ecosystems teach humans about how to manage their industrial systems?

10. Distinguish between bioaccumulation and biomagnification as they apply to lipid-soluble organic compounds.

11. What are six characteristics shared by all living organisms?

12. What are the four basic kinds of molecules that comprise living organisms?

13. Photosynthesis is the reaction that provides food and energy to keep biological systems going. What important biological process is the opposite of photosynthesis?

14. What are the six kingdoms of living organisms?

15. Justify the statement that human beings are oxic heterotrophs.

16. What is the general effect of good living conditions, such as mild climate and abundant nutrients, on ecosystems?

17. Give four organelles found in eukaryotic cells.

18. What huge effect did photosynthesis by cyanobacteria have upon the atmosphere in the early years of life on earth?

19. In order to use the food that humans eat, it must undergo digestion and respiration. What is the distinction between these two phenomena?

20. What is the explanation of high levels of persistent organic compounds in nonindustrialized polar regions?

21. Describe the overall process of enzyme action.

22. Name two important aspects of enzymes as they relate to green chemistry.

23. Which three elements are commonly regarded as plant fertilizers?

24. Name two ways in which messages are sent in the body of an animal. Do they have about the same speed?

25. Give examples of organs that produce hormones.

26. Describe a concern pertaining to synthetic chemicals and hormones.

27. Name a concern other than mutations regarding exposure to mutagens.

28. In order for an organism to live and thrive, its internal environment must be maintained within acceptable limits. Give the name of this state.

29. Name some of the critical factors in an ecosystem. How do functioning ecosystems handle materials?

30. Tropical rain forests, temperate deciduous forests, and grasslands are all examples of_________.

31. Name four characteristics that enable life systems to respond well to stress.

32. What are symbiotic relationships between organisms? Give an example.

33. Name several factors that have contributed to the increased agricultural productivity of biomass and another factor that promises such increases in the future.

34. Define the human genome and give reasons why it is so important.

35. What are the relationships among cell DNA, RNA, and ribosomes in protein synthesis?

36. Name some substances that are beneficial to human health that are made by genetically engineered organisms. Name the organism often used for this purpose.

37. What was the “green revolution?” What technology will likely result in a “second green revolution?”

38. How is transgenic technology distinguished from conventional breeding techniques? What kind of biomolecule makes transgenic technology possible?

39. Distinguish between bioaccumulation and biomagnification

40. What are xenobiotic substances? What kind of metabolic process is largely responsible for their biodegradation?

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CHAPTER OVERVIEW

13: The Anthrosphere, Industrial Ecology, and Green Chemistry

“We are addicted to growth. That addiction to growth stokes the greed that drives the endless and often pointless consumption that we have defined as economic success. The problem with being addicted to growth is that we live on a finite planet. No matter what growth’s apologists claim about finding more resources or harnessing new technology, an addiction to growth, by definition, must at some point collide with reality” (Rudy Baum, *Chemical and Engineering* News, *June 28, 2010*).

13.1: Industrial Ecology and Industrial Ecosystems
13.2: Metabolic Processes in Industrial Ecosystems
13.3: Life Cycles in Industrial Ecosystems
13.4: Kinds of Products
13.5: Attributes Required by an Industrial Ecosystem
13.6: The Kalundborg Industrial Ecosystem
13.7: Environmental Impacts of Industrial Ecosystems
13.8: Green Chemistry and Industrial Ecology
13.9: Predicting and Reducing Hazards
13.10: The E-Factor in Green Chemistry
13.11: Catalysts and Catalysis
13.12: Biocatalysis with Enzymes
13.13: Energizing Chemical Reactions and Process Intensification
13.14: Solvents and Alternate Reaction Media
13.15: Feedstocks and Reagents
Literature Cited and Supplementary References
Questions and Problems

13.1: Industrial Ecology and Industrial Ecosystems

Recall that the *anthrosphere* has been defined as a fifth sphere of the environment, the one made and modified by human activities. As such, it has developed in ways that are often in conflict with other spheres of the environment, including even the human denizens of the biosphere who have constructed the anthrosphere. This has given rise to the many environmental, resource, and sustainability problems that afflict the world today.

It is crucial for humankind and, indeed, the Earth as a whole, that the anthrosphere be brought into a state of compatibility with the other environmental spheres and with Earth. Green chemistry has a key role to play in this endeavor. In a sense, green chemistry is all about the greening of the anthrosphere. In order to understand how this may occur, it is necessary to introduce and explain the key concept of **industrial ecology**. Industrial ecology integrates the principles of science, engineering, and ecology in industrial systems through which goods and services are provided in away that minimizes environmental impact and optimizes utilization of resources, energy, and capital. In so doing, industrial ecology considers every aspect of the provision of goods and services from concept, through production, and to the final fate of products remaining after they have been used. Industrial ecology considers industrial systems in a closed-loop model rather than a linear one thereby emulating natural biological ecosystems, which are sustainable by nature. Industrial ecology is above all a **sustainable** means of providing goods and services.

Industrial ecology works through groups of industrial concerns, distributors, and other enterprises functioning to mutual advantage, using each others' products, recycling each others' potential waste materials, and utilizing energy as efficiently as possible. By analogy with natural ecosystems, such a system is an **industrial ecosystem**. Successful industrial ecosystems achieve the maximum possible degree of recycling. To quote Kumar Patel of the University of California at Los Angles, "The goal is *cradle to reincarnation*, since if one is practicing industrial ecology correctly there is no grave." As has been the case with natural ecosystems, the best means of assembling industrial ecosystems is through natural selection in which the various interests involved work out mutually advantageous relationships. However, with a knowledge of the feasibility of such systems, external input and various kinds of incentives can be applied to facilitate the establishment of industrial ecosystems. A key measure of the success of such a system can be given by the following relationship:

$$\frac{\text{Market value of products}}{\text{Consumption of material and energy}} \tag{13.1.1}$$

Just as organisms in natural ecosystems develop strong symbiotic relationships — the inseparable union of algae and fungi in lichens growing on rock surfaces, for example — concerns operating in industrial ecosystems develop a high degree of **industrial symbiosis**. It is the development of such mutually advantageous interactions between two or more industrial enterprises that result in the self-assembly of an industrial ecosystem in the first place. The recycling components of an industrial ecosystem are absolutely dependent upon symbiotic relationships with their sources of supply.

Figure 13.1 outlines a general industrial ecosystem. The major inputs to such a system are energy and virgin raw materials. A successful system minimizes use of virgin raw materials and maximizes efficiency of energy utilization. The materials processing sector produces processed materials such as sheet steel or synthetic organic polymers. These in turn go to a goods fabrication sector in which the processed materials are formed and assembled or, in the case of consumables such as detergents, formulated to give the desired product. Scrap materials, rejected

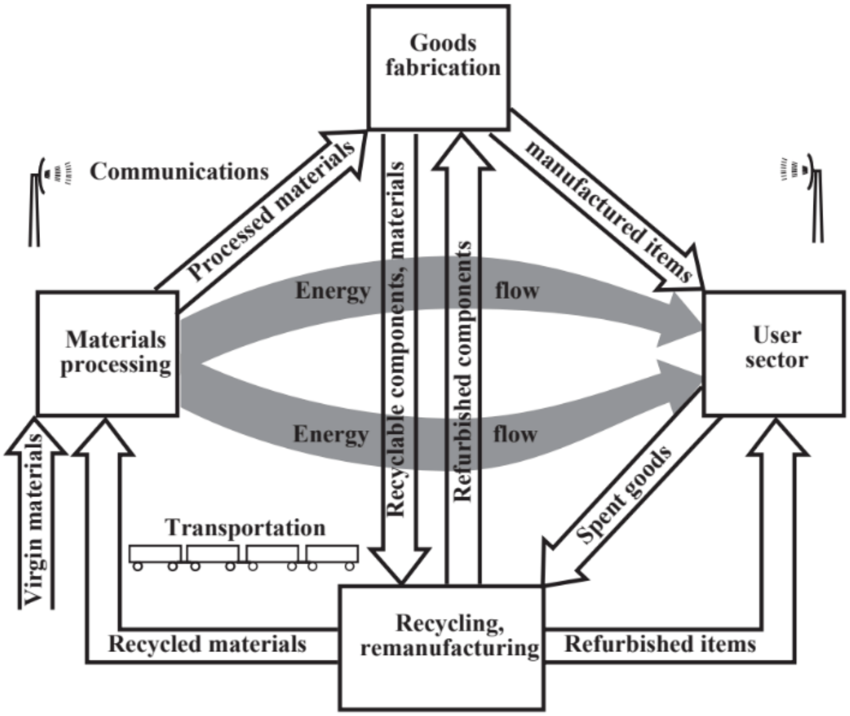

Figure 13.1. Outline of the major components of an industrial ecosystem.

components, and off-specification consumables generated during goods fabrication may go to recycling and remanufacturing. From goods fabrication, manufactured items or formulated substances are taken to a user sector, which includes consumers and industrial users. In a successful system of industrial ecology, waste materials from the user sector are minimized and, ideally, totally eliminated. Spent goods from the user sector are taken to recycling and remanufacturing to be introduced back into the materials flow of the system. Such items may consist of automobile components that are cleaned, have bearings replaced, and otherwise refurbished for the rebuilt automobile parts market. Another typical item is paper, which is converted back to pulp that is made into paper again. In some cases the recycling and remanufacturing sector salvages materials that go back to materials processing to start the whole cycle over. An example of such a material is scrap aluminum that is melted down and recast into aluminum for goods fabrication. Communications are essential to a successful industrial ecosystem, as is a reliable, rapid transportation system. It is especially important that these two sectors work well in modern manufacturing practice which calls for “just in time” delivery of materials and components to avoid the costs of storing such items.

An important characteristic of an industrial ecosystem is its **scope**. A regional scope large enough to encompass several industrial enterprises, but small enough for them to interact with each other on a constant basis is probably the most satisfactory scale to consider. Frequently such systems are based around transportation systems. Segments of interstate highways over which goods and materials move between enterprises by truck may constitute industrial ecosystems.

13.2: Metabolic Processes in Industrial Ecosystems

Industrial metabolism refers to the processes to which materials and components are subjected in industrial ecosystems. It is analogous to the metabolic processes that occur with food and nutrients in biological systems. Like biological metabolism, industrial metabolism may be addressed at several levels. A level of industrial metabolism at which green chemistry, especially, comes into play is at the molecular level where substances are changed chemically to give desired materials or to generate energy. Industrial metabolism can be addressed within individual unit processes in a factory, at the factory level, at the industrial ecosystem level, and even globally.

A significant difference between industrial metabolism as it is now practiced and natural metabolic processes relates to the wastes that these systems generate. Natural ecosystems have developed such that true wastes are virtually nonexistent. For example, even those parts of plants that remain after biodegradation of plant materials form soil humus (see “Soil Organic Matter” in Chapter 11, Section 11.8) that improves the conditions of soil on which plants grow. Anthropogenic industrial systems, however, have developed in ways that generate large quantities of wastes, where a waste may be defined as *dissipative use of natural resources*. Furthermore, human use of materials has a tendency to dilute and dissipate materials and disperse them to the environment. Materials may end up in a physical or chemical form from which reclamation becomes impractical because of the energy and effort required. A successful industrial ecosystem overcomes such tendencies.

Organisms performing their metabolic processes degrade materials to extract energy(catabolism) and synthesize new substances (anabolism). Industrial ecosystems perform analogous functions. The objective of industrial metabolism in a successful industrial ecosystem is to make desired goods with the least amount of byproduct and waste. This can pose a significant challenge. For example, to produce lead from lead ore for the manufacture of lead/acid storage batteries requires mining large quantities of ore, extracting the relatively small fraction of the ore consisting of lead sulfide mineral, and roasting and reducing the mineral to get lead metal. The whole process generates large quantities of lead-contaminated tailings left over from mineral extraction and significant quantities of byproduct sulfur dioxide, which must be reclaimed to make sulfuric acid and not released to the environment. The recycling pathway, by way of contrast, takes essentially pure lead from recycled batteries and simply melts it down to produce lead for new batteries; the advantages of recycling in this case are obvious.

There are some interesting comparisons between natural ecosystems and industrial systems as they now operate. The basic unit of a natural ecosystem is the organism, whereas that of an industrial system is the firm or, in the case of large corporations, the branch of a firm. Natural ecosystems handle materials in closed loops; with current practice, materials traverse an essentially one-way path through industrial systems. It follows that natural systems completely recycle materials, whereas in industrial systems the level of recycling is often very low. Organisms have a tendency to concentrate materials. For example, carbon in carbon dioxide that is only about 0.04% of atmospheric air becomes concentrated in organic carbon through photosynthesis. Industrial systems in contrast tend to dilute materials to a level where they cannot be economically recycled, but still have the potential to pollute. Aside from maintaining themselves during their limited lifetime, the major function of organisms is reproduction. Industrial enterprises do not have reproduction of themselves as a primary objective; their main function is to generate goods and services in a manner that maximizes monetary income.

Unlike natural ecosystems in which reservoirs of needed materials are essentially constant(oxygen, carbon dioxide, and nitrogen from air as examples) industrial systems are faced with largely depleting reservoirs of materials. For example, the lead ore cited above is a depleting resource; more may be found, but only a finite amount is ultimately available. Fossil energy resources are also finite. For example, much more fossil energy from coal may be available, but its utilization as the world’s main source of energy over the long term would come at an unacceptable cost of global warming from carbon dioxide emissions. Again, industrial metabolic processes that emphasize recycling are desirable because recycling gives essentially constant reservoirs of materials in the recycling loop. Ideally, even in the case of energy, renewable energy resources such as wind and solar power provide an essentially constant, non-depleting energy source.

As discussed under “Control in Organisms” under Section 12.4 of Chapter 12, biological ystems have elaborate systems of control. Considering the metabolism that occurs in an entire natural ecosystem, it is **self-regulating**. If herbivores that consume plant biomass become too abundant and diminish the stock of the biomass, their numbers cannot be sustained, the population dies back, and their food source rebounds. The most successful ecosystems are those in which this self-regulating mechanism operates continuously without wide variations in populations. Industrial systems do not inherently operate in a self-regulating manner that is advantageous to their surroundings, or even to themselves in the long run. Examples of the failure of self-regulation of industrial systems abound in which enterprises have wastefully produced large quantities of goods of marginal value, running through limited resources in a short time, and dissipating materials to their surroundings, polluting the environment in the process. Despite these bad experiences, within a proper framework of laws and regulations designed to avoid wastes and excess, industrial ecosystems can be designed to operate in a self-regulating manner. Such self-regulation operates best under conditions of maximum recycling in which the system is not dependent upon a depleting resource of raw materials or energy.

Obviously, recycling is the key to the successful function of industrial metabolism. Figure13.2 illustrates the importance of the **level of recycling**. In low-level recycling, a material or component is taken back to near the beginning of the steps through which it is made. For example, an automobile engine block might be melted down to produce molten metal from which new blocks are then cast. With high-level recycling, the item or material is recycled as close to the final product as possible. In the case of the automobile engine block, it may be cleaned, the cylinder walls rehoned, the flat surfaces replaned, and the block used as the platform for assembling a rebuilt engine. In this example and many others that can be cited, high-level recycling uses much less energy and materials and is inherently more efficient. The term given to the value attributed to an item or material recycled near the top of the energy/materials pyramid shown in Figure 13.2 is called its **embedded utility**.

13.3: Life Cycles in Industrial Ecosystems

In conventional industrial systems, a product is manufactured and marketed after which the vendor forgets about it (unless some product defect, such as sticking accelerator pedals on an automobile forces a recall). In a system of industrial ecology, however, the entire **life cycle** of the product is considered. An important aspect of such a consideration is the **life-cycle assessment**. The overall goal of a life-cycle assessment is to determine, measure, and minimize environmental and resource impacts of products and services.

An important decision that must be made at the beginning of a life-cycle assessment is determination of the **scope** of the assessment. Parameters included in the scope include the time period to be considered, the area (space) to be considered, and the kinds of materials, processes, and products that will go into the assessment. As an example, consider the chemical synthesis of an insecticide that releases harmful vapors and generates significant quantities of waste material. A narrowly focussed life-cycle assessment might take account of control measures to capture released vapors and the best means of disposing of the waste byproducts. A broader scope would consider a different synthetic process that might not cause the problems mentioned. An even broader scope might consider whether or not the insecticide even needs to be made and used; perhaps there are more acceptable alternatives to its use.

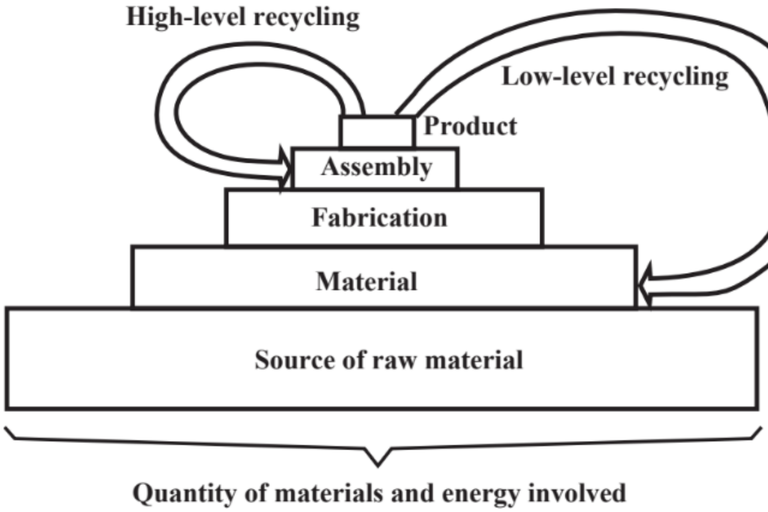

Figure 13.2. The level at which recycling occurs strongly influences the amount of energy required and the quantity of materials that must be processed.

Life cycle assessment involves an **inventory analysis** to provide information about the consumption of material and release of wastes from the point that raw material is obtained to make a product to the time of its ultimate fate, an **impact analysis** that considers the environmental and other impacts of the product, and an **improvement analysis** to determine measures that can be taken to reduce impacts. A life-cycle assessment gives a high priority to the choice of materials in a way that minimizes wastes. It considers which materials and whole components can be used or recycled. And it considers alternate pathways for manufacturing processes or, in the case of chemical manufacture, alternate synthesis routes.

In doing life-cycle assessments it is useful to consider the three major categories of **products**, **processes**, and **facilities**, all of which have environmental and resource impacts. Products are obviously the things and commodities that consumers use. They are discussed further in Section13.4. Processes refer to the ways in which products are made. Facilities consist of the infrastructural elements in which products are made and distributed.

Some of the greater environmental impacts from commerce result from the processes by which items are made. An example of this is paper manufacture. The environmental impact of the paper *product* tends to be relatively low. Even when paper is discarded improperly, it does eventually degrade without permanent effect. But the *process* of making paper, beginning with harvesting of wood and continuing through the chemically intensive pulping process and final fabrication has significant environmental impact. In addition to potential air and water pollution, paper making consumes energy and requires large amounts of water. Processes can be made much more environmentally friendly by application of the principles of industrial ecology enabling maximum recycling of materials that otherwise would have significant pollution potential.

The impact of facilities can vary over a wide range. A specialized facility such as a steel mill or petroleum refinery can have a significant environmental impact. Abandoned sites of these facilities can be blighted and difficult and expensive to restore for some other use. (The term

“brownfields” is sometimes used to describe sites of abandoned industrial facilities, and restoration of blighted “brownfields” is often a major goal of urban renewal projects.) One of the more challenging kinds of facilities to decommission are sites of nuclear power reactors in which there is a significant amount of radioactivity to deal with in dismantling and disposing of some of the reactor components. The impact of facilities can be minimized by designing them with future use and eventual decommissioning in mind. Typically, well designed commercial buildings may have a number of lives during which they are used by a sequence of enterprises. A key aspect of abuilding destined for multiple use is structure flexibility so that it can easily be rearranged for new uses.

Product Stewardship

The control of the life cycle of products that are sold is difficult. Attempts are made to exercise some degree of control by facilitating return of spent products. For example, laser printer cartridges commonly come with a return address and postage to return the used cartridge to the manufacturer. Another approach is to pay for the return of spent products. The price of a new automobile battery is commonly increased to cover a modest refund paid upon return of the spent battery. Automobile tires have a financial disincentive for recycling in that the customer is commonly charged a disposal fee.

The success rate with these kinds of measures is mixed. Automobile tires are almost invariably mounted at a dealer’s place of business, so customers pay the disposal fee in order to not be responsible for used tire disposal. Customers who install their own batteries usually turn in the old ones because they do not have a good disposal option. The return rate with printer cartridges is probably lower because people do not want to go to the trouble to mail them back.

The rate of return of items at the end of their life cycles is higher in companies and institutions where returns are more readily facilitated. The presence in a large office of a recycled paper bin or an “out box” where returned laser printer cartridges can be dropped for mailing certainly increases the recycle rate of these items. One key to recycling is in product **stewardship** where there are clear lines of accountability for items and materials. A good way to ensure product stewardship for things such as office equipment is through the leasing of equipment. In such a case, the concern holding the lease, rather than the user, is responsible for the ultimate fate of the item. The same approach can even be used with some kinds of materials, such as activated carbon used in a water treatment plant. Here the concern leasing the carbon retains ownership and is responsible for picking up the spent material for recycling. Another way to help ensure product stewardship through the consumer sector is by charging deposits on items and refunding the deposit upon return for recycling.

13.4: Kinds of Products

In considering life-cycle assessments, it is useful to divide products into three major categories. The first of these are **consumable products** which, by the nature of their use, are used up or dispersed to the environment with no possibility of recovery. Such materials include laundry detergents that are flushed down the drain with wash-water or windshield washer fluid, which is squirted onto windshields, then wiped off. Another class of product consists of **recyclable commodities**. Engine antifreeze and motor oil are potentially recyclable commodities in that, in principle (though somewhat rarely in practice), they can be reclaimed after use, purified, reformulated, and sold again. **Service products** (sometimes called durable products) are usually devices that have multiple uses and last for a long time. The washing machine in which consumable laundry detergent is used is a typical service product.

Since consumable products are dispersed to the environment, it is important that they have environmentally friendly characteristics. They should first of all be **nontoxic** at the levels and manner in which organisms are exposed to them. In addition to not causing acute toxicity, they should not be carcinogenic or mutagenic and should not cause birth defects. Another characteristic that consumable products should have is that they should not be **bioaccumulative**. As discussed under the topic of “Biological Interaction with Environmental Chemicals” in Section 12.9, **bioaccumulation** is the term given to the uptake and concentration of xenobiotic materials by living organisms. Poorly biodegradable, lipid-soluble materials such as PCB compounds have a strong tendency to bioaccumulate, and such substances should be avoided in consumable products. Consumable products should also be **degradable**. The most common type of degradation is biodegradation, which occurs primarily through the action of microorganisms. The practice of green chemistry can aid in making biodegradable products by, for example, avoiding branched-chain hydrocarbon structures in organic compounds and by attaching functional groups, such as the organic carboxylic acid group, $-CO_2H$, that are amenable to microbial attack.

Recyclable commodities should be designed with durability and recycling in mind. In order for them to last through a normal life cycle, such commodities should not be as degradable as consumables. An example of making a product more amenable to recycling is the use of bleachable and degradable inks on newsprint, which makes it easier to recycle the newsprint to produce a grade of recycled paper that meets acceptable color standards.

Although service products are designed to last for relatively long times, they do reach a stage requiring disposal or recycling. A key factor in recycling is the availability of channels through which such products can be recycled. Proposals have been made for “de-shopping” centers where items such as old computers and broken small appliances can be returned for recycling. Service products should be designed and constructed to facilitate disassembly so that various materials can be separated for recycling.

13.5: Attributes Required by an Industrial Ecosystem

Under the heading of “Response of Life Systems to Stress” in section 12.6, is a discussion of the *inertia* of biological communities, which is their resistance to alteration and damage. The key factors involved in inertia were mentioned as *productivity* of basic food materials, *diversity* of species, *constancy* of numbers of various organisms and *resilience* in the ability of populations to recover from loss. Industrial ecosystems likewise have key attributes that are required for their welfare. These include **energy**, **materials**, and **diversity**. One big difference between biological and industrial ecosystems is the time scale involved. In the evolution of organisms, a time period of several thousand years is very brief, whereas in industrial systems several decades may be a very long time.

Energy

With enough energy, almost anything is possible (see Chapter 15, “Sustainable Energy: The Essential Basis of Green Systems”). Therefore, the provision of adequate amounts of energy that can be used without damaging the environment too much is essential for the function of industrial ecosystems. And the energy that is available has to be used as effectively and efficiently as possible. It was once believed that the world’s vast coal resources would provide enough energy to meet human needs for several centuries. Now it is apparent that consuming most of these energy resources would cause unacceptable global warming effects. Solar energy and wind energy, which derives from solar energy, come about as close as any energy source to offering ideal renewable sources of energy. But there are major problems with the intermittent nature of these sources and the need that they present for short-term energy storage. Furthermore, they both require vast areas of land in order to provide a significant share of energy needs. Then there are unexpected problems, such as the one arising from the accumulation of dead insects on windmill blades, spoiling their finely tuned aerodynamic characteristics and reducing power output by about half in strong winds. Properly run nuclear power facilities can provide abundant energy for many decades, but this source comes with its own set of problems and is strongly opposed by many.

Cogeneration represents the most efficient energy use within an industry or within an industrial ecosystem. The two major reasons that an industrial plant uses energy are (1) for steam used in processing, such as heating chemical reaction mixtures to cause a reaction to go faster, and(2) to generate electricity. Traditionally, industrial operations, such as petroleum refineries, have bought electricity from external power plants to run pumps and compressors, for lighting, and other purposes that consume electricity. Steam, which can only be shipped economically for relatively short distances, is normally generated by burning fossil fuels in boilers on the site. Since a maximum of only approximately 40% of the heat generated in burning a fuel in a power plant can be converted to electricity, and because of losses in electrical transmission lines, obtaining electricity from an external source is a relatively inefficient means of getting power. Much greater efficiencies can be attained by burning fuels, such as natural gas, in large turbines connected to an electrical generator and using the hot exhaust from the turbine to raise steam. This approach can double the overall efficiency of energy utilization.

Materials

There are several approaches to providing materials. These can be classified as **dematerialization** in which less material is used for a specific purpose, **substitution** of abundant materials for scarce ones, **recycling** materials, and **waste mining** in which needed materials are extracted from wastes.

Examples abound of areas in which the need for materials has been reduced in recent decades. Higher voltage electrical transmission carries more power over thinner copper or aluminum wires, the switch from 6-volt to 12-volt electrical systems in automobiles has enabled lighter wiring in automotive electrical systems, modern photographic film uses much less silver than in years past(and the almost complete switch to digital photography has virtually eliminated the use of silver in photography), and the switch from biased-ply to radial tires has greatly extended tire life, so that much less rubber is required (as well as saving fuel by lowered rolling resistance). Dematerialization has been spectacular in the electronics area. The popular laptop computer has far more computing power than did the earliest vacuum-tube-equipped computers that each required an entire air conditioned building for housing.

Material substitution is an area in which green chemistry has made a significant contribution and will continue to do so at an accelerating pace in the future. The most spectacular advances have been made in electronics where material substitution, which enabled dematerialization to occur, has provided electronic circuits with many orders of magnitude more capability than the circuits that they replaced. The glowing, electricity-consuming vacuum tubes, capacitors, resistors, and transformers of the receiver circuit of a 1950s table-top radio have been replaced with a tiny circuit almost invisible to the human eye. The huge numbers of copper wires that carried telegraph and telephone messages in the 1940s have now been replaced by fiber optic signal conductors that carry unimaginably more information per unit mass of carrier. Polyvinylchloride (PVC) pipe, synthesized from inexhaustible world resources of chlorine and potentially from biomass hydrocarbon sources, has replaced copper and steel for water and wastewater transmissions. Toxic liquid sulfur dioxide and ammonia used in early refrigerator models were replaced by nontoxic, nonflammable chlorofluorocarbons (CFCs). When the CFCs were found to deplete stratospheric ozone, substitutes were developed containing at least one bound H atom per molecule (HCFCs) that break down in the troposphere before reaching stratospheric altitudes. Many more similar examples could be cited.

Recycling is of course one of the major objectives of a system of industrial ecology and one in which significant progress is being made. There are some consumable items that are not practical to recycle and for which the raw materials are abundant enough that recycling is not required. Household detergents are in this category. A second group of recyclables are those that are not particularly scarce, but for which recycling is feasible and desirable. Wood and paper fall into this category. A third category of recyclable materials consists of metals, particularly the more valuable and scarce ones, such as chromium, platinum, and palladium. These metals definitely should be recycled. A fourth category of recyclables consists of parts and apparatus that can be refurbished and reused.

Waste mining, the extraction of useful materials from wastes, provides more materials while benefitting the environment. One of several important examples of waste mining is the extraction of combustible methane gas, a low-polluting premium fossil fuel, from municipal refuse landfills in which the biodegradation of organic matter in the absence of oxygen generates the gas. Sulfur in sulfur dioxide extracted from the flue gases generated in burning coal that contains sulfur can be reclaimed and used to make sulfuric acid. Methods have been developed to extract aluminum from finely divided coal fly ash generated in coal combustion. In this case, the finely divided, homogeneous, dry nature of the fly ash is a definite advantage in processing it. It is anticipated that growing scarcity of resources combined with the need to dispose of a variety of wastes will lead to the development of additional waste mining processes in the future.

Diversity

Diversity in industrial ecosystems, tends to impart a **robust** character to them, which means that if one part of the system is diminished, other parts will take its place and keep the system functioning well. Many communities that have become dependent upon one or just a few major enterprises have suffered painful economic crises when a major employer leaves or cuts back. The fouling of beaches in Louisiana, Mississippi, Alabama, and Florida from the 2010 BP Deepwater Horizon has devastated the tourist trade and forced painful economic adjustments. In many parts of the world, water supply from a single vulnerable source threatens diversity.

13.6: The Kalundborg Industrial Ecosystem

Industrial ecosystems of various degrees of sophistication have existed ever since the first industries were established, although they were not called industrial ecosystems or even recognized as such until the latter 1980s. The system most commonly cited as a fully developed industrial ecosystem is the one that developed spontaneously in Kalundborg, Denmark. This system is centered around two very large energy enterprises. The first of these is the ASNAES electrical plant fired by coal and with a capacity of 1,500 megawatts. The second enterprise is the Statoil petroleum refinery, processing 4–5 million tons per year. The initial relationships in the Kalundborg system consisted of exchanges between these two enterprises. The power plant sold steam to the refinery to use in processing, and the refinery provided the power plant with fuel gas and cooling water. Both enterprises produce low-level energy in the form of steam that is used for district heating of homes and commercial buildings. The heat is also used in a large greenhouse operation, as well as in a fish-farming enterprise. Another big player in the Kalundborg industrial ecosystem is the Novo Nordisk pharmaceutical plant, which receives steam from the energy suppliers. This huge enterprise makes 40% of the world's supply of insulin as well as industrial enzymes. Fermentation processes in this plant generate excess yeast, which is used as protein supplement for swine. The plant produces large quantities of biological sludge, which, along with wastewater treatment sludge from the waste and wastewater treatment plant associated with the fish farm, is used as fertilizer and soil conditioner in area farms.

The Kalundborg industrial ecosystem is often cited for the spontaneous way in which it developed, beginning in the 1960s with steam and electricity provided to the petroleum refinery from the power plant then branching out to a large variety of other enterprises in the vicinity. Some of the enterprises were driven by required measures to lower pollution. As a result of the requirement for lime scrubbing of the stack gas from the power plant, large quantities of calcium sulfate were produced, which were used to manufacture gypsum wallboard for buildings. Air pollution control measures resulted in the substitution of clean burning hydrocarbons from the petroleum refinery in place of some of the coal to generate electricity in the power plant. The requirement to remove sulfur from petroleum led to the construction of a sulfuric acid plant.

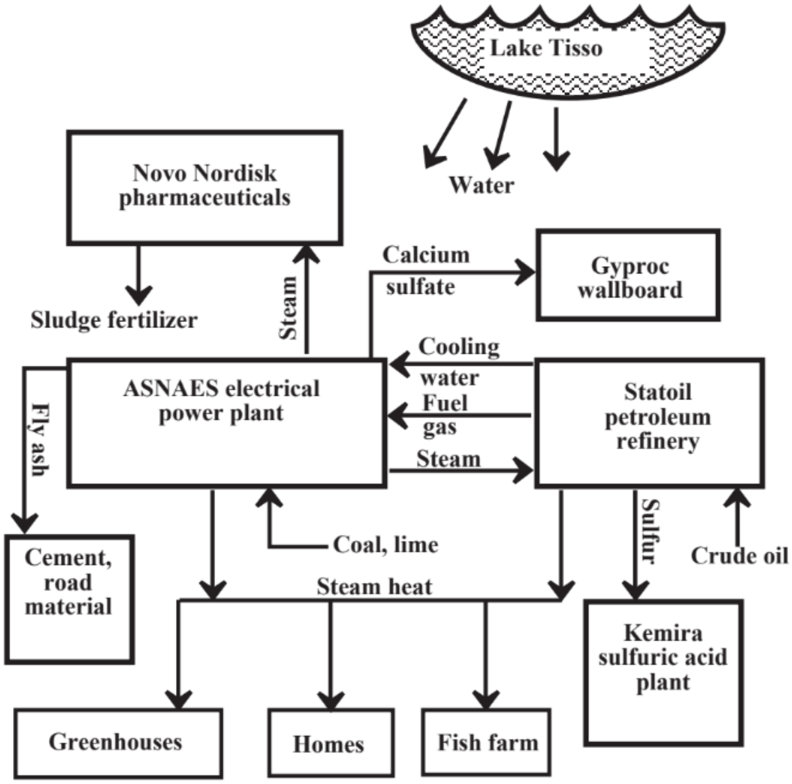

Figure 13.3. The industrial ecosystem in Kalundborg, Denmark, is commonly cited as an example of a functioning system of industrial ecology. The figure shows the numerous mutually advantageous operations in this system. It developed spontaneously beginning with exchanges of materials and energy between the electrical power plant and the petroleum refinery.

It is interesting to consider the conditions that lead to such a well developed industrial ecosystem at Kalundborg. First of all, the Kalundborg industrial ecosystem did not develop from directives from any centralized authority mandating cooperation. Instead it arose from agreements between various entities acting in their own corporate self-interests. A rather close social system that promoted contact between individuals was helpful. The relatively small geographic area involved has been helpful in enabling facile communication and the transfer of materials and energy among the various enterprises. This is especially so in that several of the main commodities involved — steam, water, waste treatment sludge — cannot be shipped economically for any great distances.

13.7: Environmental Impacts of Industrial Ecosystems

The practice of industrial ecology in the anthrosphere certainly has profound potential effects upon the atmosphere, hydrosphere, geosphere, and biosphere. Anthrospheric influences may range from highly localized effects to global effects, such as greenhouse warming or stratospheric ozone depletion. The magnitude of the effects may be minor, or they may be catastrophic. Until relatively recently, the effects of human activities on the surrounding environment were of relatively little concern, resulting in neglect that is the cause of many of the environmental problems that exist even today. However, the proper practice of industrial ecology requires that consideration be given to the various influences that anthrospheric activities have upon the surrounding environment.

Consider the kinds of effects that industrial activities may have upon the natural environmental spheres. One of the most obvious influences is upon the atmosphere because of the emission to the atmosphere of pollutant gases, vapors from volatile compounds, and particles. Released carbon dioxide and vapors such as those of fluorinated hydrocarbons have a high potential to cause greenhouse warming. Particles obscure visibility and cause adverse health effects in people who must breathe the air in which they are contained. Chlorofluorocarbons lead to stratospheric ozone depletion and hydrocarbons and nitrogen oxides released to the atmosphere can cause formation of photochemical smog. Industrial activities often utilize large quantities of water for cooling and other purposes. Water may become polluted or warmed excessively when used for cooling (thermal pollution).

Many industries require large quantities of materials that are taken from the Earth by the extractive industries. This may result in disruption of the geosphere from mining, dredging, and pumping of petroleum. The other major effect upon the geosphere results from the need to dispose of wastes. Scarce land may be required for waste disposal dumps and the geosphere may become contaminated with pollutants from disposal of wastes.

The biosphere is most affected by industrial activity when toxic substances are released. Other effects upon the biosphere may be indirect as the result of adverse effects upon the atmosphere, hydrosphere, or geosphere.

Industrial systems are largely dependent upon the utilization of fossil fuels, so many environmental effects are due to fossil fuel extraction and combustion. Greenhouse-warming carbon dioxide emissions, acid gas emissions, smog-forming hydrocarbons and nitrogen oxides, and deterioration of atmospheric quality from particles released from fossil fuel combustion are all atmospheric effects associated with fossil fuel combustion. Coal mining activities have the potential to release acid mine water to the hydrosphere, petroleum production can release brines or result in ocean oil spills, acid precipitation may acidify isolated lakes, and water used as cooling water in power plants may become thermally polluted. The geosphere may be disrupted by fossil fuel extraction, especially in the surface mining of coal. Coal is extracted from some areas of West Virginia by cutting off entire mountain tops overlying coal seams and dumping the overburden into valleys below in order to get to the coal. Effects upon the biosphere from fossil fuel utilization may be direct (birds coated with tar from oil spills come to mind), but are more commonly indirect, such as acidified bodies of water from acid rain resulting from sulfur dioxide emissions from coal combustion.

Agricultural activities certainly have to be considered as parts of the anthrosphere, and modern agricultural practices are part of vast agriculturally based industrial systems. Large quantities of greenhouse-warming methane are released to the atmosphere from the action of anoxic bacteria in rice paddies and in the intestines of ruminant animals. “Slash and burn” agricultural techniques practiced in some tropical countries release greenhouse gas carbon dioxide to the atmosphere and destroy the capacity of forests to sequester atmospheric carbon dioxide by photosynthesis. Enormous quantities of water are run through irrigation systems. Some of this water is evaporated and lost from the hydrosphere. The water that returns to the hydrosphere from irrigated fields picks up significant amounts of salt from the land and fertilizers applied to the land, so water salinity can become a problem. Underground aquifers become severely depleted by pumping large quantities of water for irrigation. The production of protein from livestock requires much more water overall than does the production of an equivalent amount of protein from grain. Animal wastes from huge livestock feedlots are notorious water polluters, adding oxygen-depleting biochemical oxygen demand (BOD, see Chapter 9, Section 9.3) and potentially toxic inorganic nitrogen compounds to water. The disturbance of the geosphere from crop cultivation is enormous. Raising livestock for food entails a much greater degree of land cultivation than does the cultivation of cereal grains. Agricultural production replaces entire, diverse biological ecosystems with artificial ecosystems, which causes a severe disturbance in the natural state of the biosphere. Another agricultural activity that affects the biosphere is the loss of species diversity in the raising of crops and livestock. In addition to the loss of entire species of organisms, the number of strains of organisms grown within species tends to become severely diminished in modern agricultural practice. Obviously, those varieties of crops and livestock that are mostproductive are the ones that will be used to produce grain, meat, and dairy products. However, if something happens, such as a particular variety becoming susceptible to a newly mutated virus, alternative resistant varieties may no longer be available. Finally, the raising of transgenic crops and livestock (see Section 12.12, “Agricultural Applications of Genetically Modified Organisms”)promises profound and potentially unforeseen effects upon the biosphere.

Design of Industrial Ecosystems to Minimize Environmental Impact

From the discussion above it is obvious that industrial activity, broadly defined to include agriculture as well, has a high potential to adversely affect the atmosphere, hydrosphere, biosphere and geosphere. Inherent to the nature of industrial ecosystems, however, are measures and systems designed to minimize such impacts.

Several measures may be taken to minimize the effects of industrial ecosystems upon the geosphere. Since most of the raw materials required for manufacturing originally have to be extracted from the geosphere, the recycling of materials inherent to well designed industrial ecosystems minimizes impact upon the geosphere. The selection of materials can also be important. As an example, the mining of copper to make copper wire once widely used to carry communications signals involves digging large holes in the ground and exposing minerals that tend to release metals and acidic pollutants. The silica used in the fiber optic cables that now largely substitute for copper is simply obtained from sand. The impacts of disturbing the geosphere for food and fiber production can be minimized by some of the conservation methods and agricultural practices discussed in Chapter 11.

Well designed industrial ecosystems emit much less harmful material to the atmosphere than do conventional industrial systems. Industrial atmospheric emissions have been decreasing markedly in recent years as the result of improved technology, more stringent regulation, and requirements to release information about atmospheric emissions. One of the main classes of industrial atmospheric pollutants has consisted of the vapors of volatile organic compounds (VOCs). These have been significantly reduced by modifying the conditions under which they are used to lower emissions and by measures such as activated carbon filters to trap the vapors. The practice of industrial ecology goes beyond these kinds of measures and attempts to find substitutes, such as water-based formulations, so that volatile organic compounds need not even be used.

Years of regulation have resulted in much lowered releases of water pollutants from industrial operations. These lowered levels have been due largely to sophisticated water treatment operations that are applied to water before it is released from a plant. Desirable as these “end-of-pipe” measures are, the practice of industrial ecology goes beyond such pollution control, minimizing the use of water and preventing its pollution in the first place. One way to ensure that water pollutants are not released from an industrial operation is to completely recycle water in the system—no water out, no water pollutants.

In past years, many hazardous solid and liquid wastes have been improperly disposed to sites in the geosphere, giving rise to a large number of “hazardous waste sites,” the subject of Superfund activity in the United States. The practice of industrial ecology seeks to totally eliminate any such wastes that would require disposal. Ideally, such wastes simply represent material resources that are not properly utilized, a fact that can serve as a guideline for the prevention of such wastes.

The expenditure of energy entails the potential to cause environmental harm to the various spheres of the environment. A prime goal in the proper practice of industrial ecology is the most efficient use of the least polluting sources of energy possible. More efficient electric motors in industrial operations can significantly reduce electricity consumption. The proper design of buildings to reduce heating and cooling costs can also reduce energy consumption. Many industrial operations require heat (process heat in industrial parlance) and steam. Rather than generating these separately, they can be produced in combined power cycles along with the generation of electricity, thereby greatly increasing the overall efficiency of energy utilization.

13.8: Green Chemistry and Industrial Ecology

Green chemistry has an essential role to play in the development of successful industrial ecosystems, especially in making industrial metabolism as efficient, nonpolluting, and safe as possible. A major advantage of the practice of green chemistry to reduce environmental impact is that, ideally, it is inherently safe and clean. By using nontoxic chemicals and processes that do not threaten the environment, green chemistry avoids posing threats to the people who practice it and to the surrounding environment. Of course, these are ideals that can never be completely realized in practice, but by having these ideals as goals and making constant incremental improvements, the practice of green chemistry can become increasingly safe, environmentally friendly, and sustainable. This reduces dependence upon the command and control measures that require constant vigilance to maintain. Rather than depending upon regulations imposed from the outside to maintain its safe operation, green chemistry is much more self-regulating.

As discussed in Chapter 2 and illustrated in Figure 2.3, **Green chemistry** can be defined as the practice of chemical science and manufacturing in a manner that is sustainable, safe, and non-polluting and that consumes minimum amounts of materials and energy while producing little or no waste material. In Section 2.10, twelve principles of green chemistry were presented. Following the discussion of industrial ecology and sustainability at the beginning of this chapter, green chemistry is now covered in greater detail here. Most of the modern aspects of green chemistry are discussed in a review article on the subject.[1] The major aspects of green chemistry discussed here include the following:

1. Efficient use of matter with minimum production of wastes
2. Catalysis
3. Utilization of biological processes
4. Maximization of renewable raw materials
5. Green product design
6. Minimization or elimination of solvents, use of water where possible
7. Process intensification

Green chemistry gives prime consideration to the chemical reactions and processes by which chemicals are manufactured. One approach to making chemical synthesis greener is to use existing chemical synthesis processes but make the process itself safer and less polluting while also making the reagents required for it by greener processes. An example of the former might be to substitute a less volatile, less toxic solvent as a reaction medium for a chemical synthesis reaction. In some cases, a reagent may be made more safely by using biological processes for its preparation in place of chemical processes. A second general approach to making chemical preparations greener is to use different reagents for the synthesis that are safer and less likely to pollute.

The practice of green chemistry is largely applied to the synthesis of organic chemicals. The history of organic synthesis abounds with examples of processes that are emphatically not “green.” One example that is sometimes cited is the synthesis beginning with explosive trinitrotoluene(TNT!) of phloroglucinol, a chemical used in relatively small quantities in the fine chemicals industry. The synthesis began with oxidation by dichromate (a carcinogenic substance) in fuming sulfuric acid (a highly corrosive material that causes horrid lesions to skin) followed by reduction with iron in hydrochloric acid and heating to isolate the product. Although the quantity of product made was only about 100 tons per year, the process generated about 4,000 tons per year of solid waste containing $Cr_2(SO_4)_3$, NH_4Cl, $FeCl_2$, and $KHSO_4$. Clearly, this was not an environmentally friendly process and a major objective of green chemistry has been to find substitute pathways for synthesis such as this one.

Several key parameters are calculated in quantifying green chemistry. As discussed in Section 2.6, one of these is **atom economy** defined as the fraction of reactant material that actually ends up in final product. The higher the atom economy — ideally 100% — the greener the process. Oxidation, in organic synthesis the introduction of oxygen onto organic molecules, that uses various **oxidants** is an important process in synthesis. Oxidants are rated according to **oxygen availability**, the percentage of the mass of the oxidant molecule that is available oxygen, here represented as {O}. Theoretically, the molecule with the greatest oxygen availability is molecular O_2 rated at 100% (in practice one of the two O atoms usually ends up as water, H_2O). Hydrogen peroxide, H_2O_2, adds oxygen to an organic molecule, represented as “R”, according to the reaction,

$$\mathrm{H_2O_2 + R \rightarrow R(O) + H_2O} \tag{13.8.1}$$

Since the O atom is 47% of the mass of H_2O, the oxygen availability of hydrogen peroxide is 47%. When ozone acts as an oxidant by donating one of its three O atoms,

$$O_3 + R \rightarrow R(O) + O_2 \tag{13.8.2}$$

its oxygen availability is 33.3%, the percentage of the O_3 molecule that is one O atom.

For reduction, usually the addition of H atoms to a molecule, the concept of **hydrogen availability** may be used. When lithium hydride, molecular mass 7.94, is used as a reducing agent as in the synthesis of silane,

$$SiCl_4 + LiH \rightarrow SiH_4 + 4\,LiCl \tag{13.8.3}$$

all of its hydrogen is used and its hydrogen availability is 12.6% which (because of the low atomic mass of Li, hence the low formula mass of LiH) is the highest hydrogen availability of all the metal hydrides.

The Presidential Green Chemistry Challenge Awards

The U.S. Presidential Green Chemistry Challenge Awards, administered by the Environmental Protection Agency with partial sponsorship by the American Chemical Society, are made annually to recognize efforts to reduce hazards and wastes from chemical processes and to help meet pollution prevention goals. The 77 winners of these awards since 1995 are estimated to have eliminated 97 million kg of hazardous chemicals from use, prevented the release of 26 million kg of greenhouse-warming carbon dioxide to the atmosphere, and saved 80 million liters of water. The 2010 awards included the following

- The development of genetically engineered microorganisms that can convert CO_2 to higher alcohols with more than 2 C atoms that have a lower percentage of oxygen and are more hydrocarbon-like than ethanol, therefore more useful as fuels and chemical feedstocks.

- The design of a biomaterials refinery as a substitute for a petroleum refinery that uses transgenic microorganisms to convert sugars to hydrocarbon alkanes and alkenes , long-chain fatty acids, and fatty esters

- The development of a process to use hydrogen peroxide to oxidize propylene to propylene oxide, one of the most widely used organic chemical feedstocks, using an approach that reduces capital costs, energy use, and wastewater generation.

- Alterations in the synthesis of sitagliptin, the active ingredient in Merck's Januviatype 2 diabetes drug. Sitagliptin is a chiral β-amino acid and the improved approach to its synthesis uses a genetically engineered transaminase enzyme to convert a precursor ketone to the desired product with increased yield, fewer production steps,and less overall waste.

- Development of a slow-release tablet form of insecticidal spinosad that makes it useful for mosquito control in aquatic environments where biodegradation of spinosad had been a problem with earlier forms of the insecticide

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13.9: Predicting and Reducing Hazards

The reduction of hazards from chemical processes was discussed Chapter 2, Section 2.7, “Reduction of Risk: Hazard and Exposure.”The conventional approach to making chemical processes less dangerous to workers and less harmful to the environment has emphasized *exposure reduction*. In the arena of worker safety, this has involved measures such as wearing protective gear to prevent contact with hazardous chemicals. For the environment as a whole it has consisted largely of “end-of-pipe” measures to prevent release of pollutants once they are generated.

In contrast to exposure reduction, green chemistry relies upon **hazard reduction**. The first step in hazard reduction is to know what the hazards are and where they originate. Hazards may arise from the raw materials used, the media (solvents) in which chemical processes are carried out, catalysts that enable chemical reactions to occur, and byproducts. The direct hazards posed to workers in a chemical process fall into the two main categories of toxicity hazards and hazards associated with uncontrolled events such as fires and explosions.

Toxic substances are most logically classified according to their biochemical properties that lead to toxic responses. A useful means of relating toxic effects to the chemical nature of toxic substances is through **structure activity relationships**, which use computer programs to find correlations between features of chemical structure, such as groupings of functional groups, and the toxicity of the compounds. As an example, organic compounds containing the N-N=O functional group are N-nitroso compounds, a family noted for members that cause cancer. Structural features that indicate a tendency to donate methyl (-CH3) groups are also suspect because attachment of methyl groups to cellular DNA is a major mechanism in causing cancer. This hazard may be reduced by substituting alkyl groups with more carbons for the methyl group.

Three kinds of chemicals have a high priority in eliminating the toxicity hazards in green chemistry. The first such category consists of **heavy metals**, such as lead, mercury, and arsenic (a metalloid). These indestructible elements have a variety of toxic effects, such as impaired function of renal tubules in kidneys (cadmium), neurological damage (mercury), and inhibition of the production of ATP (see Chapter 7, Section 7.8, “Biochemical Processes in Metabolism”) A second major category of toxic substance that should be avoided in the practice of green chemistry consists of **lipid-soluble organics** that are not readily degraded. These compounds often consist of relatively high molecular mass organohalides, such as PCBs, and accumulate in lipid (fat) tissue. Released into the environment, these materials can undergo **biomagnification** as they move through a food chain. **Volatile organic compounds** (**VOCs**) constitute a third class of troublesome toxic substances. These are primarily hydrocarbons, such as heptane, and low-molecular-mass organohalides, such as trichloroethylene.

Figure6.5) known to have caused liver cancer in workers exposed to the vapor in polyvinylchloride polymer manufacture.

Chemicals that pose hazards because of their potential to undergo destructive chemical reactions fall into several often overlapping categories. **Combustible** or **flammable** substances are those that are liable to burn vigorously and destructively in air or other sources of oxygen. Hydrocarbon solvents may closely resemble gasoline in their characteristics and are highly flammable. Adding to the hazards of such materials is their volatility, which enables them to form explosive mixtures of vapor in air. Destructive petroleum refinery fires fed by hydrocarbons can occur.

Whereas combustible substances are chemical *reducers*, another category of hazardous chemical substances consists of chemical **oxidizers** that provide sources of oxygen for the reaction of reducers (see Section 13.8). One such compound is ammonium perchlorate, NH_4ClO_4, a potent oxidizer used in rocket fuel. Many chemical synthesis procedures involve oxidation steps and a variety of chemical oxidizers are used for these steps. A fourth category of hazardous chemical substances are those that are **reactive**. Explosives are prime examples of reactive substances. One of the more treacherous explosives is nitroglycerin which undergoes the following reaction when it explodes.

$$4\,C_3H_5N_3O_9 \rightarrow 12\,CO_2 + 10\,H_2O + 6\,N_2 + O_2 \tag{13.9.1}$$

This reaction shows that the nitroglycerin molecule actually contains an excess of oxygen because elemental oxygen is released when the nitroglycerin explodes. Some structural features of molecules are known to be associated with reactivity. One example is the close presence of oxygen and nitrogen on the same molecule, particularly where multiple nitrogen atoms are bonded together. A final category of hazardous chemical substances consists of those that are **corrosive**. In general, a corrosive substance is one that attacks materials, including even human flesh. A more specific definition is that a corrosive substance is one that produces high concentrations of either H^+ ion (strong acid) or OH^- ion (strong base).

Often hazardous chemicals belong to two or even more of the categories outlined above. An example of such a substance is concentrated nitric acid, HNO_3. In addition to its being a strong acid, this material acts as a source of oxygen, represented as $\{O\}$ in the reaction below:

$$2\,HNO_3 \rightarrow 3\,\{O\} + H_2O + 2\,NO \tag{13.9.2}$$

Hazardous concentrated nitric acid is used in some chemical synthesis reactions in which an acidic oxidant is needed. Among the many other potentially hazardous strong oxidants used are permanganate (MnO_4^-) and oxygen-containing compounds such as potassium dichromate, $K_2Cr_2O_7$.

The ideal way to deal with hazardous substances in the practice of green chemistry is to totally avoid making or using them. A laudable goal in principle, it is often impossible to completely avoid hazardous materials in practice. In cases where dealing with hazardous substances is necessary, every effort must be made to prevent their release, exposure to humans, or circumstances in which their hazards may be manifested.

13.10: The E-Factor in Green Chemistry

Although atom economy, defined in Section 13.8, is a useful concept, one that is a more accurate measurement of environmental acceptability of a chemical manufacturing process is the **E factor** defined as the following:

$$\text{E factor} = \frac{\text{Total mass of waste from process}}{\text{Total mass of product}} \tag{13.10.1}$$

The E factor takes into account waste byproducts, leftover reactants, solvent losses, spent catalysts and catalyst supports, and anything else that can be regarded as a waste. Its calculation depends upon what is defined as waste. For example, water is a significant byproduct of many chemical processes and is generally harmless, so its mass is usually omitted from the total mass of waste in the calculation. However, it may be included in those processes in which it is severely contaminated and difficult to reclaim in a form pure enough to use or discharge to a publicly owned wastewater treatment facility. Leftover reactant that can be easily reclaimed and recycled to the process is not included as waste whereas reactant that cannot be salvaged is counted in the waste.

The ideal E factor is 0 and higher E factors are relatively less desirable. E factors that can be tolerated depend upon the value of the product and the amount of product produced. For bulk chemicals manufactured in amounts of hundreds of thousands to millions of tons per year, tolerable E factors typically range from 1 to 5. In the fine chemical and specialty chemical industry where annual quantities are typically measured as a few thousand tons per year E factors up to around 500 may be acceptable if the value of the product is high enough to justify the cost of treating and disposal of wastes. In the pharmaceutical manufacturing industry where annual quantities generated typically are measured in tens to several hundred tons per year, acceptable E factors may be up to about 4000.

Until recently, little attention had been given to amounts of wastes produced in pharmaceutical manufacturing because the prices of the products were so high and the total amounts of wastes produced were so low. However, with the realization that even the generation of a few hundred tons per year of waste can be undesirable and costly, the pharmaceutical industry is becoming a leader in the implementation of green chemical practice. It should be noted that,although they are not considered in the calculation of E factors for pharmaceutical manufacture, annual releases of post-consumer pharmaceuticals and their metabolites are not insignificant. Of greatest concern is contamination of wastewater, some of which gets back into drinking water supplies, by pharmaceuticals and their metabolites discharged with urine or simply flushed down the drain when no longer needed. By their nature, pharmaceuticals are metabolically active and their presence in drinking water can be a concern.

The Nature of Wastes

There are wastes, and then there are wastes. Production of a few thousand tons of carbon dioxide per year may be of little concern because it can be discharged to the atmosphere, contributing to the atmosphere's burden of greenhouse gases, but negligible compared to the millions of tons released by burning fossil fuels. However, generation of a few kilograms of heavy metal wastes can be a matter of concern because of heavy metal toxicity. So it matters *what kinds* of wastes are produced. Attempts have been made to assign an **environmental quotient**, **EQ**, to wastes where Q is a number assigned to a particular kind of waste which, multiplied times the E-factor provides in principle a means of weighting the potential harm of various kinds of wastes. Whereas E is easily measured by simple weighing, Q is a much more arbitrary number and subject to change as information is obtained regarding the potential harm of particular kinds of wastes.

13.11: Catalysts and Catalysis

The main components of a chemical process can be divided into the categories of catalysts, media, feedstocks, and reagents, all of which are important in the practice of green chemistry. Catalysts and catalysis are addressed in this section and the other aspects of chemical production are addressed in Sections 13.13 and 13.14.

An ideal green chemical reaction occurs with 100% atom efficiency using only reactants and no other reagents under mild conditions with only moderate input of thermal energy and without any catalysts. Unfortunately, few chemical processes meet these criteria.

In the past, especially in the synthesis of fine chemicals and pharmaceuticals where the objective has been to simply make the desired product without much consideration of waste, so-called stoichiometric reagents have been used. These have included inorganic oxidants such as MnO_2, $KMnO_4$, $K_2Cr_2O_7$; metal reductants including zinc, magnesium, sodium, and iron; and metal hydride reducing agents, especially $LiAlH_4$ and $NaBH_4$. Various organic reactions including sulfonations and nitrations employ Lewis acids (BF_3, $AlCl_3$, $ZnCl_2$) and mineral acids (HF, H_2SO_4, and H_3PO4). Many of these processes are indirect methods of adding to organic molecules hydrogen (reduction), oxygen (oxidation), carbon, and nitrogen. A problem with these reagents is the large amount of inorganic wastes produced. Where possible, it is much more desirable to employ catalysts to attach the simplest possible forms of the elements including H2 for reduction, O_2 or H_2O_2 for oxidation, CO or CO_2 for attachment of carbon, and NH_3 for attachment of N.

Instead of relying only on stoichiometric reagents, catalysts are commonly employed. As discussed in Chapter 5, Section 5.5, *catalysts*, are substances that enable reactions to proceed at significant rates without themselves being consumed. Catalysts are of great importance in the practice of green chemistry for a number of reasons including their ability to facilitate reactions and to reduce the energy required to enable reactions to proceed. There are two major approaches to contacting catalyst with a reaction mixture as shown in Figure 13.4. In **heterogeneous catalysis** the catalyst is held on a support and the reactants flow over it. In **homogeneous catalysis** the catalyst is placed in the reaction mixture and either remains in the product or is separated from the product in a separate step. In general, homogeneous catalysts have high activity and selectivity whereas heterogeneous catalysts are more easily recovered and recycled. Much of the activity in green chemistry has been in the area of catalysis, especially in the development of heterogeneous catalysts that do not contaminate the product and that can be reused multiple times. Large numbers of different catalysts are used in

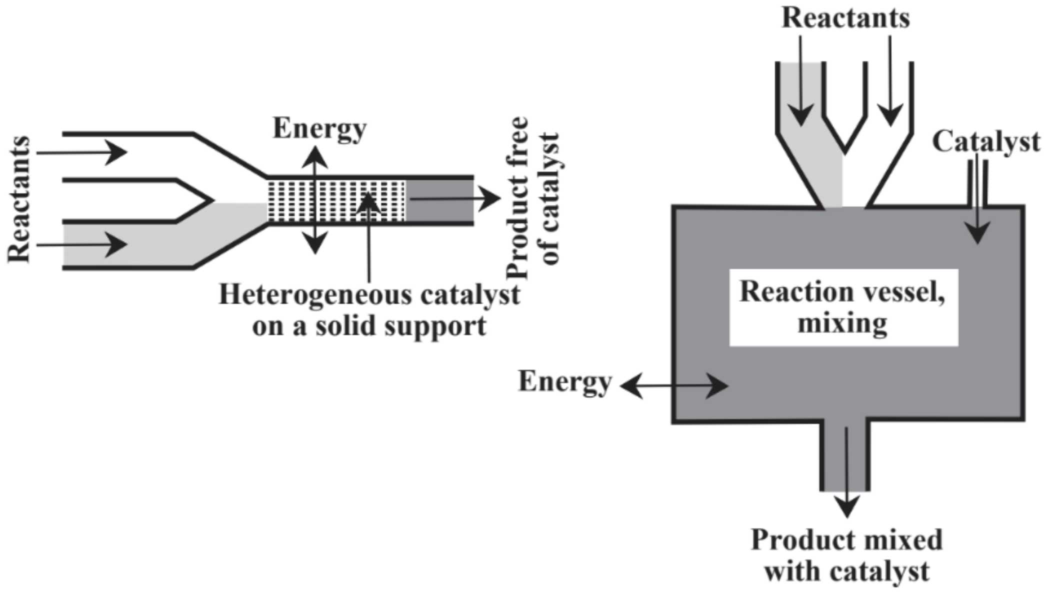


Figure 13.4. A heterogeneous catalysis (left) is held on a solid support and the reaction mixture flows over it. Inhomogeneous catalysis (right) the catalyst is mixed with the reactants and either remains in the product or is removed in a separation step. Some reactions require addition of heat energy whereas some exothermic reactions require cooling. In the practice of green chemistry energy is sometimes added as electrical current, ultraviolet radiation, microwave radiation, or ultrasound.

chemical processes and their potential toxicities, production of byproducts and contaminants, recycling, and disposal are matters of considerable importance in the chemical industry.

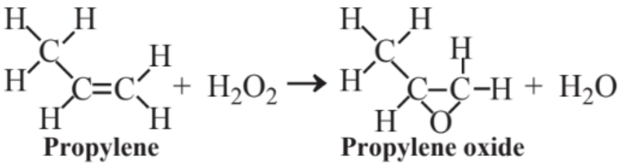
An important area of endeavor in the development of improved catalysts with respect to green chemistry is **selectivity enhancement**. Basically, this means developing a catalyst that is very selective in what it does, ideally making the right product and nothing else. A highly selective catalyst increases the percentage utilization of raw material (increased percent yield) and decreases the amount of waste byproducts from undesired side reactions.

Another important attribute of a good catalyst is related to the basic way in which a catalyst works, which is by lowering the activation energy that is required to make a reaction proceed at a significant rate. As a consequence, catalysts lower the total amount of energy that must be put into a chemical process to get it to occur. Lowered energy requirements are a basic part of the practice of green chemistry and in this respect highly efficient catalysts can be extremely beneficial in reducing energy consumption and in so doing lowering costs and environmental impact.

Numerous green industrial chemical reactions have been developed in recent years, most employing some sort of catalyst. An example is the synthesis of the widely used industrial chemical propylene oxide starting with elemental H_2 and O_2. Around 1985 it was discovered that propylene could be oxidized to propylene oxide with 30% hydrogen peroxide using a titanium silicate catalyst, but the process was not economic because of the high cost of hydrogen peroxide. A Green Chemistry Presidential Challenge prize was awarded in 2007 for an economical process to make hydrogen peroxide by combining H_2 and O_2 in a gas mixture at levels of H_2 directly below the lower flammability limit of H_2 using a catalyst composed of palladium-platinum nanoparticles:

$$\mathrm{H_2 + O_2 \rightarrow 2\,H_2O_2} \tag{13.11.1}$$

As a second step in the process the hydrogen peroxide is reacted with propylene to produce propylene oxide with water as the only byproduct:



(13.11.2)

Figure 13.5).

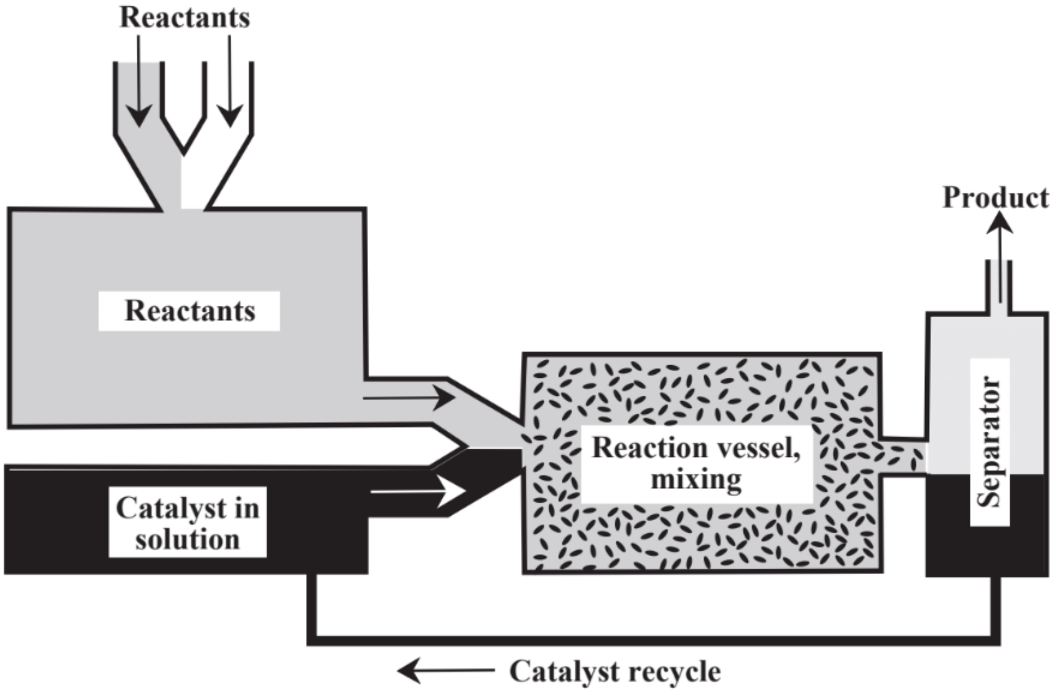


Figure 13.5. Illustration of a biphasic catalyst system. Reactants in one solution contact catalyst in another immiscible solution. After the reaction has had a chance to go to completion, the two immiscible phases are separated and the catalyst solution recycled. In the reaction vessel this kind of system provides the superior qualities of a homogeneous catalyst but with the product/catalyst separability of a heterogeneous catalyst.

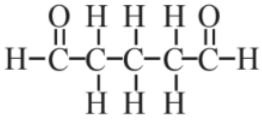
13.12: Biocatalysis with Enzymes

Nature has provided some ideal catalysts in the form of enzymes, the use of which offers some substantial advantages in green chemistry. The most obvious advantage is that enzymes have evolved to work under the mild conditions in which organisms function, especially moderate temperatures and physiological pH. Unlike precious metal catalysts that are commonly used, enzymes are made renewably from biomaterials. Enzymes have generally high activities and are highly selective in the chemical processes that they carry out. Whereas conventional organic syntheses often require activation or protection of functional groups, both of which may consume reagents and hence produce more wastes, these measures are often not needed with enzymes. The result is that biocatalyzed reactions can frequently be carried out with relatively fewer steps and less wastes making them more attractive environmentally and economically.

Although some biocatalyzed reactions have been used for production of chemicals for centuries — the production of ethanol by yeast fermentation of sugar comes immediately to mind— relatively recent advances in biotechnology have greatly increased their versatility and utility. One such advance has been with recombinant DNA in which enzymes that perform specific functions may be transferred between organisms. The other major advance has been with **directed evolution** in which the amino acid sequences in enzymes produced by genes are shuffled randomly and large numbers of the products are sampled for their activity, particularly for carrying out a particular biochemical synthetic step. This may be done within living cells, but can be carried out on a much larger scale outside of cells, a process called ***in vitro* evolution**. Obviously, most of the enzymes produced by this technique are not superior, or are even useless, but out of the enormous numbers generated, some will be superior. *In vitro* evolution is being carried out to provide enzymes with properties such as improved or different catalytic activity, catalytic specificity, thermostability, and pH optima that can be used in industrial, medical, or agricultural applications. It is proving particularly useful in developing enzymes that act upon compounds that do not occur in nature and for which enzymes have not evolved through natural evolution.

Immobilized Enzyme Catalysts

Disadvantages of catalytic enzymes include often low stability, limited storage times, difficult recovery, and product contamination, almost always a consideration with homogeneous catalysts. The stability and recyclability of enzymes may often be enhanced by immobilizing them on solid supports. A common means of immobilizing enzymes is by their precipitation from the fermentation broth in which they are generated by a buffer such as ammonium sulfate and stabilizing the precipitated aggregates with a reagent possessing two bonding functional groups, commonly glutaraldehyde a reagent that is widely used for cross-linking proteins:



$$\mathrm{H{-}C({=}O){-}CH_2{-}CH_2{-}CH_2{-}C({=}O){-}H}$$

Glutaraldehyde

The precipitation and cross-linking of the enzyme combines its isolation and immobilization into a single step. Enzymes prepared in this way are usually highly productive, stable and resistant to denaturation (loss of enzyme function by structural alteration) due to exposure to organic solvents, heating, or breakdown to shorter peptide chains or amino acids by the action of proteolytic enzymes (proteolysis).

Reduction in Synthesis Steps with Enzyme Catalysts

Typical synthesis of an organic compound, especially one as complicated as many pharmaceutical agents, may involve multiple steps. Because of factors such as product loss, the need to protect and deprotect functional groups, and generation of wastes from each step, these multistep syntheses tend to build high E factors overall. The ideal synthesis is a “one-pot” process in which all steps are carried out in the same operation without the need to isolate intermediates. Living cells are often “one-pot” synthetic factories, so it is natural to look to enzymes to accomplish the same thing in the laboratory and in chemical production using multiple enzymes ina single container and for a single multiple-step operation. Accomplishment of such a process can be complicated by incompatibility of different enzymes and the different conditions under which enzymes operate although in general they operate in water under ambient conditions compatible with life. (The relatively recent discovery of organisms that live under hot, extreme conditions on the deep ocean floor raises some interesting possibilities for the isolation of enzymes that might function under unusual conditions, particularly elevated temperatures.)

Enzyme Catalysts and Chirality

As shown by the example of the herbicide mecoprop in Figure 13.6, **chiral molecules** are three-dimensional molecules with structures such that a molecule cannot be directly imposed on its mirror image. Chiral molecules have different groups arranged around an atom, usually of carbon, that constitutes a chiral center. Two chiral molecules of the same compound are called **enantiomers** commonly designated as R and S. The physical and chemical properties of enantiomers are generally identical, having the same melting points, boiling points and solubilities. However, one enantiomer of a compound may fit exactly with an enzyme active site whereas the other does not. This results in often markedly different biochemical properties of enantiomers and consequently completely different environmental and toxicological behaviors. One enantiomer of a chiral pharmaceutical may function very well whereas the other does not work at all or may even be toxic. Biochemical differences between enantiomers may be especially pronounced for pesticides. For example, the R enantiomer of herbicidal mecoprop (Figure 13.6) kills weeds very effectively whereas the S enantiomer is inactive; therefore, the pure R enantiomer is now marketed as a herbicide in place of the racemic mixture with the S enantiomer.

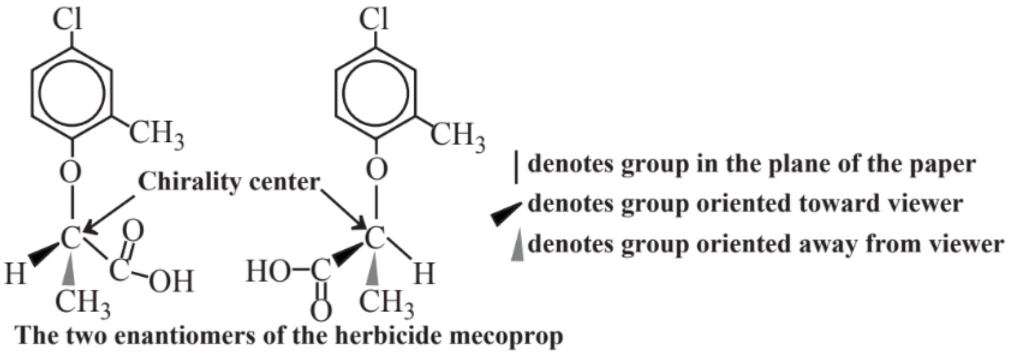


Figure 13.6. Illustration of the chiral herbicide mecoprop. Only the R enantiomer has herbicidal activity and is now marketed in the enantiometric pure form

Normally when a chiral compound is synthesized by conventional chemical means a racemic mixture of the two enantiomers is produced. Because of their essentially identical chemical properties they are very hard to separate. However, it is possible to produce enantiomerically pure chemical compounds with appropriate enzymatic catalysts. Furthermore, it is possible to use enzymatic catalysts to convert racemic mixtures of compounds to enantiomerically pure forms. In one of the larger such industrial operations, BASF now uses enzymatically catalyzed processes to prepare enantiomerically pure amines in thousand-ton quantities.

Nature’s catalysts, the enzymes in organisms, are experts in carrying out chemical processes efficiently under mild conditions. In consideration of this fact, a great deal of attention is being devoted to using organisms, especially bacteria, to carry out chemical processes. By splicing desired genes for making specific enzymes into bacteria so that they will carry out desired reactions, genetic engineering is making an increasing contribution to the development of enzyme-catalyzed green chemical processes.

Chemists are trying to use enzymes as models for synthetic catalysts that have performance characteristics of enzymes, but which are much simpler and work under conditions that would destroy enzymatic catalysts. A promising area in which this might be accomplished is the use of iron-containing catalysts to oxidize alkene (C=C) groups in organic compounds using relatively mild hydrogen peroxide reagent, H_2O_2. Organisms accomplish this task using catalysts in which the Fe^{2+} ion is bonded by four N atoms in relatively large heme porphyrin molecules. The same oxidation has now been accomplished with a catalyst in which Fe^{2+} is bound by four N atoms by an organic molecule with the formidable name of N,N'-dimethyl-N,N'bis(2-pyridylmethyl)-ethylenediamine as shown in Figure 13.7. A big advantage of this catalyst that is shared with enzyme catalysts that enable peroxide oxidations is that it does not cause the decomposition of hydrogen peroxide as do a number of synthetic catalysts.

13.13: Energizing Chemical Reactions and Process Intensification

One of the most important aspects of green chemistry is the enhancement of the speed and degree of completion of chemical reactions. One of the ways that this is done is by lowering the activation energy required to enable a reaction to proceed. That is what catalysts do as discussed in the preceding section. The other way to enhance a reaction is by adding energy as discussed in this section.

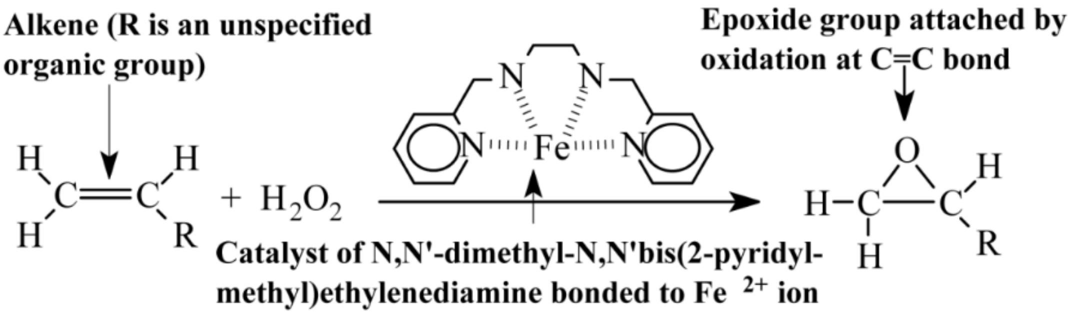


Figure 13.7. Action of an iron-containing compound modeled after iron-based enzymes as a catalyst to bring about the oxidation of an alkene hydrocarbon group with hydrogen peroxide

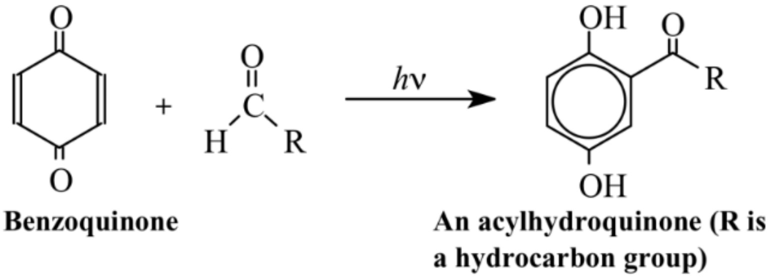
The most straightforward means to add energy to a reaction is by heating the reaction mixture. On an industrial scale this is commonly accomplished with coils of tubing immersed in the reaction mixture that are heated with steam passing through the coils. Heating by passing a current of electricity through electrically-resistant coils is also a means of adding energy to a chemical system. Much of the effort in green chemistry has been devoted to finding more sophisticated ways of energizing chemical systems.

Microwaves can be used to add energy to reactions to enhance reaction rates. Microwaves are electromagnetic radiation with wavelengths of 1 cm to 1 m (frequency 30 GHz to 300 Hz). To avoid interference with microwave bands used in communication, industrial and household microwave generators commonly operate at 2.45 GHz. Microwaves are absorbed by polar molecules, such as those of water, causing rapidly repeating re-orientation of the molecules in a microwave field. The result is a high input of energy directly into substances subjected to microwaves thereby adding energy and speeding up reactions. Microwave energy can be put directly into relatively small volumes of reaction media, reducing material requirements and minimizing wastes. Microwaves can be used to enhance reactions in (1) water media, (2) polar organic solvents such as dimethylformamide, and (3) media-free reactions, such as mixed solid reactants.

Sonochemistry adds energy by subjecting a reaction medium to ultrasound energy at frequencies between 20 and 100 KHz which introduces very high energy pulses into the medium. Commonly, the ultrasound is produced by the piezoelectric effect through which crystals of substances such as ceramic-impregnated barium titanate are subjected to rapidly reversing electrical fields converting the electrical energy to sound energy with an efficiency that can reach 95%. An advantage of sonochemistry is that it can introduce high energy into microscopic regions enabling reactions to occur without appreciably heating the reaction medium.

Electrochemistry by the passage of a direct current of electricity through a reaction medium can cause both reductions and oxidations to occur. Reduction, the addition of electrons, *e*-, occurs at the relatively negatively charged cathode, and oxidation, the loss of electrons, at the relatively positively charged anode. Electrochemical oxidation and reduction can be controlled by the electrical potentials applied, by the media in which they occur, and by the electrodes used. Because the addition of electrons to the reaction medium (reduction) and their accompanying removal (oxidation) does not add matter, electrolytic syntheses meet the goals of green chemistry. The electrolytic production of oxygen and of hydrogen, a non-polluting fuel and valuable raw material, is shown in Section 13.15 and Figure 13.10.

Photochemical reactions use the energy of photons of light or ultraviolet radiation to cause reactions to occur. The energy, E, of a photon of electromagnetic radiation of frequency,ν, is $E = h\nu$, where h is Planck's constant. Since a photon can be absorbed directly by a molecule or a functional group on a molecule, the application of electromagnetic radiation of the appropriate energy to a reaction medium can introduce a high amount of energy into a reactant species without significantly heating the medium. Photochemical energy can be used to cause synthesis reactions to occur more efficiently and with less production of waste byproducts than nonphotochemical processes. One example is the acylation of benzoquinone with an aldehyde to produce an acyl hydroquinone, an intermediate used to make some specialty polymers:



(13.13.1)

This reaction occurs with 100% atom economy. Unlike the standard Friedel-Crafts type of reaction, which utilizes the catalytic effect of Lewis acid-type acidic halides, particularly aluminum chloride, $AlCl_3$, the photochemical process does not require catalytic substances which tend to be reactive and moisture- and air-sensitive.

A reaction participant does not have to absorb a photon directly to undergo a photochemically induced reaction. In some cases photochemically reactive species are added to the reaction mixture to absorb photons, then produce reactive excited species or free radicals that carry out additional reactions. An example of this is provided with hydrogen peroxide, which absorbs photons.

$$\mathrm{H_2O_2} + h\nu \rightarrow \mathrm{HO}\cdot + \mathrm{HO}\cdot \tag{13.13.1}$$

to produce reactive hydroxyl radicals that react with a number of other species.

Process Intensification and Increased Safety with Smaller Size

Process intensification can be employed with continuous-flow reactors (Figure 13.8) used to intensify chemical processes and enable increased output of product with a smaller footprint of apparatus. This is especially the case when continuous flow is combined with heterogeneous catalysis and energy input. A big benefit to such reactors from the green chemistry viewpoint is increased safety. If something goes wrong in a large batch reactor, in the worst case an accident such as an explosion or fire with a large amount of material may occur. With a continuous-flow reactor the problem can be confined to the small volume of the reactor and the process can be shutdown immediately by stopping the inflow of the reactants.

13.14: Solvents and Alternate Reaction Media

Chemical reactions are often carried out in **media**, usually organic **solvents** or water, to provide a medium in which feedstocks and reagents can dissolve and come into close, rapid contact at the molecular level. A good solvent for chemical synthesis is one that enables facile product separation and is amenable to purification and reuse with minimum loss. Substances dissolved in a solvent are **solvated** by binding of the solvent to the molecules or ions of the dissolved substance, the **solute**. Solvation of reactants and products often plays an important role in determining the kinds and rates of reactions. Many organic feedstocks and reagents are not soluble in water or are decomposed by it, so organic solvents including hydrocarbons, chlorinated hydrocarbons, and ethers have to be used as reaction media.

Organic solvents cause several problems in chemical synthesis. Particularly because of problems associated with their containment, recovery, and reuse, organic solvents especially are major contributors to undesirably high E factors. Many of the environmental and health problems associated with making chemicals are the result of the use of organic solvents as media. Hydrocarbon solvents will burn and hydrocarbon vapors in air are explosive. Although many hydrocarbon solvents are not particularly toxic, some can cause the condition of peripheral neuropathy (damage to peripheral nerves such as those in feet and legs), and benzene is regarded as a carcinogen thought to cause leukemia. Released to the atmosphere, hydrocarbons can also participate in photochemical processes leading to the formation of photochemical smog (see Chapter 10, Section 10.11).

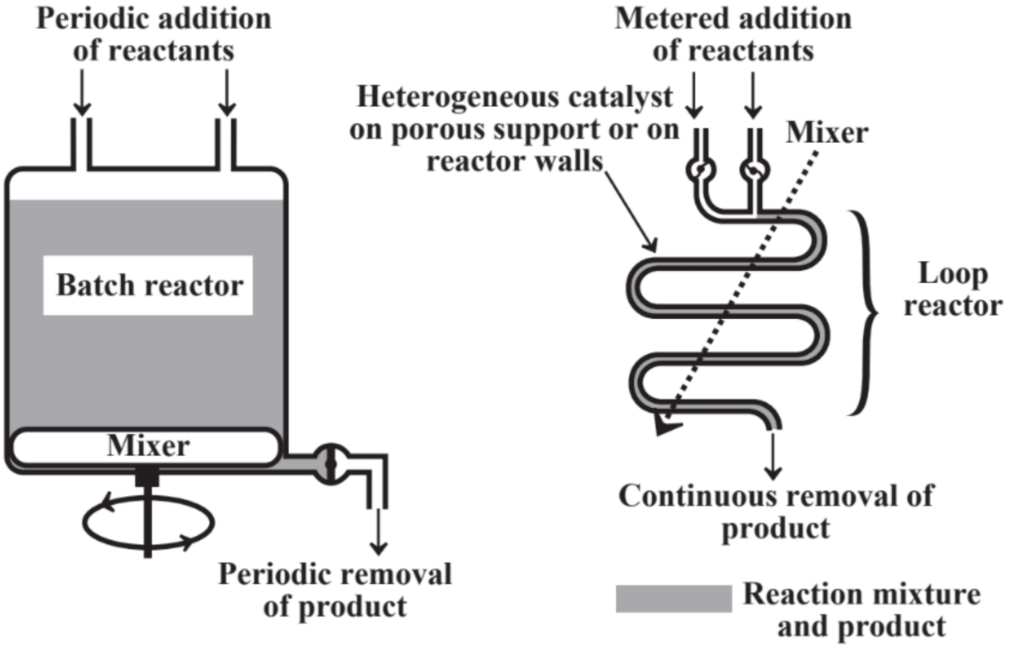
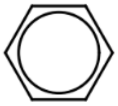
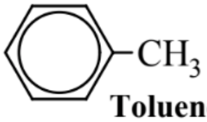


Figure 13.8. A batch reactor (left) involves mixing a large amount of reactants, often with a homogeneous catalyst, and allowing the reaction to take place for the required amount of time with the result that if anything goes wrong a large amount of material is spoiled and a considerable hazard may develop. In a continuous-flow reactor (right) only a small amount of material is reacting at any given time, heterogeneous catalysts can be used, energy input can be accurately regulated, and the process can be stopped at any time if something goes wrong.

One approach to making chemical synthesis processes greener is to replace specific solvents with less hazardous ones. For this reason, toxic benzene solvent is replaced by toluene wherever possible. As shown by their structural formulas below, toluene has a methyl group,$-CH_3$, that benzene does not possess. The methyl group in toluene can be acted upon by human metabolic systems to produce a harmless metabolite (hippuric acid) that is eliminated in the urine, whereas metabolic processes acting upon benzene convert it to a toxic intermediate that can react with cellular DNA.



Benzene



Toluene

As another example of solvent replacement, *n*-hexane, which can cause peripheral neuropathy in exposed individuals, can be replaced with 2,5-dimethylhexane, which does not cause this condition, for reactions where the higher boiling temperature of the latter compound is not a problem.

There is significant interest in reaction media other than organic solvents. The ultimate approach to eliminating problems with solvents in chemical synthesis is to do reactions without solvents of any kind. Some reactions can be performed in which the reactants are simply mixed together or are held on solid supports, such as clays. Microwave heating of such reaction mixtures has proven effective in providing energy to enable reactions to occur rapidly. However, in many cases that is not possible and solvents are required. Some alternative solvents are discussed below.

Water Solvent

Although many reagents are reactive with water making its use impossible, where applicable, the greenest solvent for green chemical processes is water. Water is abundant, cheap, not toxic, and does not burn. Because of its polar nature and the ability to form hydrogen bonds (see Chapter 9, Section 9.1 and Figure 9.1), water is an especially good solvent for ionic compounds — acids, bases, and salts. Water is particularly useful as one of the solvents in biphasic catalysis described in Section 13.11. Normally the catalyst is held in the water phase and the product in a water-immiscible organic solvent, which allows facile separation of the catalyst after the reaction is complete.

Because of water's many advantages, significant efforts have been made in replacing organic solvents used for reaction media with water. Although water does not appreciably dissolve many nonpolar organic compounds, in some cases these materials may be suspended as very small colloidal particles in water, enabling close enough contact of organic materials to undergo reactions. Water is a good solvent for some of the biological materials, such as glucose, now favored as chemical feedstocks where they can be used.

Carbon Dioxide Solvent

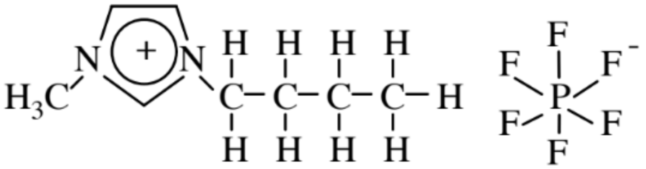
At a high pressure above 73.8 atm (73.8 times normal atmospheric pressure at sea level) and a temperature exceeding 31.1°C, carbon dioxide becomes a **supercritical fluid**, a relatively dense state of matter in which there is no longer a distinction between liquid and gas. A good solvent for organic compounds, supercritical carbon dioxide can be used as a reaction medium for organic chemical reactions. An advantage of supercritical carbon dioxide in this application is that its viscosity is only about 1/30 that of common liquid organic solvents, which enables reactant species to move much faster through the fluid, thus speeding the reactions that they undergo. At temperatures and pressures somewhat below those at which carbon dioxide becomes critical, it exists as separate gas and liquid phases while retaining many of the solvent properties of supercritical carbon dioxide. Under these conditions carbon dioxide is called a **dense phase fluid**, a term that also encompasses supercritical fluids.

Adjustment of the composition and conditions under which dense phase fluid carbon dioxide is maintained can provide significant variations in its solvent properties and adjustment of its ability to act as a reaction medium. In addition to variations in temperature and pressure, dense phase fluid carbon dioxide may be mixed with small quantities of other solvents (modifiers), such as methanol, to further vary its solvent properties.

In addition to its solvent properties, dense phase fluid carbon dioxide offers the advantage of low toxicity and low potential for environmental harm (the small amounts of greenhouse gas carbon dioxide released from its application as a solvent are negligible compared to quantities released from combustion of fossil fuels). A big advantage of dense phase fluid carbon dioxide is its volatility, meaning that it separates readily from reaction products when pressure is released. Furthermore, carbon dioxide released from a reaction mixture can be captured and recycled for the same application. Carbon dioxide can be obtained at low cost from biological fermentation processes.

Ionic Liquid Solvents

Ionic liquids present another alternative to organic solvents for use as media for chemical synthesis. Inorganic salts consisting of ions, such as NaCl composed of Na^+ and Cl^-ions, are normally hard, high-boiling solids. However, when one or both of the ions are composed of large charged organic molecules, as shown by the cation in the example of an ionic liquid below,



1-Butyl-3-methylimidazolium hexafluorophosphate

the salts can be liquids at room temperature and are called ionic liquids. These materials have the potential to act as suitable media in which substances can be dissolved and undergo reactions, and active research is underway to explore this possibility. There is an enormous variety of such ionic liquids with widely varying solvent properties because of the large number of kinds of ions that can be combined leading to almost limitless possibilities for various ionic liquids. An interesting possibility that has been tried experimentally is to use a mixed ionic liquid/supercritical carbon dioxide single fluid phase in which the reaction proceeds with a homogeneous catalyst followed by reduction of pressure that causes the supercritical carbon dioxide and ionic liquid to separate into two phases with the catalyst remaining in the ionic liquid — hence available for reuse — and the product in the supercritical carbon dioxide.

13.15: Feedstocks and Reagents

Feedstocks

Feedstocks are the main ingredients that go into the production of chemical products. As discussed below, feedstocks may be acted upon by reagents, and often there is some overlap between the two categories of materials. Feedstocks are so important in the practice of green chemistry that much of Chapter 14, “Feeding the Anthrosphere: Utilizing Renewable and Biological Materials,” is devoted to renewable feedstocks. Here they are introduced briefly as they relate to green chemistry and sustainability.

There are three major components of the process by which raw materials from a source are obtained in a form that can be utilized in a chemical synthesis, then converted to a product. The first of these is the **source** of the feedstock, an aspect that has a number of environmental and sustainability considerations. This may consist of a depleting resource, such as petroleum, in which case the lifetime of the resource and the environmental implications of obtaining it must be considered. From the standpoint of sustainability it is preferable to use recycled materials as feedstocks, although the availability of recycled materials suitable for this purpose is limited. A third source that is very desirable consists of renewable resources, particularly from materials made by photosynthesis and biological processes.

The second major aspect of converting feedstocks to final products is separation and isolation of the desired substance. An example of this step is the isolation of specific organic compounds from crude oil to provide a feedstock for organic chemical synthesis. It may be necessary to process raw materials from a source to convert it to the specific material used as a feedstock for a chemical process. Often most of the environmental harm in providing feedstocks comes during the isolation process, in large part because of the relatively large amount of waste material that often is generated in obtaining the needed feedstock.

The world chemical industry has been built primarily on fossil carbon feedstocks. Much of the impetus for the organic chemical industry was built during the late 1800s and early 1900s on the basis of organic chemicals isolated from the coal tar byproduct of coal coking. Later petroleum and natural gas became the basis of the petrochemicals industry which has produced enormous quantities of polymers, plastics, synthetic rubber, and thousands of other kinds of chemicals. Eventually this reliance on depleting fossil carbon resources must end. Therefore, one of the main goals of green chemistry has become a shift toward renewable feedstocks — biomass produced by photosynthesis — and to renewable reaction media, specifically water and supercritical and pressurized liquid carbon dioxide. In addition to being renewable, such feedstocks offer advantages over petroleum in that they are not toxic and they, and most of their products and intermediates, are biodegradable.

Biomass Feedstocks

The ongoing shift to a biobased economy offers the opportunity to design their processing and products on the basis of green chemistry and sustainability. Rather than petroleum refineries, biorefineries are used to process biobased feedstocks. Initially, the feedstocks used have been from grains of corn and oil seeds, such as soybeans. Cornstarch is hydrolyzed to sugars that are converted to alcohols by fermentation processes and to biodiesel fuel by esterification of the fatty acids in the oil seed lipids. Some commodity chemicals such as lactic acid are also made from grain sources. However, these are inefficient ways to utilize biomass, they compete with the consumption of grain for food, and the maximum production of grain requires intensive cultivation (often of marginal land), heavy use of fertilizer, and strong reliance on pesticides. A much more renewable approach is to utilize lignocellulose, the structural material of plants (such as wheat straw) either from dedicated crops or preferably from crop byproduct biomass or highly productive algae growing in water. Although attempts are being made to break down these lignocellulose materials with enzymes to produce fermentable sugars, a preferable pathway is the thermochemical route. This can be by pyrolysis of the biomass to produce a variety of organic liquids, some gas and a carbon residue that can be burned to provide heat for the pyrolysis. Alternatively, biomass can be reacted directly with hydrogen to produce liquid and gas products. Both pyrolysis and hydrogenation produce a large variety of liquids including oxygenated organics that can be run through a biorefinery. As discussed in Chapter 15 on energy, the best approach is thermochemical gasification of the biomass to produce a synthesis gas mixture of CO and H_2 that can be used with well known technology to synthesize gasoline, diesel fuel, aircraft fuel, alcohols, substitute natural gas, and various organic chemical feedstocks.

Genetic engineering can be very useful in producing biomass for feedstocks. One area in which there is much room for improvement is in enhanced efficiency of photosynthesis. Crops can be bred to increase the amount of byproduct biomass along with the grain they produce. Dedicated crops can be developed for the production of large quantities of biomass, alone. This has already been done using conventional plant breeding techniques to develop rapidly growing hybrid poplar trees that produce large quantities of lignocellulosic wood.

Carbohydrate Feedstocks

The most abundant biomass feedstocks are carbohydrates. It follows that one of the most promising pathways to obtaining useful raw materials and fuels from biomass is their synthesis directly from carbohydrates. As an example of a feedstock chemical that can be synthesized from fructose, a monosaccharide made in abundance from cornstarch and sucrose (common table sugar) is dimethylfuran (Figure 13.9) an oxygen-containing cyclic organic compound that has most of the desirable properties of hydrocarbons as a fuel and raw material. As shown in Figure 13.9, fructose and dimethylfuran have similar structural formulas and the conversion is largely a matter of removing oxygen from fructose by reaction with hydrogen. This synthesis and monosaccharide glucose as a feedstock are discussed in Chapter 14.

Green chemistry and the inevitable shift away from petroleum hydrocarbon feedstocks to biobased materials will cause a massive realignment of the chemical industry. Rather than manufacturing nondegradable materials using environmentally unfriendly technologies with depletable feedstocks, the new paradigm will employ green catalytic processes to convert biomass feedstocks to biocompatible (non-toxic, biodegradable) products.

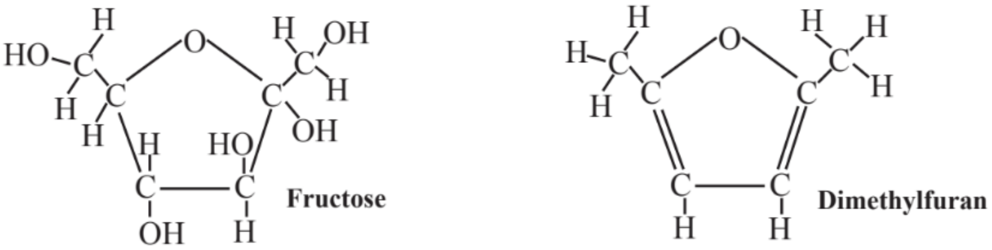


Figure 13.9. Fructose, a carbohydrate produced in abundance by plants, can be used to make dimethylfuran, a compound that resembles hydrocarbons in many of its properties and that can be used as a motor fuel and as a feedstock for organic synthesis.

Reagents

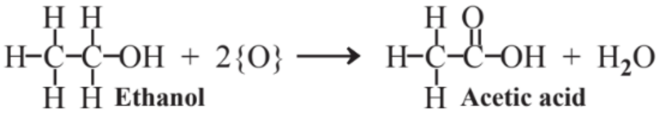
The term **reagents** is used here to describe the substances that act upon basic chemical feedstocks to convert them to new chemicals in synthetic processes. The kinds of reagents used have a very strong effect upon the acceptability of a chemical process with respect to green chemical aspects. Much of the work that has been done in developing and using green reagents has involved organic chemical processes, many of which are beyond the scope of this book. However, some of the general aspects of chemical reagents from a green chemical perspective are discussed here.

The most obvious characteristic required of a good chemical reagent is that it do what it is supposed to do completely and at an acceptable rate. A reagent with a high **product selectivity** produces a high percentage of the desired product with a low percentage of undesired byproducts. Another desirable characteristic of a good reagent is high **product yield** meaning that most of the feedstocks are converted to product. The use of reagents that provide high selectivity and yield means that less unreacted feedstock and byproduct material have to be handled, recycled, or disposed.

One of the most common measures taken in implementing green chemical processes is selection of alternative reagents. The criteria used in selecting a reagent include whether or not itis available, how efficient it is, and the effect that it has. Important considerations with the chemical transformation are whether it is stoichiometric or catalytic, the degree to which it is atom economical, and the quantities and characteristics of any wastes produced.

Reagents for Oxidation and Reduction

One of the main kinds of reactions for which reagents are used is **oxidation**, which usually consists of the addition of oxygen to a chemical compound or a functional group on a compound. (See Chapter 5, Section 5.7 for a discussion of oxidation and its accompanying phenomenon, reduction and section 13.8 regarding oxygen availability in oxidants and hydrogen availability in reductants.) An example of an oxidation reaction is the conversion of ethanol to acetic acid,



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}OH} + 2\{O\} \longrightarrow \mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH} + H_2O \tag{13.15.1}$$

where {O} is used to represent oxygen from some unspecified oxidant. Oxidation is one of the most common steps in chemical synthesis. A number of reagents are used as oxidants. Some of these reagents, such as potassium dichromate, $K_2Cr_2O_7$ are dangerous (dichromate salts are considered to be carcinogenic when inhaled for prolonged periods of time) and leave troublesome residues that require disposal.

Because of problems with oxidants that are commonly used, a major objective in the practice of green chemistry is to use more benign oxidants. Alternatives to the more traditional oxidant reagents include molecular oxygen (O2), ozone (O3), and hydrogen peroxide (H_2O_2), usually used with a suitable catalyst that enables the oxidation reaction to occur. Under the right conditions, hydrogen peroxide can be used as an alternative to elemental chlorine, Cl_2, a strong oxidant used to bleach colored materials, such as paper pulp and cloth. Since chlorine is toxic (it was used as a poison gas in World War I) and has a tendency to react with organic compounds to produce undesirable chlorinated organic compounds, hydrogen peroxide is a much preferable bleaching agent.

In contrast to the usually harsh conditions under which chemical oxidations are carried out, organisms carry out biochemical oxidations under mild conditions. In so doing, they use monooxygenase and peroxidase enzymes that catalyze the oxidizing action of molecular oxygen or hydrogen peroxide. An area of significant interest in green chemistry is to perform such oxidations in biological systems or to attempt the use of catalysts that mimic the action of enzymes in catalyzing oxidations with molecular oxygen or hydrogen peroxide.

Reduction, which consists of loss of O, gain of H, or gain of electrons by a chemical species is also a common operation in chemical synthesis. As is the case with oxidants, the reagents used to accomplish reduction can pose hazards and produce undesirable byproducts. Such reductants include lithium aluminum hydride ($LiAlH_4$) and tributyl tin hydride.

Electrons as Reagents for Oxidation and Reduction

As an alternative to the potentially troublesome oxidation and reduction procedures using reagents, **electrochemistry** provides a reagent-free means of doing oxidation and reduction. This is possible because an electrical current consists of moving electrons and oxidation consists of electron removal from a chemical species and reduction is addition of an electron. The passage of an electrical current between metal or carbon graphite electrodes through a solution resulting in oxidation and reduction reactions is called **electrolysis**. Consider the simplest possible case of electrolysis, that of water containing a non-reactive salt, such as Na_2SO_4, shown in Figure 13.10.

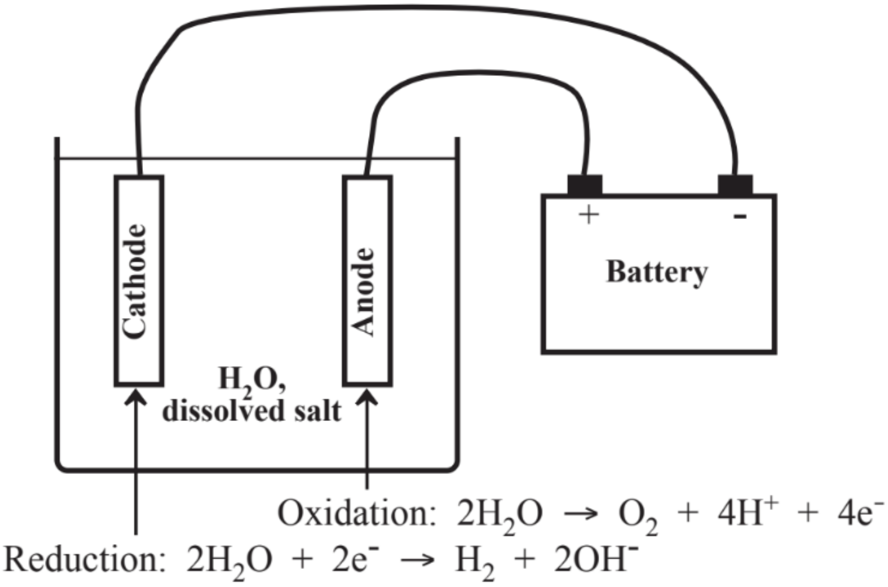


Figure 13.10. Apparatus for electrolysis in which a direct current of electricity is passed through a reaction medium, in this case water with a dissolved salt to make it electrically conducting. Reduction occurs when electrons are added to the medium at the cathode and oxidation when they are removed at the anode. Electrolysis is a reagent-free way of doing oxidation and reduction.

At the **cathode**, where electrons (e-) are pumped into the system and where reduction occurs, reduction of water occurs releasing H_2,

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \tag{13.15.1}$$

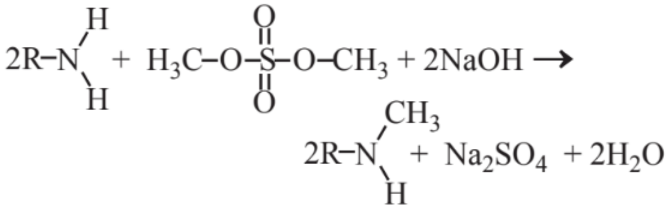
and at the **anode** where electrons are removed, O_2 is released as the water is oxidized:

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \tag{13.15.2}$$

In the setup shown, H+ion generated at the anode OH-ion generated at the anode diffuse through the solution and react upon contact to produce water again. At the cathode, a dissolved chemical species could be reduced directly or the hydrogen generated could add to a species, reducing it. And at the anode another species could be oxidized directly by loss of electrons or the oxygen generated could add to a species, oxidizing it.

Miscellaneous Reactions with Reagents

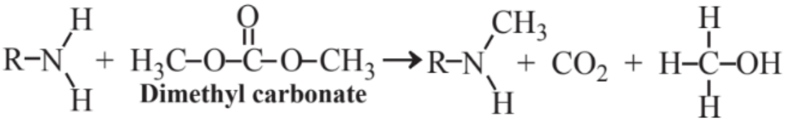
Reactions other than oxidation and reduction are carried out by reagents. As an example of a commonly performed reaction that normally requires potentially troublesome reagents, consider **alkylation** with alkylating reagents in which an alkyl group, most frequently the -CH_3 (methyl) group, is added to an atom on an organic compound. The methylation reaction,



$$2R\text{-}NH_2 + H_3C\text{-}O\text{-}S(=O)_2\text{-}O\text{-}CH_3 + 2NaOH \rightarrow 2R\text{-}N(H)CH_3 + Na_2SO_4 + 2H_2O \tag{13.15.4}$$

shows attachment of a methyl group to an amine group, -NH_2, that is part of an unspecified molecule represented “R.” Methylation of nitrogen is used in a number of chemical syntheses including preparation of analgesics such as Ibuprofen. The dimethyl sulfate reagent used to accomplish the methylation poses toxicity problems in that it is a suspect human carcinogen. The reaction also produces a byproduct of Na_2SO_4, which if contaminated with dimethyl sulfate reagent may pose disposal problems.

Dimethyl carbonate prepared by reacting methanol, CH_3OH, with carbon monoxide, CO, in the presence of elemental oxygen and a copper salt catalyst has been developed as a green alternative to dimethyl sulfate as a methylating reagent. When dimethyl carbonate acts as a methylating agent,



$$R\text{-}NH_2 + \underbrace{H_3C\text{-}O\text{-}C(=O)\text{-}O\text{-}CH_3}_{\text{Dimethyl carbonate}} \rightarrow R\text{-}N(H)CH_3 + CO_2 + H\text{-}CH_2\text{-}OH \tag{13.15.5}$$

methanol and innocuous carbon dioxide are generated as byproducts. The methanol can be recirculated through the system to generate additional dimethylcarbonate reagent.

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Questions and Problems

1. Define industrial ecology.

2. Define an industrial ecosystem.

3. Name four major parts of an industrial ecosystem

4. Give the name of the processes to which materials and components are subjected in industrial ecosystems.

5. Give a definition of wastes in terms of natural resources.

6. What is the general pathway of materials through industrial systems as they currently operate?

7. What is meant by “level of recycling” and how is it related to embedded utility?

8. Name the three kinds of analyses and three categories considered in a life-cycle assessment.

9. What are the three kinds of products, classified in part on their amenability to recycling, that are normally considered in life-cycle assessments?

10. Give three important useful characteristics of consumable products related to their potential environmental effects.

11. Name three key attributes of industrial ecosystems that largely determine the wellbeing of the systems.

12. Given that an abundant source of energy can make almost anything possible in an industrial ecosystem, in what respects do vast reserves of coal, wind power, and solar energy fall short of being ideal energy sources?

13. Explain cogeneration of energy. What are its advantages?

14. Name three approaches to providing materials other than from virgin sources.

15. Consumable items and products cannot be recycled on a practical basis. Name three other categories of goods or products that can be recycled.

16. What is Kalundborg, Denmark, noted for?

17. Name several characteristics that facilitated development of the Kalundborg industrial ecosystem.

18. Name an environmental effect of industrial activities in the anthrosphere upon each of the other four environmental spheres.

19. Name an environmental effect of agricultural activities in the anthrosphere upon each of the other four environmental spheres.

20. For each of the other four environmental spheres, name a measure that may be taken in anthrospheric activities to reduce the environmental impact of these activities.

21. What does atom economy have to do with reducing the environmental impact of industrial ecosystems?

22. Describe two general approaches to making chemical synthesis greener.

23. What are structure activity relationships applied to toxic substances?

24. Why should the use of lipid-soluble organics be reduced in the practice of green chemistry?

25. What is a characteristic of VOCs that both makes them useful in industrial applications, but also increases their hazards?

26. Distinguish between reactive and corrosive substances. May a compound be both?

28. Distinguish among feedstocks, reagents, media, and catalysts.

29. Name two desirable characteristics of reagents insofar as their ability to generate products is concerned.

30. What are two oxidants used by organisms? What catalysts are used with these oxidants?

31. What is a nonchemical alternative to the use of oxidant and reductant reagents?

32. What are the two most common media used for chemical reactions?

33. Why is toluene preferred to benzene as a solvent medium for organic reactions?

34. What is a common toxicity problem with some lighter hydrocarbons, such as hexane?

35. Normally encountered as a gas, how can carbon dioxide be used as a medium for chemical reactions?

36. What are ionic liquids and what is their potential use in green chemistry?

37. Name two general categories of catalysts based upon physical form. Which is more desirable from the green chemistry standpoint?

38. What is a desirable characteristic of catalysts that chemists try to enhance?

CHAPTER OVERVIEW

14: Feeding the Anthrosphere- Utilizing Renewable and Biological Materials

"For approximately one century from the early 1900s to the early 2000s, petroleum-based feedstocks gave rise to a vast petrochemicals industry that resulted in the production of synthetic rubber, plastics, polymers with a variety of properties, pesticides and literally hundreds of other products, many of which replaced materials biosynthesized in nature, especially by plants. Now with diminishing petroleum supplies, a new generation of materials made from biomaterials such as the lignocellulose that composes plant structural matter is developing that will take the place of many of the petroleum-based chemicals. This massive shift to renewable feedstocks is leading to a new age of green chemistry."

- 14.1: Feeding the Anthrosphere
- 14.2: Utilization of Feedstocks
- 14.3: Biological Feedstocks
- 14.4: Biological Sources of Chemicals
- 14.5: Biorefineries and Biomass Utilization
- 14.6: Monosaccharide Feedstocks - Glucose, Fructose, and Xylose
- 14.7: Cellulose
- 14.8: Feedstocks from Cellulose Wastes
- 14.9: Lignin
- 14.10: Direct Biosynthesis of Polymers
- 14.11: Bioconversion Processes for Synthetic Chemicals
- 14.12: Bamboo - Ancient Material for the Future
- Literature Cited
- Questions and Problems

14.1: Feeding the Anthrosphere

As the industrial revolution gained impetus since about 1800, and especially since about 1900 with the development of the chemical industry, the anthrosphere developed a voracious appetite for materials. This is especially true of the vast petrochemicals industry fed by materials from petroleum and producing huge quantities of polymers, plastics, synthetic detergents, agricultural chemicals and many other products. The era of petrochemicals must come to an end because sources of petroleum cannot sustain the enormous appetite of the anthrosphere for petrochemicals. The demand for the kinds of products now produced from petroleum will not go away, so alternate means of providing the materials desired by humans will have to be met. The only real alternative is biomaterials which in fact provided most of the stuff that humans used until very recently in the history of humankind. Although challenging, this shift in raw materials sources promises to be a very exciting one for chemistry. And it provides an opportunity for chemists and engineers to “get it right” by applying the principles of green chemistry, green engineering, and industrial ecology in ways that will ensure a sustainable future.

Feedstocks

Recall from Chapter 13, Section 13.15 that **feedstocks** are the main ingredients that go into the production of chemical products. Reagents act upon feedstocks and often the two are not readily distinguished. Feedstock selection largely dictates the reactions and conditions that will be employed in a chemical synthesis and is, therefore, of utmost importance in the practice of green chemistry. A feedstock should be as safe as possible. The source of a feedstock can largely determine its environmental impact, and the acquisition of the feedstock should not strain Earth’sresources. The process of isolating and concentrating a feedstock can add to the potential harm of otherwise safe materials. This is true of some metal ores in which corrosive and toxic reagents (in the case of gold, cyanide) are used to isolate the desired material.

As a general rule, it is best if feedstocks come from renewable sources rather than depletable resources A biomass feedstock, for example, can be obtained as a renewable resource grown by plants on land, whereas a petroleum-based feedstock is obtained from depletable crude oil resources. However, the environmental tradeoffs between these two sources may be more complex than first appears in that the petroleum feedstock may simply be pumped from a few wells in Saudi Arabia, whereas the biomass may require large areas of land, significant quantities of fertilizer, and large volumes of irrigation water for its production. Another important decision is whether or not the feedstock should be made entirely from virgin materials or at least in part from recycled material.

In the United States petroleum amounts to all but about two percent of the raw material used for the manufacture of organic chemicals and the many products made from them, such as textiles, plastics, and rubber. To a degree petroleum is an ideal feedstock for this purpose; during the last 100 years it has been readily available and relatively inexpensive except during times of temporary supply disruption. There are, of course, disadvantages to the use of petroleum as a feedstock, not the least of which is the fact that eventually available supplies will become exhausted. The transportation and refining of petroleum consume large amounts of energy, amounting to more than 15 percent of total energy use in United States. Chemically, a consideration with the use of petroleum as a raw material is that the hydrocarbon molecules that compose petroleum are in a highly reduced chemical state. In order to be utilized as feedstocks, petroleum hydrocarbons often must be oxidized. The oxidation process (see Section 13.15) entails a net consumption of energy and often requires the use of severe and hazardous reagents. Although commonly used oxidation processes are well contained and safe, there is always the consideration of possible combustion and explosion hazards in the partial oxidation of petroleum.

Much of the challenge and potential environmental harm in obtaining feedstocks is in separating the feedstock from other materials. This is certainly true with petroleum, which consists of many different hydrocarbons, only one of which may be needed as the raw material for a particular kind of product. Some metals occur at levels of less than 1% in their ores, requiring energy-intensive means of separating out the metals from huge quantities of rock. The smelting of copper and lead ores releases significant quantities of impurity arsenic with the flue dust, which must be collected from the smelting operation. Indeed, this byproduct arsenic provides more than enough of the arsenic needed in commerce. Biobased materials are also generally mixtures that require separation. Cellulose from wood, which can be converted to paper and a variety of chemicals, is mixed intimately with lignin, from which it is separated only with difficulty.

In evaluating the suitability of a feedstock, it is not sufficient to consider just the hazards attributable to the feedstock itself and its acquisition. That is because different feedstocks require different processing and synthetic operations downstream that may add to their hazards. If feedstock A requires use of a particularly hazardous material to convert it to product, whereas feedstock B can be processed by relatively benign processes, feedstock B should be chosen. This kind of consideration points to the importance of considering the whole life cycle of materials rather than just one aspect of them.

14.2: Utilization of Feedstocks

Before considering sources of feedstocks, it is useful to consider how those feedstocks can be used in the least polluting, most sustainable way possible. Feedstocks are modified by chemical processes to produce new chemical materials with commercial uses. The ideal feedstock is renewable and poses no hazards. And it can be converted to the desired product using few steps with 100% yield and 100% atom economy. This should be done with minimum quantities of reagent using only safe media in which the reaction occurs.

There are three major categories of reactions that are involved in chemical processing of feedstocks as shown in a general sense in Figure 14.1. In an **addition reaction**, all feedstock material becomes part of the product and there are no byproducts. These are the best kinds of reactions from the viewpoint of green chemistry because, when they work ideally, there are no wastes. A **substitution reaction** uses a reagent to replace a functional group on the feedstock molecule. As its name implies, an **elimination reaction** removes a functional group from a feedstock molecule. Both of these latter kinds of reactions produce byproduct materials from the feedstock and from spent reagent. Their impacts can be reduced by reclaiming byproducts, if a use can be found for them, and by regenerating reagent, when that is possible. In some cases,elimination reactions can be carried out without use of a reagent, reducing the impact of this kind of reaction.

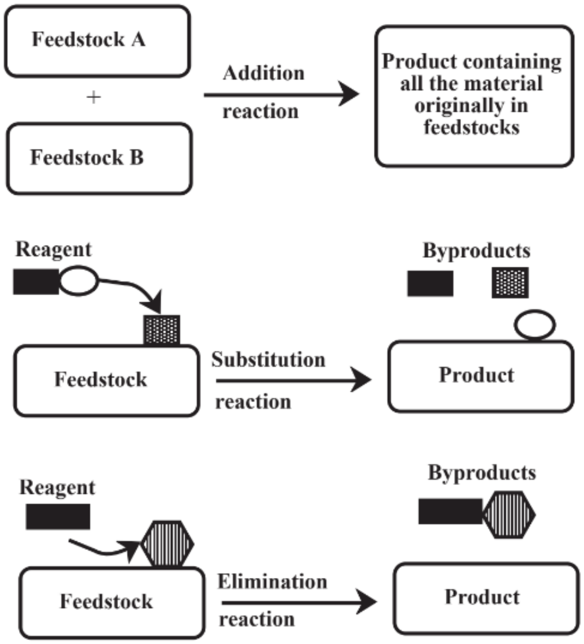


Figure 14.1. Illustration of three major categories of reaction processes by which feedstocks are acted upon by reagents to produce desired products

14.3: Biological Feedstocks

Organisms have provided a huge share of the materials used by humans throughout their existence. Trees have served as sources of wood for construction and firewood. Animals provided hides and fur to protect primitive humans from Ice Age cold. The American bison was the source of food, shelter, clothing, and a wide variety of other useful items to plains-dwelling Native Americans. Protein silk is obtained from the cocoons of insects, and protein wool from sheep and related animals.

Biomass, the plant material generated from photosynthesis is the leading candidate to replace petroleum as a feedstock for the organic chemicals industry. There are several major categories of biomass that can be used for feedstock:

1. Carbohydrate, which has the general formula of approximately CH_2O. Carbohydrate is the biomass that is produced initially as glucose sugar from water and carbon dioxide during photosynthesis. It is contained in the structural parts of plants as cellulose, a biopolymer.

2. Lignin, a biological polymer with a complex structure, which occurs with carbohydrate cellulose in woody parts of plants, binding fibers of cellulose together. Relatively few uses have been found for lignin, and it poses impurity problems in extracting cellulose for feedstock use.

3. Lipid oils extracted from seeds, including soybeans, sunflowers, and corn.

4. Hydrocarbon terpenes produced by rubber trees, pine trees, and some other kinds of plants.

5. Proteins, produced in relatively small quantities, but potentially valuable as nutrients and other uses.

Biological materials used as sources of feedstocks are usually complex mixtures, which makes separation of desired materials difficult. However, in some biological starting materials nature has done much of the synthesis. Most biomass materials are partially oxidized as is the case with carbohydrates, which contain approximately one oxygen atom per carbon atom (compared to petroleum hydrocarbons which have no oxygen). This can avoid expensive, sometimes difficult oxidation steps, which may involve potentially hazardous reagents and conditions.

There are several main pathways by which feedstocks can be obtained from biomass. The most straightforward of these is a simple physical separation of biological materials, such as squeezing oil from oil-bearing biomass or tapping latex from rubber trees. Only slightly more drastic treatment consists of extraction of oils by organic solvents. Physical and chemical processes can be employed to remove useful biomass from the structural materials of plants, which consist of lignocellulose composed of cellulose and the related carbohydrate polymer hemicellulose bound together by lignin "glue."

Carbohydrates are perhaps the most likely candidates as feedstocks for chemical processes. Carbohydrates come in several forms. Sucrose sugar, $C_{12}H_{22}O_{11}$, can be squeezed from sugar cane as sap and can be extracted from sugar beets and sugar cane with water. The exceptional photochemical productivity of sugar cane makes sucrose from this source an attractive option. Larger amounts of carbohydrates are available in starch, a polymer of glucose readily isolated from grains, such as corn, or from potatoes. An even greater source is found in cellulose, which occurs in woody parts of plants. It is relatively easy to break down starch molecules with the addition of water (hydrolysis) to give simple sugar glucose. Breaking down cellulose is more difficult, but can be accomplished by the action of cellulase enzymes.

Lipid oils are extracted from the seeds of some plants. Volatile solvents, most commonly the 6-carbon straight-chain alkane *n*-hexane, C_6H_{14}, are used to extract oils. In this process, the solvents are distilled off from the extract and recirculated through the process.

The hydrocarbon terpenes that occur in rubber trees can be tapped from the trees as a latex suspension in tree sap. Steam treatment and distillation can be employed to extract terpenes from sources such as pine or citrus tree biomass.

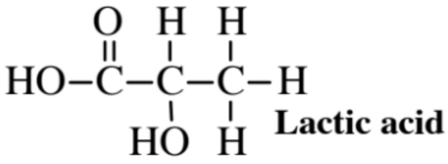
Grain seeds are rich sources of protein, almost always used for food, but potentially useful as chemical feedstocks for specialty applications. An exciting possibility just now coming to fruition in a practical sense is to transplant genes into plants so that they will make specialty proteins, such as medicinal agents.

14.4: Biological Sources of Chemicals

In the provision of specialty and commodity chemicals and feedstocks, there are two main biological sources of materials. One of these consists of plants, which make huge quantities of cellulose and lesser quantities of other materials by photosynthesis. The other source is microorganisms, especially bacteria and yeasts.

Fermentation

Fermentation refers to the action of microorganisms on nutrients under controlled conditions to produce desired products. Fermentation for some products is anoxic (absence of O2); for other products oxic fermentation may be required. Fermentation processes have been used for thousands of years to produce alcoholic beverages, sauerkraut, vinegar, pickles, cheese, yogurt, and other foods. Ethanol, the alcohol in alcoholic beverages, is the most widely produced chemical made by fermentation. Lactic acid,



$$\mathrm{HO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle HO}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}H}$$

Lactic acid

has also been produced by fermentation processes for many years. More recently, fermentation has been applied to the production of a wide variety of organic acids, antibiotics, enzymes, and vitamins.

Starting in the 1940s, one of the major products of industrial fermentation has been penicillin, of which there are several forms. Figure 14.2 shows a simplified diagram of a facility for production of this life-saving antibiotic. Following penicillin, fermentation processes were developed for the production of several other significant antibiotics.

Selection of the appropriate microorganism is the most important consideration of a successful fermentation production process. The microorganisms have to have the proper nutrients, the choice of which can affect the kind and yield of the product. Sterile conditions must be maintained, and sterilization of equipment and media is accomplished by heating to 125–150°C for appropriate lengths of time. Air entering the fermenter must be filtered and sterilized. The temperature of fermentation is important, with fermentation rates increasing up to an optimum temperature, after which they decrease sharply with increased temperatures as the enzymes used by the microorganisms are destroyed (denatured). This kind of temperature relationship has increased interest in the use of thermophilic microorganisms that exist at boiling water temperatures in hot springs. If such organisms can be engineered to produce desired products, the rate of product generation may increase markedly. Both the levels of oxygen (which must be excluded from anoxic processes) and pH must be controlled precisely. Modern fermentation processes use a variety of sensors to continuously monitor conditions in the fermentation tank and computerized control to accurately control all the parameters.

Fermentation is undergoing tremendous development with the use of transgenic microorganisms to which genes have been transferred to make specific kinds of substances. The most common and valuable substances made by transgenic microorganisms consist of a variety of proteins. These include proteins and smaller molecule polypeptides that are used as pharmaceuticals. The best example of such a substance is human insulin, which is now produced in large quantities by transgenic microorganisms.

Until recently, fermentation has not been widely employed to make commodity chemicals used on a large scale. An exception is the large-scale production of ethanol from the fermentation of glucose sugar by yeasts. Now mandated as a gasoline additive in the U. S. by law, huge and growing quantities of ethanol are made by fermentation of glucose derived from corn and this use is an important market for corn. It is not clear that this is a truly green technology and some authorities believe that the energy consumed and the environmental damage from more intensive cultivation of corn outweigh the benefits of using this grain to produce ethanol fuel. Advances in transgenic microbiology have increased the possibilities for using fermentation to produce a variety of chemicals and chemical feedstocks, several examples of which are discussed in this chapter.

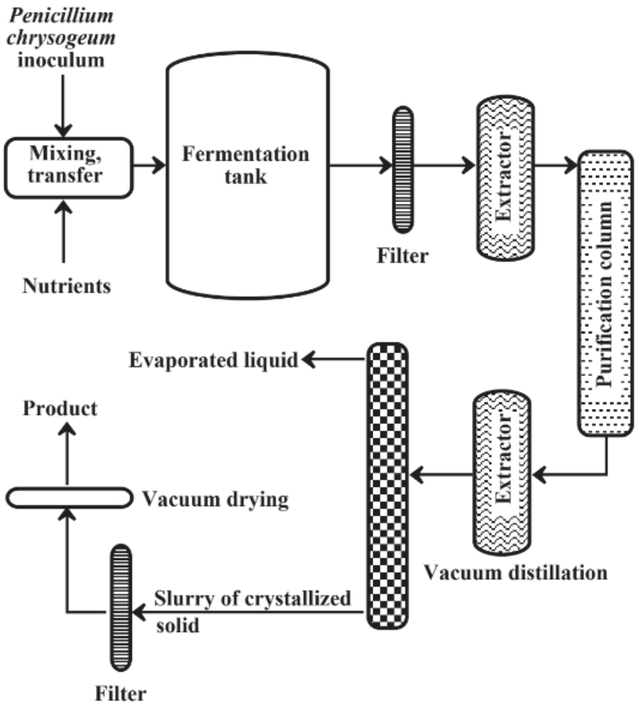


Figure 14.2. Simplified schematic diagram of the process for making penicillin by fermentation

Production of Materials by Plants

The uses of microorganisms operating in fermentation processes to generate commodity chemicals were discussed above. Plants are the other kind of organism that can be used for producing chemicals. Indeed, the nutrients used for fermentation processes come originally from plants. Fermentation is in a sense not a very efficient means of producing chemicals because of the consumption of nutrients to support the microorganisms and their reproduction and because of the generation of large quantities of byproducts. Plants, which generate their own biomass from atmospheric carbon dioxide and water are very efficient producers of materials. Wood and the cellulose extracted from it are prime examples of such materials.

In addition to their efficient production of biomass, plants offer distinct advantages in their production and harvesting. Genetics determine the materials that a plant makes, and once a crop is growing in a field, the products it is programmed for will be produced without fear of contamination by other organisms, which is always a consideration in fermentation. Plants can be grown by relatively untrained personnel using well known agricultural practices. Plant matter is generally easy to harvest in the form of grains, stalks, and leaves, which can be taken to a biorefinery (see below) to extract needed materials.

The production of feedstocks and other chemical commodities from plants has been limited by the genetic restrictions inherent to plants. Now, however, transgenic plants can be bred to produce a variety of materials directed by genes transplanted from other kinds of organisms. For example, as discussed in Section 14.10, plants have even been developed to synthesize plastics. Another limitation of the production of materials by plants has been the mixture of these materials with other matter generated by plants. The intimate mixture of useful wood cellulose with lignin, for which uses are still being sought, is a prime example of this problem. Again, transgenic technology can be expected to be helpful in developing plants that produce a relatively pure product (such as the almost pure cellulose in cotton.)

The potential of plants to produce useful products has been greatly increased by the development of hybrid plants with spectacular capacities to generate biomass by photosynthesis. Corn is one of the more productive field crops, and hybrid varieties produce large quantities of grain and plant biomass (leaves, stalks, husks and cobs commonly called corn stover). Sugar cane is noted for its ability to produce biomass, some in the form of sugar, much more in the cane stalk biomass. The sugar cane stalk residues left after extracting sugar from it (bagasse) has had relatively few uses, other than for fuel but potentially can produce large quantities of chemical feedstocks in biorefineries. One of the more exciting developments of productive hybrid plants is the hybrid poplar tree which, nourished by minimal amounts of fertilizer and watered by economical trickle irrigation systems, grows within a few years to a harvestable size for the production of wood pulp and wood for plywood. The ability of these trees to generate cellulose that can be converted to glucose means that they may serve as the basis of an entire plant-based chemicals industry. The possibility exists that they can be genetically engineered to produce other chemicals as well.

14.5: Biorefineries and Biomass Utilization

Just as crude oil is a complex mixture of hydrocarbons and other organic compounds that must be run through a petroleum refinery to separate and chemically modify the materials in it to produce fuel and petrochemical feedstocks, chemicals from biological sources are usually complex mixtures that require refining and chemical processing to provide needed feedstocks. The separation and processing of biomaterials from plants or from bacteria cultured in digesters is accomplished in a **biorefinery** the output of which consists of organic chemicals and fuels. In a biorefinery the various products that can be obtained from biomass are separated and subjected to chemical treatment, generally with the objective of reducing the chemically bound oxygen contents of the organic liquids. Although the large number of compounds generated from biomass poses a challenge for separations, it also provides the opportunity to produce smaller quantities of high-value chemicals.

Figure 14.3 illustrates a biorefinery showing four ways in which feedstocks may be obtained from biomass. The simplest and least energy-consumptive of these is extraction in which an organic solvent or, in more sophisticated operations, supercritical carbon dioxide is used to dissolve materials from biomass. This approach is widely used to extract oils from some kinds of oil seeds. Terpene hydrocarbons can be extracted from pinewood and other terpene-producing plants. Some of the greatest potential is to extract hydrocarbons and other oils from algae that produce these materials. Single-cell algae are particularly efficient photosynthesizers and the potential is high to genetically engineer strains that can produce specific classes of extractable organics.

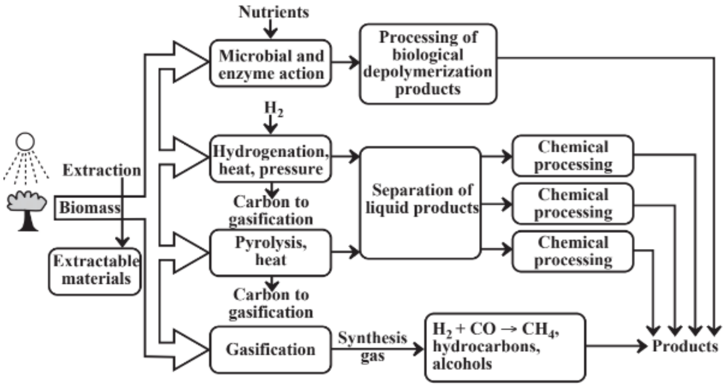


Figure 14.3. General outline of a biorefinery in which organic feedstocks and fuels are obtained by the action of microorganisms or enzymes that depolymerize large biomass molecules, extraction, hydrogenation, pyrolysis, or gasification of biomass.

Other than by extraction, the pathway to useful chemicals from biomass involves breaking down the complex biomass polymers. One way in which this is done is with microbial action or the action of isolated enzymes, for example, to produce glucose sugar from starch or cellulose. This step may require addition of nutrients including nitrogen, phosphorus, and potassium to enable microorganisms to grow. The glucose and other monomers isolated by enzymatic action can be subjected to additional processing, the most common example of which is fermentation of glucose to alcohol.

Hydrogenation of biomass involves reaction with elemental H_2 under high pressure and at elevated temperatures. This approach can be used with hydrogen generated relatively inexpensively by electrolysis of water employing renewable sources of electricity, especially from wind power. Direct hydrogenation of biomass produces a wide variety of organics including oxygenated compounds, some of which have direct uses and others of which may be chemically modified to give desired product.

Pyrolysis involves heating biomass externally or with a hot gas stream to evolve liquid and gas products. An external heat source including even solar energy focussed and concentrated on a reactor may be employed. As with hydrogenation, pyrolysis generates a variety of products including oxygenated compounds. It also produces large amounts of residual carbon, which can be used directly as fuel or gasified with steam and oxygen to produce synthesis gas.

Gasification, which is discussed in more detail in Chapter 15, Section 15.6, involves the reaction of hot carbon with steam,

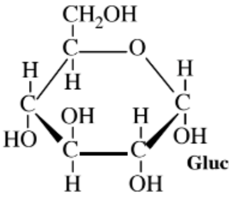
$$H_2O + C \rightarrow H + CO_2 \tag{14.5.1}$$

yielding a synthesis gas mixture of H_2 and CO. The carbon is usually heated by partial combustion with O_2 and the CO in the synthesis gas is reacted with steam to increase the ratio of H_2 to CO. Biomass can be gasified directly by reaction with a minimal amount of O_2. Since biomass has the approximate empirical formula of $\{CH_2O\}$ the “water” required for gasification is largely in the biomass, itself. Such direct gasification of biomass also produces large quantities of organics that are processed downstream in the biorefinery.

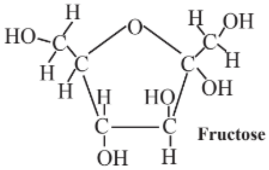
An important consideration in biorefineries is the use of catalysts. Insofar as possible biorefineries should use heterogeneous catalysts that do not get into the product and enzyme catalysts that operate at moderate temperatures.

14.6: Monosaccharide Feedstocks - Glucose, Fructose, and Xylose

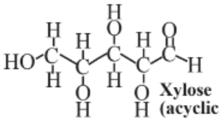
The monosaccharides such as glucose and fructose, as well as xylose, the monomer of hemicellulose, which makes up almost 1/3 of typical plant biomass,



Glucose



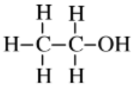
Fructose



Xylose (acyclic form)

are produced in abundance by plants. These compounds are excellent platforms for a number of different organic syntheses. As partially oxidized materials, they are particularly advantageous where a partially oxidized product is made, as is often the case in organic synthesis. Monosaccharides contain hydroxyl groups (-OH) around the molecule, which act as convenient sites for the attachment of various functionalities. Glucose is metabolized by essentially all organisms, so it serves as an excellent starting point for biosynthesis reactions using enzymes, and it and many of its products are biodegradable, adding to their environmental acceptability.

Glucose can be obtained by enzyme-catalyzed processes from other sugars, including sucrose and fructose. A large fraction of the glucose that is now used is obtained from the enzymatic hydrolysis of cornstarch. It is also possible to obtain glucose by the enzymatic hydrolysis of cellulose, although it has not proven economically practical to do so on an industrial scale because of the refractory nature of the cellulose polymer. Nevertheless, the enormous quantities of cellulose available in wood and other biomass sources make glucose from cellulose an attractive prospect. The greatest use of glucose and fructose (which is readily converted to glucose by enzymes) for synthesis is by fermentation with yeasts to produce ethanol,



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$$

Ethanol

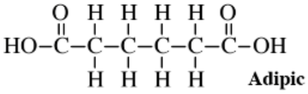
an alcohol widely used as a gasoline additive, solvent, and chemical feedstock. A byproduct of this fermentation process is carbon dioxide, the potential of which in green chemical applications as a supercritical fluid solvent are discussed in Section 13.14.

Glucose is widely used as a starting material for the biological synthesis of a number of different biochemical compounds. These include ascorbic acid, citric acid, and lactic acid. Several amino acids used as nutritional supplements, including lysine, phenylalanine, threonine, and tryptophan, are biochemically synthesized starting with glucose. The vitamins folic acid,ubiquinone, and enterochelin are also made biochemically from glucose.

In addition to the predominantly biochemical applications of glucose mentioned above, monosaccharides can be used to make feedstocks for chemical manufacture. The possibilities for so doing are now greatly increased by the availability of genetically engineered microorganisms that can be made to express genes for the biosynthesis of a number of products. Sophisticated genetic engineering is required to make chemical feedstocks because these are materials not ordinarily produced biologically.

A study by the U.S. Department of Energy Pacific Northwest Regional Laboratory has identified "top twelve value added chemicals" that can be made enzymatically from monosaccharides, especially glucose and fructose.[1] Listed in Table 14.1, these chemicals could form the main feedstocks for future biorefineries that would generate an abundance of products currently made largely from petrochemicals. Several specific syntheses of commercially valuable chemicals are discussed below.

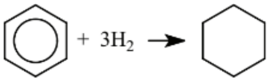
As an example of the potential of glucose for making important feedstocks, consider the synthesis from glucose of adipic acid,



$$\mathrm{HO-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH}$$

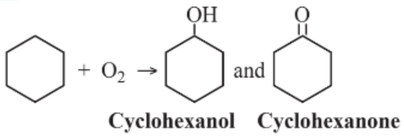
Adipic acid

a feedstock consumed in large quantities to make nylon. The conventional synthesis of this compound starts with benzene, a volatile, flammable hydrocarbon that is believed to cause leukemia in humans. The synthesis involves several steps using catalysts at high pressure and corrosive oxidant nitric acid, which releases air pollutant nitrous oxide, N_2O. The first step is the addition to benzene over a Ni/Al_2O_3 catalyst at a pressure 25 to 50 times atmospheric pressure of explosive hydrogen gas, H_2,



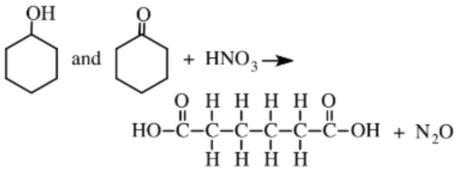
(14.6.1)

to produce cyclohexane, which is then subjected to oxidation in air at 9 atm pressure over a cobalt catalyst



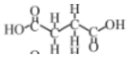
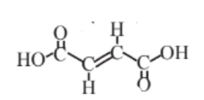
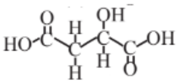
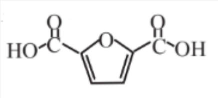
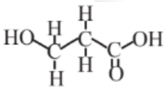
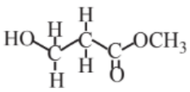
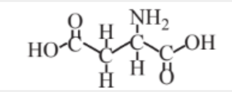
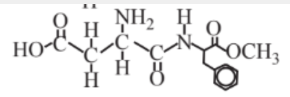
(14.6.2)

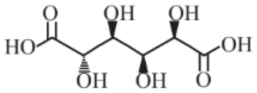
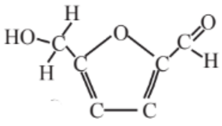
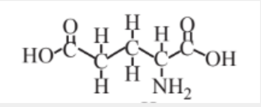
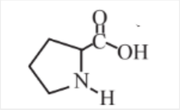
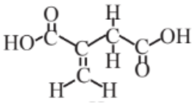
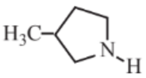
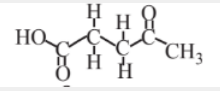
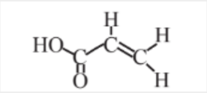
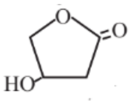
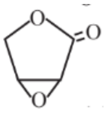
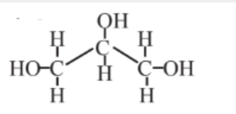
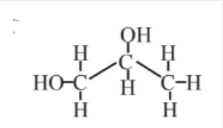
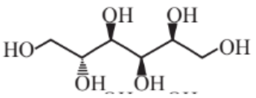
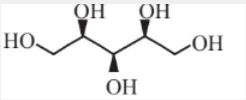
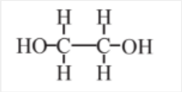
to produce a mixture of cyclohexanol, a cyclic alcohol, and cyclohexanone, a cyclic ketone. This mixture is then reacted with oxidizing, corrosive, 60% nitric acid over a Ni/Al_2O_3catalyst at 25–50 atm pressure to give the adipic acid feedstock:



(14.6.3)

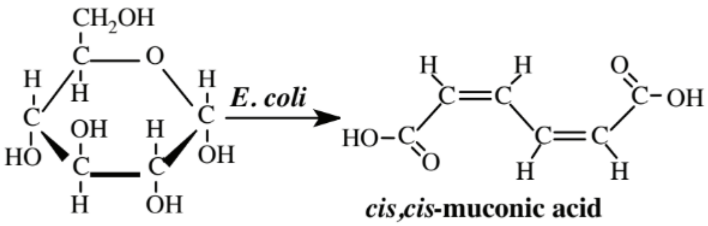
Table 14.1. Top Twelve Chemical Feedstock That Can be Made Enzymatically from Monosaccharide

Name and structural formula	Examples of Products
Four carbon 1,4-diacids	Tetrahydrofuran 
Succinic acid 	
Fumaric acid 	
Malic acid 	
2,5-Furandicarboxylic acid 	2,5-Bis(aminomethyl)-tetrahydrofuran 
3-Hydroxypropionic acid 	Methyl acrylate 
Aspartic acid 	Aspartame (artificial sweetener) 

Glucaric acid 	5-Hydroxymethyl-furfural 
Glutamic acid 	Proline 
Itaconic acid 	3-Methylpyrrolidine 
Levulinic acid 	Acrylic acid 
3-Hydroxybutyrolactone 	Epoxylactone 
Glycerol 	Propylene glycol 
Sorbitol 	Sorbitol itself has numerous uses in foods(as a low-calorie sweetener) and in cosmetics
Xylitol 	Ethylene glycol 

Throughout the synthesis process, elevated temperatures of approximately 250°C are employed. The N_2O released by the synthesis of adipic acid in the manufacture of nylon accounts for a significant fraction of worldwide N_2O releases. The potential dangers and environmental problems with this synthesis are obvious.

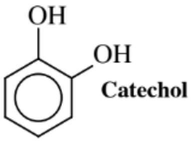
As an alternative to the chemical synthesis of adipic acid described above, a biological synthesis using genetically modified *Escherichia coli* bacteria and a simple hydrogenation reaction has been devised. The bacteria convert glucose to *cis,cis*-muconic acid:



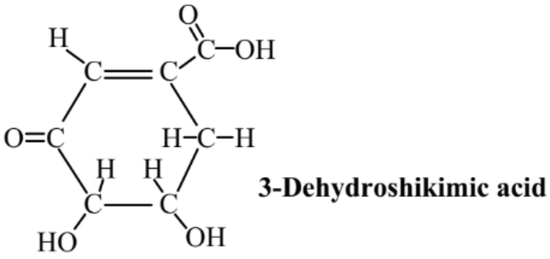
(14.6.4)

The muconic acid is then treated under relatively mild conditions with H_2 under 3 atm pressure over a platinum catalyst to give adipic acid.

Another organic chemical that potentially can be produced by the action of transgenic microorganisms on glucose is catechol, used as a feedstock to make flavors, pharmaceuticals, carbofuran pesticide, and other chemicals. About 20 million kilograms per year worldwide of this compound are now manufactured chemically starting with propylene and carcinogenic benzene, both derived from depleting petroleum sources. Toxic phenol is generated as an intermediate, and it is oxidized to catechol with 70% hydrogen peroxide, which at this concentration is a violently reactive, hazardous oxidant. These steps require some rather severe conditions and stringent precautions in handling hydrogen peroxide reagent.*E. coli* bacteria of a genetically modified strain designated AB2834/pKD136/pKD9/069A, produce catechol from glucose and, if yields can be gotten to acceptable levels, biosynthesis could become a major source of this important chemical.



Another potentially important organic feedstock that has now been synthesized from glucose using transgenic *E. coli* is 3-dehydroshikimic acid:



This compound is an important intermediate in the production of aromatic amino acids, gallic acid, vanillin, and other chemicals. It also has antioxidant properties. Antioxidants are organic compounds that react with oxygen-containing, reactive free radical species, such as hydroxyl radical, HO•. With their unpaired electrons (which make them free radicals), these species oxidize materials such as oils, fats, and lubricating oils and greases, causing deterioration in quality. By reacting with the free radicals, antioxidants stop their action. An abundant source of 3-dehydroshikimic acid could lead to its much wider application as an antioxidant.

The most abundant biomass feedstocks are carbohydrates. It follows that one of the most promising pathways to obtaining useful raw materials and fuels from biomass is their synthesis directly from carbohydrates. One of the more promising end products from chemical modification of carbohydrates is dimethylfuran, an oxygen-containing cyclic organic compound that has most of the desirable properties of hydrocarbons as a fuel and raw material. Compared to ethanol, dimethylfuran has a relatively low boiling temperature, has a high energy content per unit mass, does not absorb water, and exhibits combustion characteristics comparable to those of commonly used hydrocarbon fuels. Structurally, dimethylfuran with its 5-membered ring resembles the abundant monosaccharide fructose, which also has a 5-membered ring,

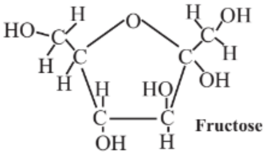


Figure 14.4.

14.7: Cellulose

The most abundant natural material produced by organisms is **cellulose** synthesized biologically by the joining of glucose molecules with the loss of 1 H_2O molecule for each bond formed (see Figure 14.5). This makes the chemical formula of cellulose $(C_6H_{10}O_5)_n$, where n ranges from about 1500 to 6000 or more. Most cellulose is made by plants, with total amounts exceeding 500 *billion* metric tons per year world-wide. Cellulose makes up the sturdy cell walls of plants. Wood is about 40% cellulose, leaf fibers about 70%, and cotton, one of the purest sources of cellulose, about 95%. Cellulose occurs in different forms and is generally associated with hemicellulose (a material also composed of carbohydrate polymers) and lignin, a biopolymer of varied composition and bonding composed largely of aromatic unit.

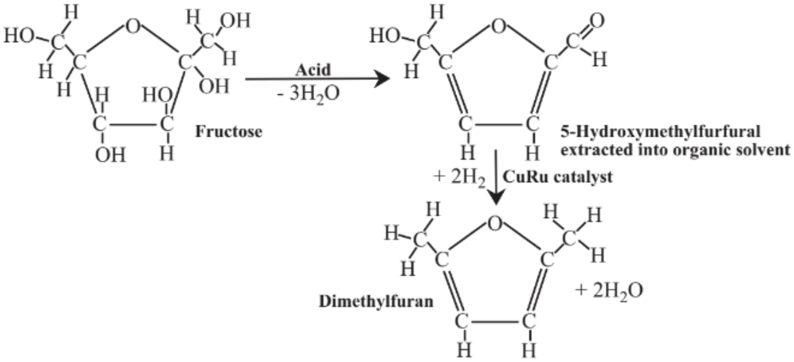


Figure 14.4. Synthesis of dimethylfuran, an organo-oxygen compound with many of the desirable properties of petroleum hydrocarbons, from fructose, a carbohydrate produced in abundance by plants.

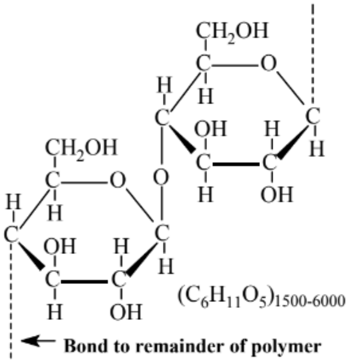


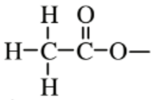
Figure 14.5. Segment of the cellulose molecule in which from 1500 to several thousand an hydroglucose units (glucose molecules less H_2O) are bonded together.

The first major step in cellulose utilization, such as extraction of cellulose fibers for making paper, consists of separating the cellulose from its matrix of lignocellulose (hemicellulose and lignin). This step has been the cause of many problems in utilizing cellulose because of the harsh chemical processing that has been employed. Lignin residues impart color to the cellulose, so wood pulp used in making paper has to be bleached with oxidants that alter the structure of the coloring agents. Bleaching used to be done almost entirely with elemental chlorine, Cl_2, and salts of hypochlorite ion, ClO^-. However, bleaching of biomass with these chlorine-based materials produces chlorinated organic impurities and pollutants. Therefore, ozone and hydrogen peroxide are preferred bleaching agents.

A finely divided form of cellulose called **microcrystalline cellulose** is produced by appropriate physical and chemical processing of cellulose. This material has many uses in foods in which it impart smoothness, stability, and a quality of thickness. Microcrystalline cellulose is also used in pharmaceutical preparations and cosmetics. Added to food, indigestible cellulose contributes bulk and retains moisture.

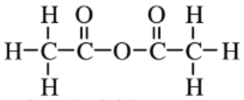
Chemically modified cellulose is used to make a wide variety of materials. Like the glucose that comprises it, cellulose has an abundance of -OH groups to which various other groups can be bonded to impart a variety of properties. One of the oldest synthetic fabrics, rayon, is made by treating cellulose with base and carbon disulfide, CS_2, then extruding the product through fine holes to make thread. In a similar process, chemically treated cellulose is extruded through a long narrow slot to form a sheet of transparent film called cellophane.

As seen by the structural formula in Figure 14.5, each unit of the cellulose polymer has three–OH groups that are readily attached to other functional groups leading to chemically modified cellulose. One of the most common such products is cellulose acetate, an ester (see Section 6.4and Reaction 6.4.1) used primarily for apparel and home furnishings fabrics in which most of the -OH groups on cellulose are replaced by acetate groups by reaction with acetic anhydride (see below):



$H{-}\underset{H}{\overset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}$

Acetate group



$H{-}\underset{H}{\overset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\overset{H}{C}}{-}H$

Acetic anhydride reagent

Although the cellulose feedstock for cellulose acetate synthesis is certainly a “green” material, acetic anhydride used to make the acetate is a corrosive, toxic chemical that produces poorly chealing wounds on exposed flesh. Furthermore, potentially hazardous solvents, such as dichloromethane, are used in some processes for making cellulose acetate.

Another cellulose ester that has been widely manufactured is cellulose nitrate in which the$-$OH groups on cellulose are replaced by $-ONO_2$ groups by treating cellulose with a mixture of nitric acid (HNO_3) and sulfuric acid (H_2SO_4). Cellulose nitrate makes transparent film and was used in the early days of moving pictures for movie film. However, one of the other major uses of this material is as an explosive, so cellulose nitrate can burn violently giving off highly toxic fumes of NO_2 gas. In years past this characteristic has lead to several tragic fires involving human fatalities. Its use is now largely restricted to lacquer coatings, explosives and propellants. Although the cellulose raw material is green, neither the process for making cellulose nitrate involving strong acids, nor the flammable product would qualify as green.

From the discussion above, it is apparent that cellulose is an important raw material for the preparation of a number of materials. The reagents and conditions used to convert cellulose to other products are in some cases rather severe. It may be anticipated that advances in the science of transgenic organisms will result in alternative biological technologies that will enable conversion of cellulose to a variety of products under relatively mild conditions.

14.8: Feedstocks from Cellulose Wastes

Large quantities of cellulose-rich waste biomass are generated as byproducts of crop production in the form of straw remaining from grain harvest, bagasse residue from the extraction of sucrose from sugar cane, and other plant residues. This biomass represents a large amount of essentially free raw material that potentially can be converted to valuable chemical feedstocks. One way in which this can be done is by the use of enzyme systems to break the cellulose down into glucose sugar used directly as a feedstock or fermented to produce ethanol. Direct conversion of cellulose wastes to feedstocks is another route. Fortunately, nature has provided efficient microorganisms for this purpose in the form of rumen bacteria that live in the stomachs of cattle and related ruminant animals. It has been found that these bacteria function well in large fermenters from which oxygen is excluded if the plant residues are first treated with lime(chemical formulas $Ca(OH)_2$ and $CaCO_3$), producing short-chain organic acids that exist as their calcium salts in the presence of lime.

The organic acids produced by rumen bacteria in animals that can use cellulose as food are absorbed from the digestive systems of the animals and used as food. The acids produced in fermenters are in the form of calcium salts, the main ones of which consist of calcium acetate, calcium propionate, and calcium butyrate. These calcium salts of organic acids can be processed in several ways to produce feedstocks for a variety of organic syntheses. As shown in Figure 14.6, acidification of the salts yields the corresponding organic acids. Reaction of these acids with elemental hydrogen (hydrogenation) can be used to convert them to alcohols. Heat treatment(pyrolysis) of the calcium salts of the organic acids at 450°C produces ketones, such as those shown in Figure 14.6. These compounds are valuable feedstocks for a number of different chemical synthesis operations.

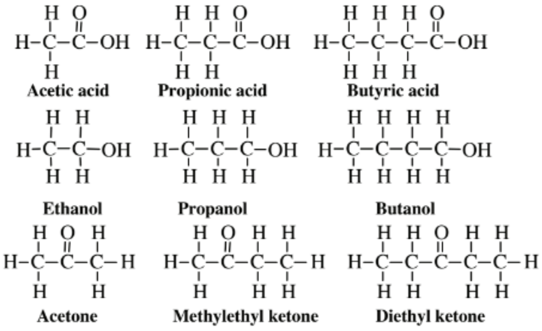


Figure 14.6. Production of organic chemicals from cellulose beginning with its breakdown by bacteria isolated from the rumen in animals capable of digesting cellulose. The first products are carboxylic acids, which can be converted to alcohols by hydrogenation and to ketones by pyrolysis

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14.9: Lignin

Lignin, a chemically complex biopolymer that is associated with cellulose in plants and serves to bind cellulose in the plant structure, ranks second in abundance only to cellulose as a biomass material produced by plants. Lignin is normally regarded as a troublesome waste in the processing and utilization of cellulose. The characteristic that makes lignin so difficult to handle in chemical processing is its inconsistent, widely variable molecular structure as shown by the segment of lignin polymer in Figure 14.7. This structure shows that much of the carbon is present in aromatic rings that are bonded to oxygen-containing groups, and lignin is the only major plant biopolymer that is largely aromatic. Because of this characteristic, lignin is of considerable interest as a source of aromatic compounds including phenolic compounds, which have the−OH group bonded to aromatic rings or even aromatic hydrocarbons. The abundance of hydroxyl (−OH), methoxyl ($-OCH_3$), and carbonyl (C=O) groups in lignin also suggests potential chemical uses for the substance. A significant characteristic of lignin is its resistance to biological attack. This property, combined with lignin's highly heterogeneous nature makes it a difficult substrate to use for the enzyme-catalyzed reactions favored in the practice of green chemistry to give single pure products useful as chemical feedstocks.

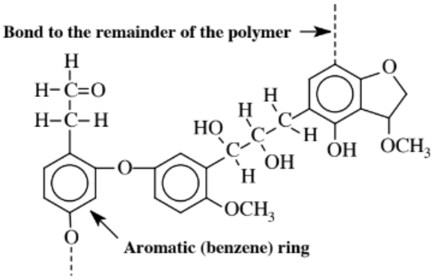


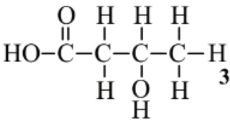
Figure 14.7. Segment of a lignin polymer molecule showing aromatic character and the disorganized, variable chemical structure that makes lignin a difficult material to use as a feedstock

Since lignin is a significant fraction of all plant biomass, significant fractions of this biopolymer must be dealt with in biorefineries. Lignin generated as a byproduct in the extraction of cellulose from wood is now largely burned for fuel, the lowest level of use for this material. By retaining much of the lignin molecule intact, use may be made of larger molecular mass segments of the molecule, such has been done for some uses for binders to hold materials together incoherent masses, fillers, resin extenders, and dispersants. There is also some potential to use lignin as a degradation-resistant structural material, such as in circuit boards. Potentially the most profitable use for lignin is to make small aromatic molecules useful for chemical synthesis. For this to be practical, special techniques will need to be developed to partially break down the lignin molecule without destroying the aromatic molecule segments in it.

14.10: Direct Biosynthesis of Polymers

Cellulose in wood and cotton is only one example of the numerous significant polymers that are made biologically by organisms. Other important examples are wool and silk, which are protein polymers. A big advantage of these kinds of polymers from an environmental viewpoint is that polymers made biologically are also the ones that are most likely to be biodegradable. Attempts have been made to synthesize synthetic polymers that are biodegradable, These efforts have centered on those prepared from biodegradable monomers, such as lactic acid.

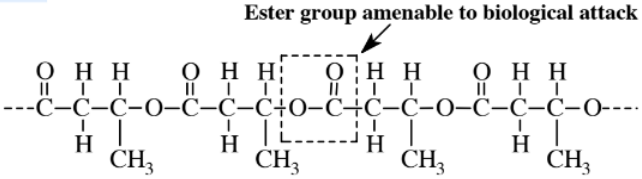
From the standpoint of green chemistry, it is ideal to have polymers that are made by organisms in a form that is essentially ready to use. Recently, interest has focussed on poly (hydroxyalkanoate) compounds, of which the most common are polymers of 3-hydroxybutyricacid:



$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle \overset{\displaystyle O}{H}}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-H$$

3-Hydroxybutyric acid

This compound and related ones have both a carboxylic acid (-CO_2H) and an alcohol (-OH) group. As discussed in Section 6.4 and shown in Reaction 6.4.1, a carboxylic acid can bond with an alcohol with the elimination of a molecule of H_2O forming an *ester linkage*. Since the hydroxyalkanoates have both functional groups, the molecules can bond with each other to form polymer chains:



Ester group amenable to biological attack

Segment of poly(3-hydroxybutyrate) polymer

Ester groups are among the most common in a variety of biological compounds, such as fats and oils, and organisms possess enzyme systems that readily attack ester linkages. Therefore, the poly(hydroxyalkanoate) compounds are amenable to biological attack. Aside from their biodegradability, polymers of 3-hydroxybutyric acid and related organic acids that have -OH groups on their hydrocarbon chains (alkanoates) can be engineered to have a variety of properties ranging from rubberlike to hard solid materials.

It was first shown in 1923 that some kinds of bacteria make and store poly(hydroxy-alkanoate) ester polymers as a reserve of food and energy. In the early 1980s it was shown that these materials have thermoplastic properties, meaning that they melt when heated and resolidify when cooled. This kind of plastic can be very useful, and the thermoplastic property is rare in biological materials. One commercial operation was set up for the biological synthesis of a polymer in which 3-hydroxybutyrate groups alternate with 3-hydroxyvalerate groups, where valeric acid has a 5-carbon atom chain. This process uses a bacterium called *Ralstonia eutropia* fed glucose and the sodium salt of propionic acid (structural formula in Figure 14.6) to make the polymer in fermentation vats. Although the process works, costs are high because of problems common to most microbial fermentation synthesis processes: The bacteria have to be provided with a source of food, yields are relatively low, and it is difficult to isolate the product from the fermentation mixture.

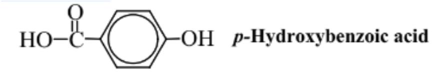
Developments in genetic engineering have raised the possibility of producing poly(hydroxyalkanoate) polymers in plants. The plant *Arabidopsis thaliana* has accepted genes from bacterial *Alcaligenes eutrophus* that have resulted in plant leaves containing as much as 14% poly(hydroxybutyric acid) on a dry weight basis. Transgenic *Arabidopsis thaliana* and *Brassica napus* (canola) have shown production of the copolymer of 3-hydroxybutyrate and 3-hydroxyvalerate. If yields can be raised to acceptable levels, plant-synthesized poly(hydroxyalkanoate) materials would represent a tremendous advance in biosynthesis of polymers because of the ability of photosynthesis to provide the raw materials used to make the polymers.

14.11: Bioconversion Processes for Synthetic Chemicals

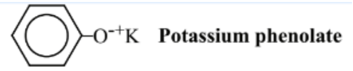
Most of the biochemical operations described so far in this chapter pertain to natural products which, by their nature, would be expected to be amenable to the action of enzymes. The mild conditions under which enzymes operate, the readily available, safe reagents that they employ, such as molecular O_2 for oxidations, and the high specificity of enzyme catalysts make biocatalyzed reactions attractive for carrying out chemical processes on synthetic chemicals, such as those from petroleum sources. This section discusses two examples of enzyme-catalyzed processes applied to chemical processes on synthetic chemicals that would otherwise have to be performed with chemical reagents under much more severe conditions.

p-Hydroxybenzoic Acid from Toluene

The potential for use of biosynthesis applied to synthetic chemicals can be illustrated by the synthesis of *p*-hydroxybenzoic acid

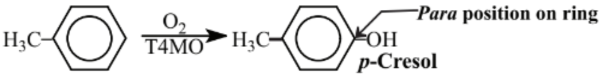


an important intermediate used in the synthesis of pharmaceuticals, pesticides, dyes, preservatives, and liquid crystal polymers currently made by reacting potassium phenolate,



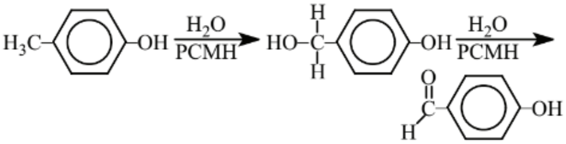
with carbon dioxide under high pressure at 220°C, which converts slightly less than half of the potassium phenolate to the desired product and produces substantial impurities. The process dates back to the early 1860s almost 150 years ago, long before there were any considerations of pollutants and wastes. It requires severe conditions and produces metal and phenol wastes. Reactive alumina powder (Al_2O_3) used to catalyze the process has been implicated in a 1995 explosion at a facility to produce *p*-hydroxybenzoic acid that killed 4 workers.

A biosynthetic alternative to the synthesis described above has been attempted with *Pseudomonas putida* bacteria genetically engineered to carry out several steps in the synthesis of *p*-hydroxybenzoic acid starting with toluene. A key to the process is the attachment at the *para* position on toluene of a hydroxyl group by the action of toluene-4-monooxygenase (T4MO) enzyme system transferred to *Pseudomonas putida* from *Pseudomonas mendocina*:



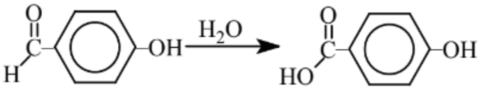
(14.10.1)

The next step is carried out by *p*-cresol methylhydroxylase (PCMH) enzyme from a strain of *Pseudomonas putida* that yields *p*-hydroxybenzyl alcohol followed by conversion to *p*-hydroxybenzaldehyde:



(14.10.2)

The last step is carried out by an aromatic aldehyde dehydrogenase enzyme designated PHBZ also obtained from a strain of *Pseudomonas putida* and consists of the conversion of the aldehyde to the *p*-hydroxybenzoic acid product:

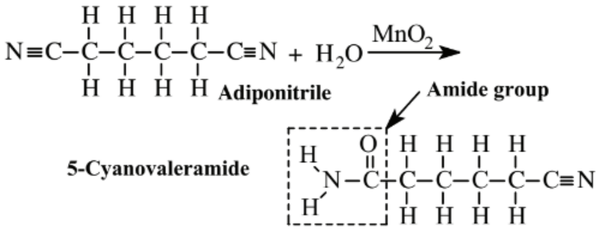


(14.10.3)

Through elegant genetic manipulation, the chemical processes described above were achieved leading to the desired product. In addition to providing the enzymes to carry out the desired steps, it was also crucial to block steps that would consume intermediates and give undesired byproducts that would consume raw material and require separation from the product. Although it is a long way from showing that the complex biochemical synthesis process actually gives the desired product to the final goal of having a practical process that can be used on a large scale, the results described above certainly show the promise of transgenic organisms in carrying out chemical syntheses.

Production of **5-Cyanovaleramide**

The second biocatalyzed process to be considered is the conversion of adiponitrile to 5-cyanovaleramide. This conversion was required for the synthesis of a new chemical used for crop protection. This process can be carried out chemically with a stochichiometric mixture of adiponitrile with water and a manganese dioxide catalyst under pressure at 130°C as shown by the following reaction:



(14.10.4)

If the reaction is run to 25% completion, an 80% selectivity for the 5-cyanovaleramide is achieved, with the other fraction of the adiponitrile that reacts going to adipamide, in which the second C≡N functional group is converted to an amide group. Carrying the reaction beyond 25%completion resulted in unacceptable levels of conversion to byproduct adipamide.

The isolation of the 5-cyanovaleramide product from the chemical synthesis described above entails dissolving the hot reaction mixture in toluene solvent, which is then cooled to precipitate the product. The unreacted adiponitrile remains in toluene solution from which it is recovered to recycle back through the reaction. For each kilogram of 5-cyanovaleramide product isolated, approximately 1.25 kg of MnO_2 required disposal; this is definitely not a green chemical process!

As an alternative to the chemical synthesis described above, a biochemical synthesis was developed using organisms that had nitrile hydratase enzymes to convert the C≡N functional group to the amide group.[2] The microorganism chosen for this conversion was designated *Pseudomonas chloroaphis* B23. The cells of this organism were immobilized in beads of calcium alginate, the salt of alginic acid isolated from the cell walls of kelp. It was necessary to run the process at 5°C above which temperature the enzyme lost its activity. With this restriction, multiple runs were performed to convert adiponitrile to 5-cyanovaleramide. During these runs, 97% of the adiponitrile was reacted with only 4% of the reaction going to produce byproduct adipamide. The water-based reaction mixture was simply separated mechanically from the calcium alginate beads containing the microorganisms, which were then recycled for the next batch of reactant. The water was distilled off of the product to leave an oil from which the 5-cyanovaleramide product was dissolved in methanol, leaving adipamide and other byproducts behind. In contrast to the enormous amount of waste catalyst produced in the chemical synthesis of 5-cyanovaleramide, only 0.006 kg of catalyst waste residue was produced per kg of product. The waste microbial catalyst was 93% water, so its disposal was not a problem.

14.12: Bamboo - Ancient Material for the Future

Bamboo is a term given to large, fast-growing woody grasses including 1250 species within 75 genera ranging from small grassy plants that can substitute for lawn grass to giant bamboo or tree bamboo with stems 30 cm thick and comparable to trees in size. Bamboo has been used since ancient times and has approximately 1,500 applications, especially in Asia. These include structural and reinforcing fiber materials, paper, textiles, food, and fuel. Bamboo is a very strong material with a tensile strength comparable to that of steel. Bamboo textiles are now being used as substitutes for cotton. Although the separation from bamboo of fibers suitable for fabrics is a challenge, the fact that bamboo produces these fibers at a rate several times that of cotton makes bamboo fabrics very attractive as a cotton substitute.

Bamboo propagates primarily by rhizomes, underground stems that grow horizontally and that produce shoots and roots as they spread (good for reproduction but not desirable for neighboring areas where bamboo growth is not wanted). After harvesting, bamboo re-grows from its underground rhizome structure. Bamboo plants typically increase in biomass by 10-30% per year compared to 2-5% annually for trees. The annual yield of bamboo wood is about twice that of loblolly pine, a tree noted for its high productivity. The growth rate of some bamboo varieties under favorable conditions can be spectacular, exceeding 20 meters per year in some cases. Bamboo stalks sequester significantly more carbon dioxide and release correspondingly greater amounts of oxygen compared to trees of the same size.

Bamboo almost certainly has a bright future for sustainability as an attractive renewable source of biomass for materials and energy. There are several reasons for this related to the unique and diverse properties of bamboo, its high productivity, and the relatively short cycles over which bamboo can be produced. The production cycle of bamboo is generally much shorter than that of trees and the bamboo is generally harvested after 5-7 years of growth. Arguably, the greatest contribution that bamboo can make is for erosion control because of the dense underground soil-anchoring rhizome systems possessed by some of the more prominent bamboo varieties. Haiti, especially, could benefit from widespread growth of bamboo on eroded slopes denuded of once abundant forests to provide for firewood for cooking.

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1. Werpy, T. and G. Petersen, *Top Value Added Chemicals from Biomass*, U.S. Department of Energy Pacific Northwest Regional Laboratory, Richland, WA, 2004, Vol. 1, available from www.osti.gov/bridge(Vol. 2 on lignin 2007).

2. DiCosimo, Robert, “Biocatalytic Production of 5 Cyanovaleramide from Adiponitrile,”*Green Chemical Syntheses and* Processes, Oxford University Press, New York, 2000, pp.114–125.

Questions and Problems

Access to and use of the internet is assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be "right."

1. Discuss advantages that biological feedstocks have over petroleum. Are there disadvantages?

2. What is a fundamental chemical difference between petroleum and biological feedstocks?

3. Potassium permanganate, sodium dichromate, and hydrogen peroxide may all three be used as reagents to react with organic molecules. What kind of reaction to they cause to occur? Which of these would be regarded as the greenest reagent and why is that so?

4. Name three kinds of reactions used in processing feedstocks. Which is best from the viewpoint of green chemistry?

5. Name several fractions of biomass that can be used for feedstocks. Which of these is the least useful?

6. How are oils extracted from plant sources?

7. Use chemical formulas to make the argument that carbohydrates are a more oxidized chemical feedstock than hydrocarbons.

8. Before the petrochemicals industry developed, the use of coal in making steel gave rise to a major organic chemicals industry? Explain why this was so and list some of the products that were made

9. Name some categories of chemicals routinely produced by fermentation.

10. Which pharmaceutical material has been produced by fermentation for many years?

11. What is the first, most important consideration in developing a fermentation process for production of a chemical?

12. What is the significance of temperature in fermentation processes? What happens if temperature is too high?

13. Which chemical is made in largest quantities by fermentation?

14. In which fundamental respect are plants more efficient producers of material than fermentation?

15. Which relatively recent advance in biotechnology has greatly increased the scope of materials potentially produced by plants?

16. Why are hybrid poplar trees particularly important in the production of raw materials?

17. Describe the structural characteristics of glucose and other carbohydrates that make them good platforms for chemical synthesis.

18. Give a disadvantage and an advantage of the use of cellulose as a source of glucose.

19. List some of the hazards associated with the chemical synthesis of adipic acid used to make nylon.

20. Give a major concern with the use of benzene as a feedstock.

21. What is a chemical characteristic of 3-dehydroshikimic acid that could lead to much greater uses for it?

22. Although the chemical formula of glucose is $C_6H_{12}O_6$, that of the cellulose polymer made from glucose is $(C_6H_{10}O_5)_n$ where n is a large number. Since cellulose is made from glucose, why is the cellulose formula not $(C_6H_{12}O_6)_n$?

23. Why is wood pulp consisting mostly of cellulose, treated with oxidants? Which oxidants are preferred, and which has lost favor?

24. Give some examples of useful chemically modified cellulose. Which of these has proven to be rather dangerous?

25. In ruminant animals that have bacteria in their stomachs that digest cellulose, the rumen bacteria and the organic acids they generate are passed on through the digestive tract where the bacterial biomass is dissolved, with the products and the organic acids previously generated absorbed by the animal as food. Suggest why basic limestone is used in the large batch processes that use rumen bacteria in digesters to produce organic acids from cellulose.

26. Why is it difficult to deal with lignin as a source of chemical feedstocks? What is the current main use of waste lignin?

27. Using internet resources, try to find an example of an operational biorefinery that is either in commercial operation or at a pilot plant level. What materials does it process and how does it process them? What are its main products?

28. Give the main advantage of biopolymers from an environmental viewpoint.

29. Which structural feature of hydroxyalkanoates enables them to make polymeric molecules?

30. What was the original source of poly(hydroxyalkanoate) polymers? How is it now proposed to produce them?

31. Although enzymes have not developed specifically to act upon synthetic compounds, they have some specific advantages that make them attractive for carrying out chemical processes on synthetic compounds. What are some of these advantages?

32. Name two chemicals for which it has been shown that enzymatic processes can actually convert synthetic raw materials to chemical products normally made by nonbiological chemical reactions.

CHAPTER OVERVIEW

15: Sustainable Energy- The Essential Basis of Green Systems

“If enough energy is available by means that are sustainable and that do not end up ruining theenvironment, virtually all sustainability needs may be met.”

15.1: Sustainability and Energy
15.2: What is Energy?
15.3: Radiant Energy from the Sun
15.4: Sources of Energy Used in the Anthrosphere
15.5: Conversions Between Forms of Energy
15.6: Green Technology for Energy Conversion
15.7: Energy Conservation
15.8: Depletable Fossil Fuels
15.9: Carbon Sequestration for Fossil Fuel Utilization
15.10: Nuclear Energy
15.11: Renewable Energy Sources - Solar Energy
15.12: Energy from Wind and Water
15.13: Biomass Energy
15.14: Geothermal Energy
15.15: Hydrogen for Energy Storage and Utilization
Literature Cited and Supplementary References
Questions and Problems

15.1: Sustainability and Energy

Excluding the social and institutional problems of sustainability (as examples those of overpopulation or of vested economic interests that are environmentally counterproductive), sustainability issues are overwhelmingly energy issues. Most environmental and sustainability problems can be solved if abundant sources of energy are available and if they can be used without doing unacceptable harm to the environment. Consider the following:

•Material resources: With abundant energy, materials can be obtained in adequate quantities from sources normally considered to be marginal, such as metals from low-grade ores and organics from unconventional sources (even carbon dioxide can be converted to organics if energy is not an issue).

•Water: Earth has large quantities of water that is not suitable for domestic and other uses. If enough energy is available, saline ocean and ground water can be desalinated by distillation or reverse osmosis and wastewater can be purified to drinking water standards.

• Wastes: With enough energy the volume of municipal wastes can be greatly reduced and converted to a harmless mineral residue. Hazardous wastes can be made nonhazardous, their volume greatly reduced, and placed where they will do no harm.

•Food: Abundant energy enables production of adequate amounts of food. Water desalination, wastewater purification, and pumping water for long distances can provide needed irrigation water. Marginal land can be leveled and terraced and rocks crushed to a size that permits cultivation. High-value specialty foods can be grown inheated greenhouses even during winter.

•Transportation: Sustainable transportation is all about energy and can be achieved with energy-efficient vehicles and electrified rail systems.

•Fuels: Concentrated forms of carbon including biomass and even carbon dioxide can be converted to hydrocarbon fuels for applications for which there are no viable alternatives (such as aircraft) without adding any net amounts of greenhouse-gas carbon dioxide to the atmosphere.

• Dwellings and workplaces: The places where humans live and work can be maintained at comfortable temperatures regardless of harsh conditions outside.

Energy supply as such is not the problem; for example, world coal resources can meet energy needs for several centuries. The problem is that current patterns of energy use are not sustainable. Earth’s peak petroleum production has probably already been reached. Using the remaining petroleum and switching to coal will almost certainly lead to global warming that might destroy Earth as we know it. The great challenge, therefore, is to develop sources of energy that are renewable and sustainable and that do not significantly damage Earth and its environment. A top priority must remain conservation of energy and greatly increased efficiency of energy utilization. Energy alternatives include wind, solar, biomass, geothermal, and nuclear energy sources along with some minor sources such as tidal energy. The use of fossil fuels will not cease and may continue for a long time with sequestration of carbon dioxide from combustion. This chapter discusses the energy alternatives listed above with emphasis upon energy sustainability.

15.2: What is Energy?

Energy is the ability to move matter around, that is, to do work. The movement of atoms and molecules is also a form of energy called **heat**. The energy contained in a moving mass of matter is **kinetic energy**. For example, energy collected from sunlight during the day can be accumulated in rapidly rotating spinning flywheels, then used at night when solar energy is not available. Water pumped into an elevated reservoir is an example of **potential energy** that can be run through a hydroelectric turbine to generate electricity as needed.

Chemical energy is a form of potential energy stored in the bonds of molecules. This energy can be released during chemical reactions, usually as heat but sometimes as electrical or light energy, as bonds are broken and new bonds are formed.

A crawler tractor equipped with a bulldozer for earth-moving illustrates the definition of energy and several forms of energy (Figure 15.1). **Chemical energy** in the form of petroleum hydrocarbons is used to fuel the tractor's diesel engine. In the engine the hydrocarbons combine with oxygen from air,

$$2\,C_{16}H_{34} + 49\,O_2 \rightarrow 32\,CO_2 + 34\,H_2O + \text{heat energy} \tag{15.2.1}$$

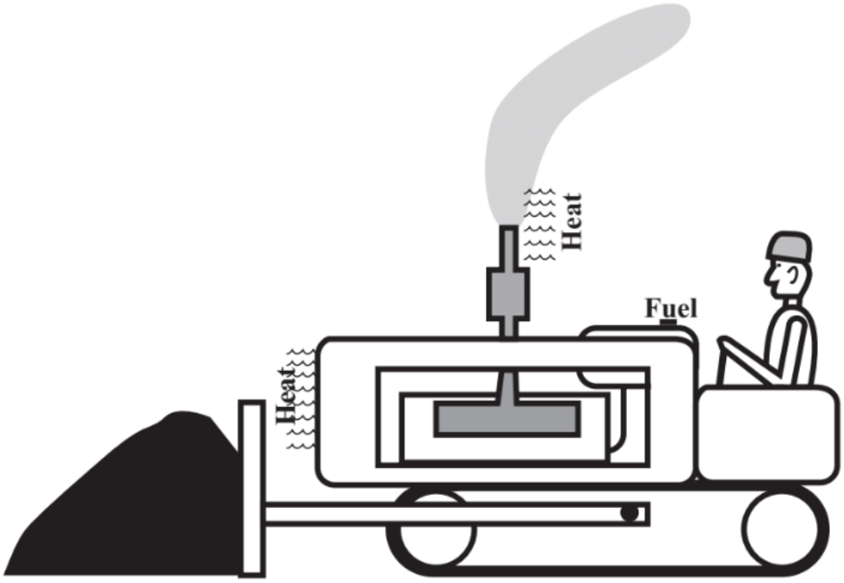


Figure 15.1. Conversion of chemical energy in diesel fuel to mechanical energy in an earth-moving operation through the intermediate production of heat energy. More than half of the chemical energy released in the combustion of the fuel in the tractor's engine is dissipated as heat dispersed through the engine's exhaust and cooling system

to produce **heat energy**. As the hot gases in the engine's cylinders push the pistons down, some of this heat energy is converted to **mechanical energy**, which is transferred by the engine crankshaft, gears, axle, and tracks to propel the tractor forward. A blade or other implement attached to the tractor moves soil.

The energy released in a chemical reaction results from the difference in energies between the bonds in the reactants and the energy of the bonds in the products. An example calculation is shown for the combustion of a mole of methane in Chapter 5, Section 9.5.

Energy Units and Thermodynamics

The standard unit of energy is the **joule**, abbreviated **J**. A total of 4.184 J of heat energy will raise the temperature of 1 g of liquid water by 1°C. This amount of heat is equal to 1 **calorie** of energy (1 cal = 4.184 J), the unit of energy formerly used in scientific work. A joule is a small unit, and the kilojoule, kJ, equal to 1000 J is widely used in describing chemical processes. The"calorie" commonly used to express the energy value of food (and its potential to produce fat) is actually a kilocalorie, kcal, equal to 1000 cal.

Power refers to energy generated, transmitted, or used per unit time. The unit of power is the **watt** equal to an energy flux of 1 joule per second (J s-1). A compact fluorescent light bulb adequate to illuminate a desk area might have a rating of 21 watts. A large powerplant may put out electricity at a power level of 1000 **megawatts** (mw, where one mw is equal to 1 million watts).

Power on a national or global scale is often expressed in **gigawatts**, each one of which is equal to a billion watts or even **terawatts**, where a terawatt is equal to a trillion watts.

The science that deals with energy in its various forms and with work is **thermodynamics**. There are some important laws of thermodynamics. The **first law of thermodynamics** states that energy is neither created nor destroyed. This law is also known as the **law of conservation of energy**. As an example of the application of this law, consider Figure 15.1. The energy associated with moving earth enters the system as chemical energy in the form of diesel fuel, and the oxygen from the air required for its combustion. This is a valuable form of concentrated chemical energy that can be used to propel a tractor or locomotive, in a turbine attached to a generator for the generation of electrical energy, or as a fuel to generate heat in an oil-fired furnace. The fuel is burned in the tractor’s engine, and more than half of its energy is dissipated as heat to the surroundings. The rest is used to move the tractor and dirt. The energy originally contained in a concentrated useful form in the diesel fuel is not destroyed, but it is dissipated in a dilute form, mostly to warm the surroundings very slightly.

The first law of thermodynamics must always be kept in mind in the practice of green chemistry. The best practice of green chemistry and, indeed, of all environmental science, requires the most efficient use of energy as it goes through a system. The availability of energy is often the limiting factor in using and recycling materials efficiently.

15.3: Radiant Energy from the Sun

The sun is the ultimate source of most of the energy that we use. How much energy does Earth receive from the sun? If the sun were to abruptly "go out" (not to worry, it won't happen for another billion years or so) we would quickly find out, because within hours Earth would become a frozen rock in space. In fact, the **solar flux**, which is the rate at which solar energy is transmitted through space at Earth's distance from the sun is 1.34×103watts/m2. What this means, as illustrated in Figure 15.2, is that a 1 square meter area (a square just over 3 feet to the side) with the sun shining perpendicular to it just above Earth's atmosphere receives energy at a rate of 1,340 watts. A watt is a measure of power, that is, energy per unit time. A power level of 1,340 watts is enough to easily power an electric iron or toaster and would provide the energy equivalent to 13100-watt incandescent bulbs plus a 40-watt bulb.

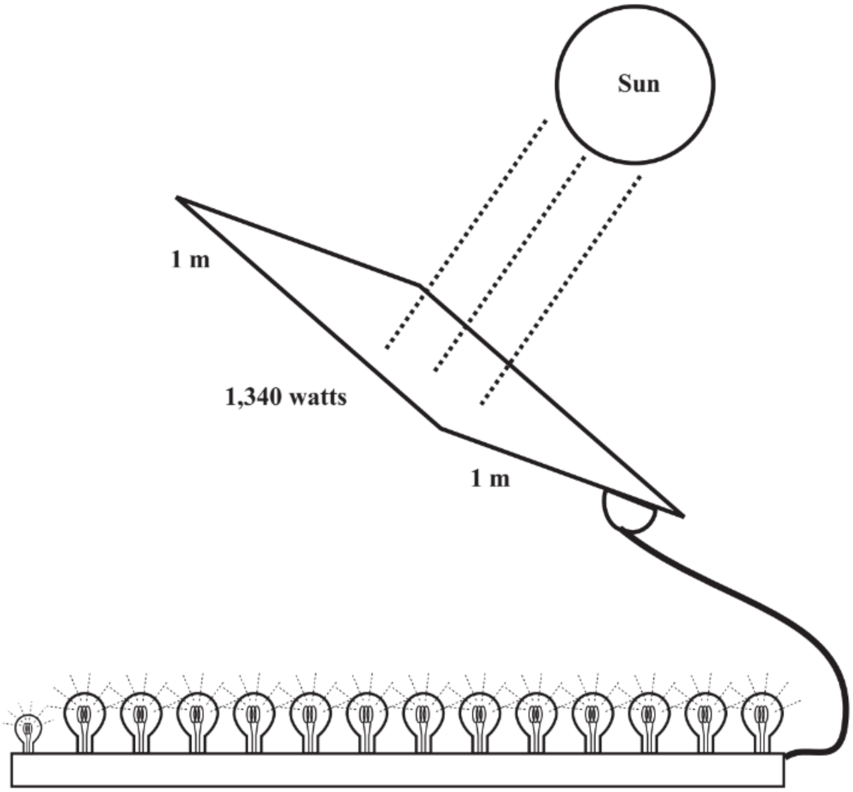


Figure 15.2. The solar flux at the distance of Earth from the sun is 1,340 watts/m2. This amount of power is equivalent to that consumed by 13 100-watt incandescent light bulbs plus a 40-watt bulb

Where does the sun get all this energy? It gets it by consuming itself in a gigantic thermonuclear fire, the same basic process that gives a "hydrogen bomb" its enormous destructive force. The fuel for the sun is ordinary hydrogen. But the energy-yielding reaction is not an ordinary chemical reaction. Instead, it is a **nuclear reaction** in which the nuclei of 4 hydrogen atoms fuse together to produce the nucleus of a helium atom of mass number 4, plus 2 positrons, subatomic particles with the same mass as the electron, but with a positive, instead of a negative, charge. There is a net loss of mass in the process (in nuclear reactions mass **can** change) and this loss translates into an enormous amount of energy. The fusion of only 1 gram of hydrogen releases as much energy as the heat from burning about 20 tons of coal. Using superscripts to express mass number and subscripts for charge, the thermonuclear fusion of hydrogen in the sun may be expressed as follows:

$$4\,{}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1}\mathrm{e} + \mathrm{energy} \tag{15.3.1}$$

15.4: Sources of Energy Used in the Anthrosphere

Until about 1800 the sun provided virtually all of the energy used by humans. Biomass produced by photosynthesis was burned for heat or used to feed horses, oxen, and even human who provided muscle power. Wind resulting from uneven solar heating of air masses powered sailing ships and windmills. The solar powered hydrologic cycle produced running water that drove water wheels.

Around 1800 the dramatically increased use of coal began the era of fossil fuel energy sources. This use was enabled by the invention of the steam engine, which provided abundant and reliable power for stationary sources and locomotives and the power used for mining the coal. By 1900 coal was the dominant energy source in industrialized societies, but petroleum, especially well suited as fuel for the newly developed internal combustion engine, began a century of rapid development, becoming the favored fuel for transportation. Often encountered in wells drilled for petroleum, natural gas also developed during the 1900s, predominantly as a fuel for non-transportation needs. During this century hydroelectric power took on a significant share of electrical power production and remains a substantial renewable energy source. By around 1975, nuclear energy was supplying significant amounts of electricity and has maintained an appreciable share worldwide until the present. Miscellaneous renewable sources including geothermal and, more recently, solar and wind energy are making increasing contributions to total energy supply. Biomass still contributes significantly to the total of the sources of energy used and will become even more important as emphasis on renewable sources increases.

Figure 15.3 shows U.S. and world energy sources as of 2009. The overwhelming reliance on **fossil fuel** petroleum, natural gas, and coal are obvious. These are non-renewable energy sources. Figure 15.4 shows estimated original amounts of these fuels based on data from around 1970. Although the amounts of these fuels based upon more modern estimates would certainly differ, the proportions should be roughly the same. The predominance of coal and lignite is obvious.

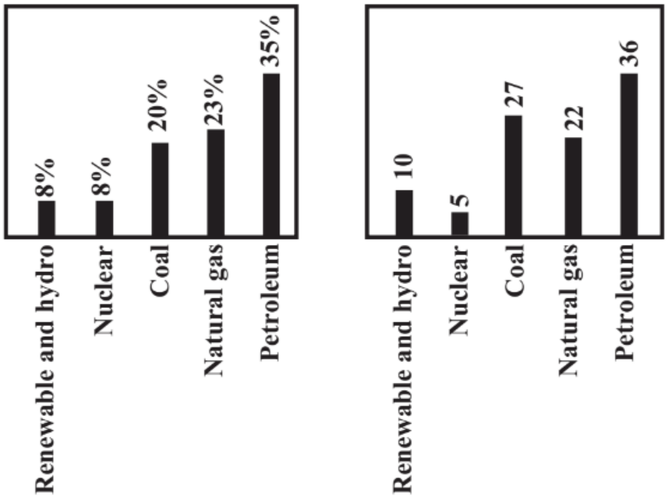


Figure 15.3. U.S. (left) and world (right) sources of energy. Percentages of total rounded to the nearest 1%.

Coal and lignite are the fuels that contribute the most carbon dioxide to the atmosphere per unit of energy generated. A measure of this contribution for fossil fuels is the ratio of water produced per molecule of carbon dioxide generated; greater relative amounts of water mean that more of the energy comes from burning chemically bound hydrogen which does not produce carbon dioxide. The best fuel in this respect is natural gas composed of methane, CH_4, which burns according to the reaction

$$\mathrm{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O + energy} \tag{15.4.1}$$

producing two molecules of water per molecule of carbon dioxide. For liquid petroleum, approximate empirical formula CH_2, there is one molecule of H_2O generated per molecule of CO_2 and for coal, approximate empirical formula $CH_{0.8}$, there is somewhat less than 1/2 of a molecule of H_2O for each CO_2 molecule released.

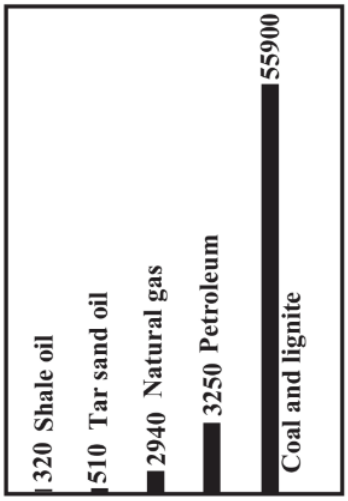
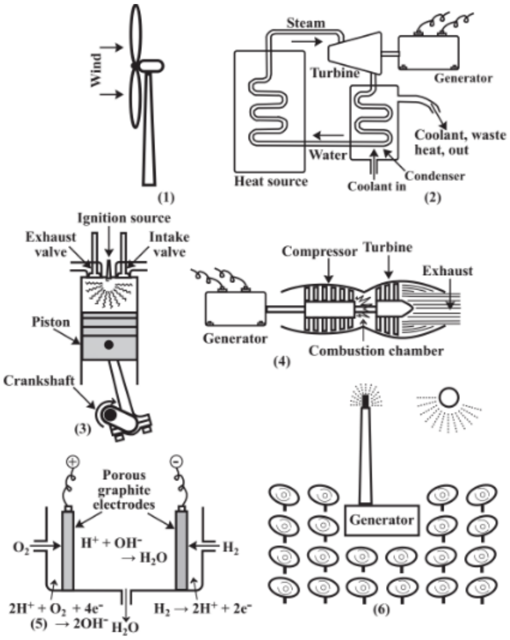


Figure 15.4. Estimated original amounts of the world's recoverable fossil fuels from 1971 (quantities in thermal petawatt hours of energy based upon data taken from M. K. Hubbert, "The Energy Resources of the Earth," in *Energy and Power*, W. H. Freeman and Co., San Francisco, 1971. A petawatt is 10^{15} watts).

15.5: Conversions Between Forms of Energy

The most abundant sources of energy are usually not directly useful and must be converted to other forms. Therefore, much of what is done with energy involves changing it from one form to another. As an example, the nuclear energy that can be extracted from a few kilograms of natural uranium is enormous. But in order to get any benefit from it, the uranium must first be enriched in the isotope whose nucleus can undergo fission (split) to release the energy, the enriched uranium must be placed in a nuclear reactor where fission occurs, converting the nuclear energy to heat, this heat is used to produce steam, the steam is run through a turbine to produce mechanical energy, and the turbine is coupled to a generator to convert its mechanical energy to electrical energy. The various conversions of energy from one form to another occur with different efficiencies. The successful practice of industrial ecology tries to maximize the efficiencies of energy conversion.

Figure 15.5 shows some of the most common devices for converting energy from one form to another and Figure 15.6 illustrates important energy conversions along with the percentage efficiencies with which some of these conversions can be carried out. Examination of the different percentage efficiencies for energy conversion given in Figure 15.6 shows differences ranging from very low to almost 100%. But they point to areas in which improvements may be sought. For example, photosynthesis is less than about 0.5% efficient in converting light energy to chemical energy. Despite this dismal figure, photosynthesis has generated the fossil fuels from which industrialized societies now get their energy and provides a significant fraction of energy in areas where wood and agricultural wastes are used. The intriguing possibility is suggested that genetically modified plants may be developed with much higher photochemical efficiencies, leading to greatly increased use of renewable biomass as an energy source. The poor efficiency of conversion of electricity to light in the incandescent light bulb points to the need to replace these wasteful devices with fluorescent bulbs that are 5 or 6 times more efficient.



(1) A turbine converts kinetic energy in a moving fluid to mechanical energy then to electrical energy through a generator; (2) a steam power plant in which high-energy fluid is produced by vaporizing water in a heat source such as a fossil-fueled boiler, nuclear reactor core, or solar heat collector; (3) reciprocating piston internal combustion engine; (4) internal combustion gas turbine engine from which kinetic energy of hot exhaust gases may be used to propel an aircraft; (5) fuel cell; (6) electricity generation from a solar-heated boiler and turbine generation system

Figure 15.5. Devices for conversion of energy

The most common kind of energy conversion carried out in the anthrosphere is the conversion of heat, produced by chemical combustion processes, to mechanical energy used to propel a vehicle or run an electrical generator. This occurs, for example, when gasoline in a gasoline engine burns, generating hot gases that move pistons in the engine connected to a crankshaft that converts the up-and-down movement of the pistons to rotary motion that drives a vehicle’s wheels. It also occurs when hot steam generated at high pressure in a boiler flows through a turbine connected directly to an electrical generator. Unfortunately, the laws of thermodynamics dictate that the conversion of heat to mechanical energy is always much less than 100% efficient. The Carnot equation,

`\textrm{Percent efficiency} = \frac{T_{1} -T_{2}}{T_{1}} \times 100}`

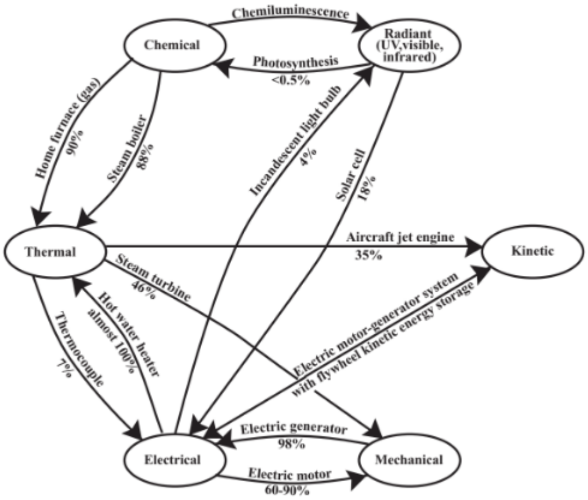


Figure 15.6. Conversion of energy between various forms and energy conversion efficiencies

states that the percent efficiency is a function of the inlet temperature (for example, of steam), T1, and the outlet temperature, T2, both expressed in Kelvin (°C + 273). Consider a steam turbine in which steam impinges on vanes attached to a rapidly rotating shaft. If the inlet temperature is 850K and the outlet temperature is 330 K, substitution into the Carnot equation gives a maximum theoretical efficiency of 61%. An inability to introduce all the steam at the highest temperature combined with friction losses of energy reduce the energy conversion efficiency of most modern steam turbines to just below 50%. Since only about 80% of the chemical energy used to raise steam by combustion of fossil fuel in a boiler is actually transferred to water to produce steam, the net efficiency for conversion of chemical energy in fossil fuels to mechanical energy to produce electricity is about 40%. Fortunately, essentially all the mechanical energy in a rotating turbine can be converted to electricity in the generator to which it is connected, so the overall efficiency of conversion of fossil fuel chemical energy to electricity is about 40%. The conversion of nuclear energy to mechanical energy in a reactor-powered steam turbine is only about 30% because reactor peak temperatures are limited for safety reason.

Another example of the application of the Carnot equation is provided by the internal combustion piston engine shown in Figure 15.5(3) in which a complete cycle consists of (1) a downward stroke sucking air into the cylinder, (2) a compression stroke during which fuel is injected, (3) ignition of the air/fuel mixture forcing the piston down, and (4) an exhaust stroke in which the exhaust gases are forced out through the open exhaust valve as the piston moves upward. The efficiency of the internal combustion engine increases with the peak temperature reached by the burning fuel, which increases with the degree of compression during the compression stroke. This temperature is highest for the diesel engine in which the compression is so high (up to around 20:1) that fuel injected into the combustion chamber ignites without a sparkplug ignition source. Whereas a standard gasoline engine is typically about 25% efficient in converting chemical energy in fuel to mechanical energy, a diesel engine is typically 37%efficient, with some reaching higher values.

Fuel Cells

Fuel cells convert the energy released by electrochemical reactions directly to electricity without going through a combustion process and electricity generator. Fuel cells are the primary means for utilizing hydrogen fuel and are becoming more common as electrical generators. The electrode reactions in a fuel cell are shown in Figure 15.5(5) and the net reaction is

$$2\,H_2 + O_2 \rightarrow 2\,H_2O + \text{electricalenergy} \tag{15.5.1}$$

the only product of which is water. A number of different fuel cell types are at various stages of development.[1] Development is underway of solid-oxide fuel cells, operating around 1000°C that produce an exhaust that is hot enough to drive a turbine or cogenerate steam. with steam cogeneration, such systems may be able to develop overall efficiencies of up to 80%

15.6: Green Technology for Energy Conversion

Green technologies have much to do with the important processes by which energy is converted between various forms. Some of the more important aspects of such conversions are discussed here.

Energy Conversion **Efficiency**

Energy is best conserved by efficient energy conversion. Vastly improved energy conversion efficiencies have been achieved in heat engines such as automobile engines and gas turbines by higher combustion temperatures made possible by improved materials and heat-resistant lubricating oils. Computerized design and operation of engines enabling optimum ignition timing, valve timing, and fuel injection have made possible extremely efficient engines.

As noted in the discussion of the Carnot equation above, heat engines typically dissipate more than half of the energy in fuel as heat. A small fraction of this heat is used by heaters in automobiles. In stationary power plants much of this energy can be reclaimed for heating buildings or chemical processes with **combined power cycles**. as illustrated in Figure 15.7. Typically, in combined power cycle installations gas or fuel oil is burned in a turbine engine that is much like the engine of a turboprop airplane, and the rotating shaft of this engine is coupled to a generator to produce electricity. The hot exhaust gases from the combustion turbine can be injected into a boiler where their heat turns liquid water to steam. This steam can be run through a steam turbine coupled to a generator to produce more electricity. Steam leaving the steam turbine still contains a lot of heat, and can be conveyed to homes and other structures for heating. The water condensed from this steam is pure and is recycled to the boiler, thus minimizing the amount of makeup boiler feedwater, which requires expensive treatment to make it suitable for use in boilers. Such a system as the one described is in keeping with the best practice of industrial ecology. Heating with steam that has been through a steam turbine, a concept known as **district heating**, is commonly practiced in Europe (and many university campuses in the U.S.) and can save large amounts of fuel otherwise required for heating.

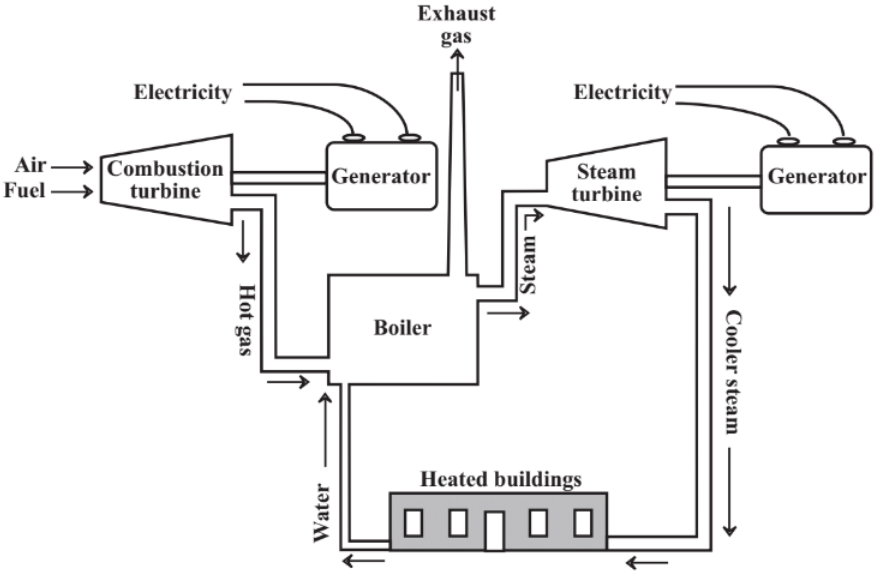


Figure 15.7. A combined power cycle in which natural gas or oil is first used to fire a gas turbine connected to an electrical generator. The hot exhaust gases from this turbine are fed to a boiler to produce steam, which drives a steam turbine, also connected to a generator. The still hot exhaust steam from the steam turbine is distributed to residential and commercial buildings for heating. The water condensed from the steam used to heat buildings is returned to the power plant to generate more steam, which conserves water and also prevents the necessity of treating more water to the high standards required for a boiler

Conversion Efficiency of Chemical Energy

In some cases a need exists to convert chemical energy from one form to another so that it can be used in a desired fashion. The generation of hydrogen gas from fossil fuels is an important chemical energy conversion process that may become much more widely practiced as fuel cells, which use elemental hydrogen as a fuel, come into more common use. Hydrogen can be obtained from a number of sources. The cheapest and most abundant raw material for hydrogen generation is coal and the same general processes can be applied to other carbon-containing materials, especially renewable biomass. When carbon-based materials are used to generate hydrogen, the hydrogen actually comes from steam. In this process, known as **coal gasification** part of the coal is burned in an oxygen stream,

$$\mathrm{C(coal)} + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{heat} \tag{15.6.1}$$

leaving a solid residue of very hot carbon from the unburned coal. This material reacts with water in steam,

$$\mathrm{C(hot)} + \mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{CO} \tag{15.6.2}$$

to generate elemental H_2 and CO in a reaction that absorbs heat. The CO can be reacted with more steam over an appropriate catalyst,

$$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{CO_2} \tag{15.6.3}$$

to increase the ratio of H_2 to CO.

The reactions shown above for the generation of elemental hydrogen from coal and water have been used for well more than a century in the coal gasification industry. Before natural gas came into common use, steam blown over heated carbon was used to generate a **synthesis gas** mixture of H_2 and CO that was piped into homes and burned for lighting and cooking. The mixture burned well, but, in addition to forming treacherous explosive mixtures with air, it was lethal to inhale because of the toxic carbon monoxide. But the process may have a future for the generation of elemental hydrogen for use in fuel cells. By using pure oxygen as an oxidant, it raises the possibility of producing greenhouse gas carbon dioxide in a concentrated form that can be pumped underground or otherwise prevented from getting into the atmosphere. Retention of carbon dioxide in this manner is called **carbon sequestration** and is the subject of some intense research.

The synthesis gas mixture of H_2 and CO_2 is a good raw material for making other chemicals, including hydrocarbons that can be used as gasoline or diesel fuel. Combined in the correct ratios over a suitable catalyst, these two gases can be used to make methane, the main constituent of natural gas:

$$\mathrm{CO} + 3\,\mathrm{H_2} \rightarrow \mathrm{CH_4} + \mathrm{H_2O} \tag{15.6.4}$$

15.7: Energy Conservation

Particularly with the development of an automobile-based economy and society, energy has been wasted to a shocking extent in the U.S. and some other industrialized nations. This points to the opportunity afforded by energy conservation as the most effective means of providing adequate energy. The potential for energy conservation is illustrated by the fact that some nations that have living standards near or even exceeding those of the U.S. have much lower energy consumption per capita.

On a positive note, energy use in the U.S. fell 5% to 94.6 quadrillion British thermal units (BTU) in 2009 from 99.2 quadrillion BTU in 2008, the largest year-to-year drop since the U.S.government started keeping track of energy consumption in 1949. Declines were registered in residential, commercial, industrial, and transportation sectors. Although much of the decline was due to a sharp decrease in economic activity, a significant portion was due to more energy-efficient appliances, automobiles, and other energy-consuming devices. The year also showed a significant increase in renewable wind, solar, and hydro power sources.

As illustrated in Figure 15.8, increases in the efficiency of energy utilization can contribute favorably to higher economic standards. This plot shows past and realistic future estimates of trends of the ratio of energy use per unit of gross domestic product reflecting a steady decrease in energy required per unit of economic output. Furthermore, well developed economies are more efficient users of energy. For the year 2000, the production of $1000 of gross domestic product in developed nations required 1.7 barrels of oil equivalents compared to 5.2 barrels for nations with less developed economies that lack means to utilize energy efficiently. This indicates that as the economies of less industrially advanced nations evolve with energy conservation as a top priority significant economic development with reduced energy consumption can be achieved. This kind of development combined with more efficient energy utilization in developed nations including measures such as smaller, more fuel efficient dwellings and vehicles can make a major favorable impact on energy demand.

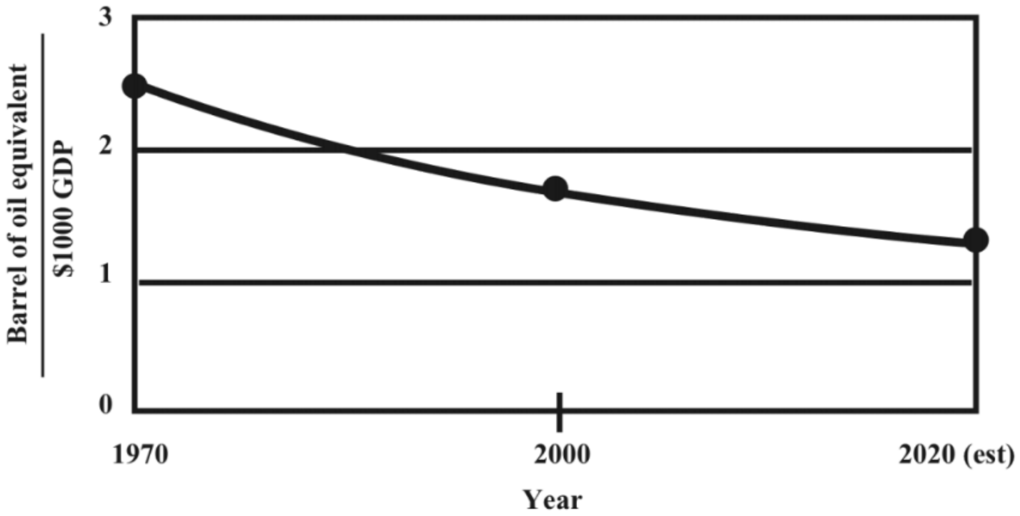


Figure 15.8. Plot of barrel of oil equivalent required per $1000 gross domestic product (GDP) as a function of year in industrialized nations.

Although household and commercial uses of energy are relatively efficient they present significant potential for increased energy efficiency. Considering the energy wasted in generating electricity, the all-electric home requires much more energy than one heated directly with fossil fuels. A compactly constructed home (more in the shape of a cube with a full basement) uses significantly less energy than a rambling “ranch style” house constructed on a slab. Apartments and row houses are much more energy-efficient than free-standing homes. Measures such as increased insulation and sealing around windows can save fuel. Waste heat from centrally located electrical power plants can be used for commercial and residential heating and cooling. With proper pollution control, these plants can use municipal refuse for a significant fraction of their fuel thereby reducing quantities of solid wastes requiring disposal.

Saving Energy in the Transportation Sector

The economic sector with the greatest potential for increased energy efficiency is transportation. Private automobiles and commercial aircraft are only about one-third as efficient as trains and buses in moving people. Movement of freight by truck requires 5-6 times as much energy as transport by train. Furthermore, electrified railways are much better adapted to using renewable sources of energy than are private automobiles. trucks, and aircraft.

As illustrated in Figure 15.9, U.S. automobile fuel economy increased impressively from the first "energy crisis" of the 1970s until about 1990. This was achieved along with much lower emissions of exhaust pollutants. Unfortunately, the trend toward better fuel economy, which, if continued would have meant average mileage figures of at least 40 miles per gallon (MPG) by 2010, stopped moving up with increased popularity of outsized vehicles, especially the "sport utility vehicle" type. In 2007 the U.S. Congress passed legislation mandating improved fuel economy for automobiles sold in the U.S. An average of 40 MPG is readily achievable without significantly compromising safety and comfort and has the added benefit of substantially reduced emissions of greenhouse gas carbon dioxide.

Hybrid vehicles that are propelled by an electric motor connected to a battery rechargeable with a small internal combustion engine now deliver impressive fuel economy (Figure 15.10). The improvement is especially pronounced for stop-and-go driving in traffic where at least 50% better mileage figures have been achieved. In operation, the main battery in the vehicle, which is much larger than a conventional automobile battery, but smaller than one required for an all-electric vehicle, is kept charged by the onboard internal combustion engine coupled to a generator. A contribution is also made by regenerative braking that generates electricity during braking. When the vehicle is slowing, coasting downhill, or stopped, the internal combustion engine turns off, which saves fuel.

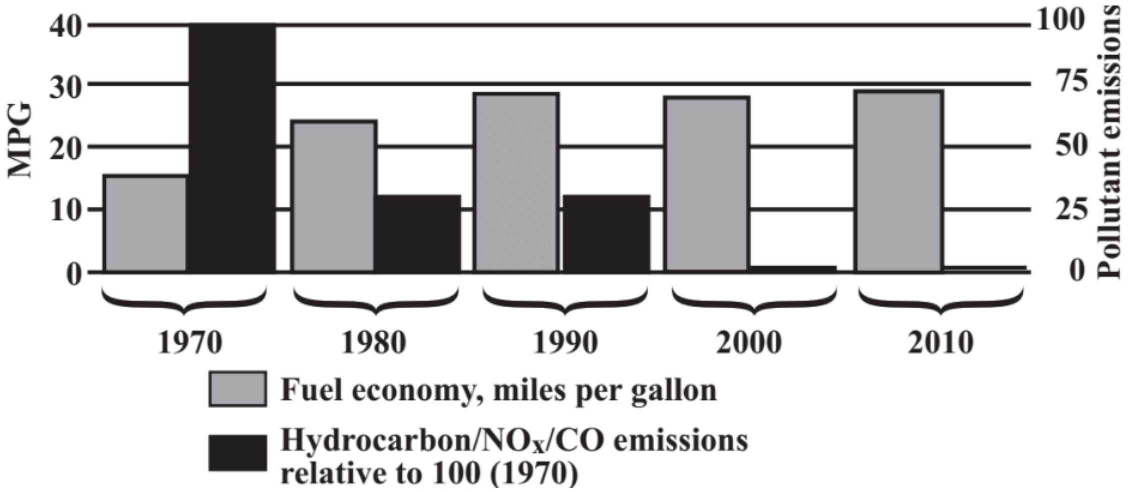


Figure 15.9. U.S. auto fleet fuel economy and emissions over 4 decades. showing a trend of generally higher fuel economy with greatly reduced emissions.

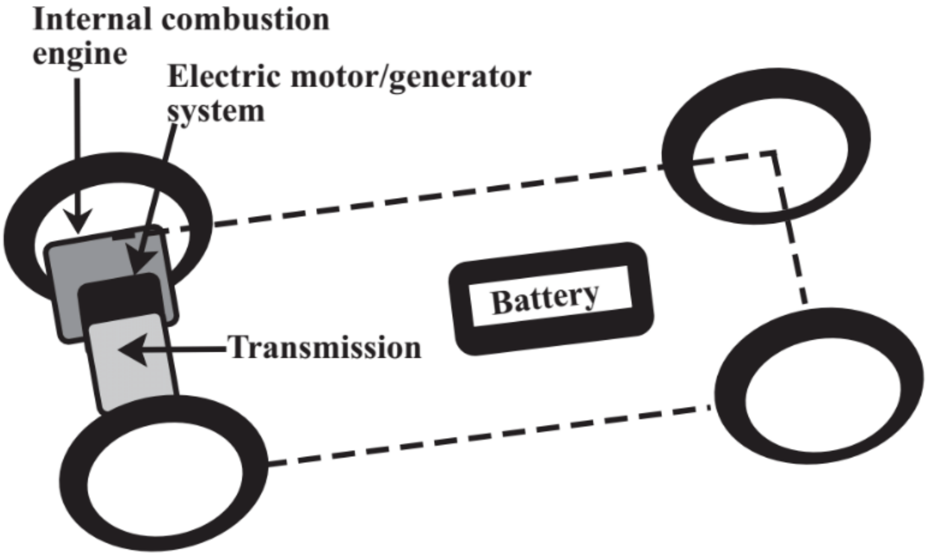


Figure 15.10. Major components of a hybrid automobile. Electrical energy to propel the car and to keep the battery charged is provided by a generator/motor system powered by an internal combustion engine. Energy regenerated during braking is also used to help charge the battery.

Until recently the battery of choice for hybrid vehicles has been the nickel-metal-hydride battery. As of 2010, development was actively underway on hybrid vehicles using lithium ion batteries, which hold a relatively greater charge per unit mass. These batteries can be charged from an external source of electricity providing 40-50 km of driving range before the onboard internal combustion engine has to engage. Charging the battery from an external source is much less expensive than using an internal combustion engine affording rather spectacular fuel economy.

The ultimate in fuel economy could be achieved with an externally rechargeable hybrid vehicle using a diesel engine for onboard recharging. The highly efficient diesel engine, which idles on remarkably little fuel, could be left running at a steady rate for relatively long periods of time, staying hot and greatly reducing emissions, which are highest for a diesel engine during startup, shutdown, and abrupt changes in engine speed.

A natural gas (methane) fueled engine could be an excellent choice for a hybrid vehicle. With recent developments in the exploitation of abundant shale sources of natural gas, this fuel has become readily available in a number of countries including the U.S. A big advantage with methane is that it is a very low pollutant fuel. A limitation with a natural gas engine is the relatively low cruising range. But, coupled with an externally rechargeable battery in a hybrid vehicle, a natural gas engine could provide impressive range and fuel economy. The economy could be further enhanced using stratified charge ignition in which the fuel is injected directly onto the spark plug enabling extremely efficient combustion with a very lean overall fuel/air mixture.[2]

15.8: Depletable Fossil Fuels

Hydrocarbons from Wells

Currently, the most widely used sources of energy are liquid and gaseous hydrocarbons from underground. It is readily seen why liquid petroleum and natural gas became so popular because they are so easy to obtain from holes drilled into the ground, easy to transport by pipeline, and easy to use, especially in home furnaces (natural gas) and internal combustion engines (refined petroleum). But these sources suffer two major disadvantages: (1) They will eventually run out and (2) they contribute greenhouse gas carbon dioxide to the atmosphere.

Liquid petroleum occurs in pores of rock having a porosity of 10-30%, over half of which is normally occupied by water. Primary recovery typically removes about 30% of the crude oil. more advanced recovery techniques by injecting water or pressurized carbon dioxide can remove around 50% of the crude oil. A very sustainable technique is to burn petroleum in a pure oxygen atmosphere to generate electricity, collect the relatively pure CO_2 product, and inject it back into the petroleum-bearing formation to remove more oil. By using advanced techniques that recover up to 60% of the available petroleum, oil fields that have been depleted by formerly used processes can be given a second life and yield as much more oil as they did originally.

The most exciting relatively recent development in utilizing hydrocarbons pumped from below ground consists of the development of methods to remove natural gas (CH_4) from tight shale formations such as the natural-gas-rich Marcellus Shale deposits extending for 600 miles through sections of Virginia, West Virginia, Ohio, Pennsylvania, and New York. Methods have been developed for hydraulic fracturing (“hydrofracking”) these formations and enabling natural gas to flow by injecting water containing additives into the formations under very high pressures. Widespread development of these sources since approximately 2000 has led to a relative abundance of natural gas. Furthermore, since about 1990 natural gas has been extracted from coal seams, many of which are not suitable for mining. There are environmental issues involving water with both of these methods of natural gas extraction. There is some potential with hydrofracking shale formations to contaminate well water with natural gas and a search of the internet can bring up rather spectacular pictures of “burning water” in which natural gas coming out of a water faucet can be lit resulting in a substantial flame. Natural gas withdrawn from coal seams is usually mixed with copious quantities of water which in some cases is polluted.

Fossil Fuels Dug from Below Ground

Large quantities of fossil fuels are dug from below ground, either from underground mines or from surface pits. The largest source of petroleum that is imported into the U.S. is from **tar sands** in the Canadian province of Alberta. These are deposits of sand covered with heavy crude petroleum that are extracted from pits and carried by enormous trucks to locations where the oil is extracted by hot water or steam leaving immense quantities of relatively clean sand.

Another petroleum substitute that can be obtained by mining is **shale oil**, a material bound to oil shale rock in the form of complex organic material of biological origin called kerogen. Shale oil is removed from these rocks by heating in the absence of air. It is believed that as much as1.8.trillion barrels of shale oil could be recovered from deposits in Colorado, Wyoming, and Utah. The story is told that oil shale was discovered in this region by an earlier settler who constructed a fireplace and chimney in a cabin from the shale and was very much distressed when the first fire in the heating facility resulted in its burning, along with the surrounding cabin. Although large amounts of petroleum substitute could be recovered from oil shale, this resource is not likely to be developed on a large scale because the pyrolysis releases enormous amounts of greenhouse gas carbon dioxide and leaves a residue of ash from which salts such as sodium sulfate are readily leached. Furthermore, the liquid shale oil product contains a high content of potentially carcinogenic organonitrogen compounds.

Coal and Lignite

Coal and related solids are solid carbonaceous fossil fuels formed by the partial biodegradation of ancient biomass followed by geochemical processes involving heat and high pressures. Coal is differentiated largely by **coal rank** based upon percentage of fixed carbon, percentage of volatile matter, and heating value. Although “coal” gives the appearance of being pure carbon, it is actually a complex hydrocarbon-like material, typically with an empirical formula of around $CH_{0.8}$ and containing from 1 to several percent sulfur, nitrogen, and oxygen. Of these elements, sulfur bound to the organic coal molecule and mixed with coal as mineral pyrite, FeS_2, presents major environmental problems because of production of air pollutant sulfur dioxide during combustion. Much of the FeS_2 can be removed physically from coal prior to combustion and sulfur dioxide can be removed from stack gas by various scrubbing processes. Lower rank brown coal and lignite typically have high moisture and bound oxygen contents. Most commonly, coal classified as brown coal is relatively closer in its constitution to the vegetation from which it was formed.

The greatest fraction of electricity production worldwide is from coal burned in boilers to raise steam that runs turbines connected to electrical generators. The potential is high for air pollution from this technique including especially fly ash and sulfur dioxide. These two pollutants are now generally well controlled. However, burning coal releases more greenhouse gas carbon dioxide per unit energy output than any other energy-yielding process and this release can only be controlled by extraordinary (and expensive) means.

Coal Conversion

A sustainable approach to utilizing the coal energy resource is **coal conversion** in which coal is converted to gaseous or liquid fuels or low-sulfur solids. Starting with the house of William Murdocks at Redruth, Cornwall, England, illuminated with coal gas in 1792, coal conversion has along history. Pall Mall in London was lit with gas from the first municipal coal-gas system in1807. The coal-gas industry began in the U.S. in 1816. The first coal gas plants operated by heating coal in the absence of air leaving a solid residue consisting mostly of carbon (that could be used as stove fuel) and produced a hydrocarbon-rich fuel especially effective for lighting. During the 1800s a gasification process was developed in which steam reacted with hot carbon to produce a mixture consisting primarily of H_2 and CO (synthesis gas) to which it was necessary to add volatile hydrocarbons to make the fuel suitable for lighting. There were 11,000 coal gasifiers operating in the U.S. in the 1920s and the industry peaked in 1947 after which it was rapidly replaced by abundant natural gas sources. During World War II Germany made synthetic petroleum from synthesis gas, reaching a capacity of 100,000 barrels per day in 1944. The largest coal-based synthetic fuels plant operating today is in Sasol, South Africa, and now produces hydrocarbons and feedstocks equivalent to about 150,000 barrels of petroleum per day.

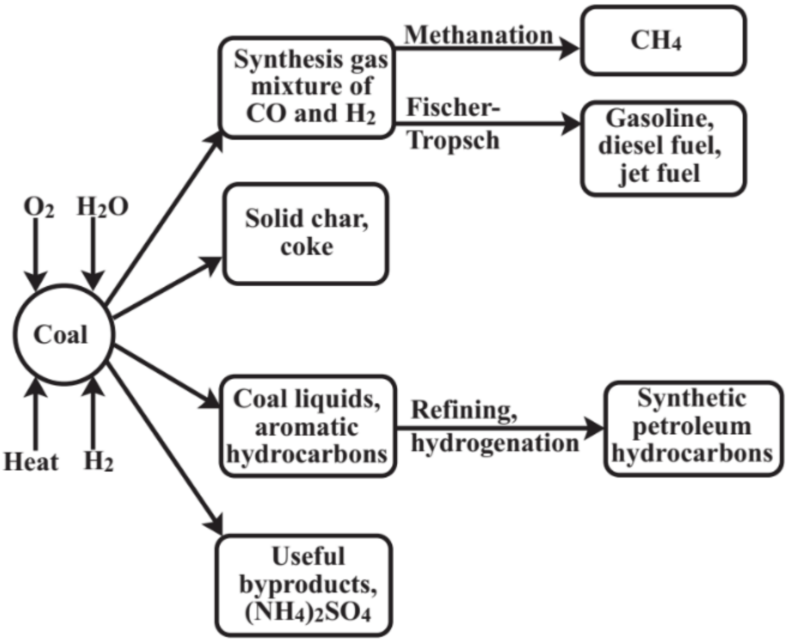


Figure 15.11. Routes to coal conversion. BTU refers to British thermal units, a measure of the heat energy that can be obtained from a fuel. Methanation means synthesis of CH_4 gas. Hydrogenation and hydrotreating refer to reaction with elemental H_2 gas.

Although coal conversion could be developed as a substitute for petroleum, it is by no means a green process considering the environmental costs of coal mining, the production of toxic coal tar byproducts, and the enormous amounts of carbon dioxide generated during the conversion process. As discussed in the following section, the byproduct carbon dioxide can be captured and pumped underground where it can aid in petroleum recover.

15.9: Carbon Sequestration for Fossil Fuel Utilization

Fossil fuels can be used sustainably by employing **carbon sequestration** to retain greenhouse gas carbon dioxide produced in fuel combustion or coal conversion, which by preventing carbon dioxide generated by fossil fuels from entering the atmosphere holds the promise of enabling utilization of fossil fuels without contributing to greenhouse warming. Carbon dioxide can be captured and sequestered deep in the ocean or pumped into porous formations underground. A major concern with oceanic disposal of carbon dioxide is the tendency of this gas to lower pH resulting in thinner shells in shellfish.

The most promising approach to carbon sequestration is to pump carbon dioxide gas into underground formations at depths exceeding 1000 meters. If the formations are overlain with impermeable layers of rock that are not breached by improperly abandoned oil wells, the carbon dioxide will remain in place indefinitely. Sequestration is aided by the presence of saline groundwater and by chemical reaction with minerals.

Carbon dioxide from natural gas that contains a high content of CO_2 has been sequestered since 1996 in the Sleipner oil and gas field about 240 km off the Norwegian coast. The gas is pumped into the 200-m thick Utsira sandstone formation located about 1000 km below the seabed. A mixture of carbon dioxide and toxic hydrogen sulfide is now being disposed underground in Alberta, Canada.

Carbon dioxide is best captured and sequestered in processes such as fermentation of sugars to make ethanol that produce the gas in high concentrations. Because of the high nitrogen contents exhaust gases from combustion are not suitable for carbon dioxide sequestration. Using pure oxygen instead of air for combustion does produce a relatively pure carbon dioxide product and one commercial power plant using coal burned in pure oxygen is now planned with support of the U.S. Department of Energy.

The most promising approach for large-scale carbon dioxide sequestration is through coal gasification (see Section 15.8). There are two major sources of carbon dioxide from coal gasification. The first of these is coal combustion with pure oxygen oxidant,

$$\mathrm{C(coal) + O_2 \rightarrow CO_2 + heat} \tag{15.9.1}$$

which generates the heat required for gasification of the hot carbon residue of coal with steam:

$$\mathrm{C(coal) + H_2O \rightarrow CO + H_2} \tag{15.9.2}$$

The second reaction that produces carbon dioxide is reaction of steam with CO to increase the ratio of H_2 to CO in the synthesis gas product:

$$\mathrm{CO + H_2O \rightarrow H_2 + CO_2} \tag{15.9.3}$$

The largest carbon dioxide sequestration process now operating in the U.S. is the Great Plains Synfuels Plant near Beulah, North Dakota. This plant gasifies 16,000 tons per day of lignite coal and sends approximately 4.3 million cubic meters of carbon dioxide per day (3 million tons per year) through a 330 km pipeline to the Weyburn and Midale oilfields in Saskatchewan, Canada, for sequestration and petroleum recovery.

An integrated coal gasification plant with carbon dioxide sequestration is shown in Figure 15.12. This plant uses the reaction of steam with hot carbon from coal to produce elemental hydrogen (reaction 15.9.2) and reacts the CO product with steam to produce more H_2; both of

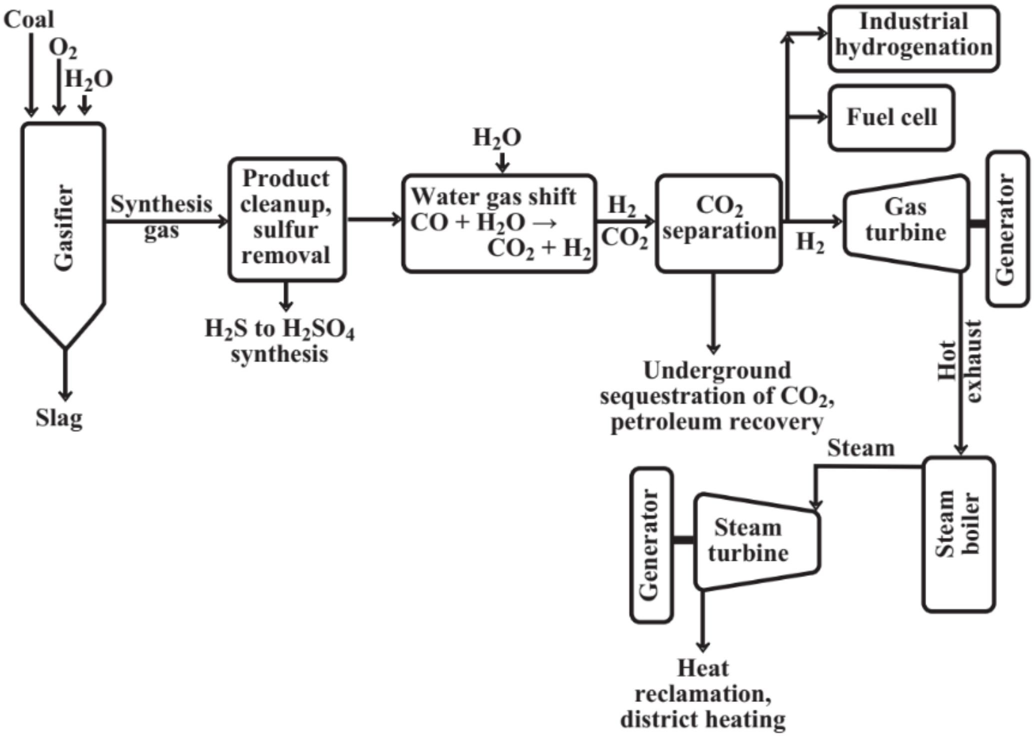


Figure 15.12. An integrated coal gasification plant with carbon dioxide sequestration

these reactions produce CO_2. A gas turbine fueled with H_2 coupled to a generator produces electricity. Hot exhaust gas from the gas turbine is used to raise steam in a boiler and this steam powers a steam turbine that is also coupled to a generator. This combination results in very efficient electrical power generation. The elemental H_2 generated can be used in fuel cells, as a chemical reagent to produce synthetic hydrocarbon fuels, or to synthesize ammonia, NH_3. Some ammonia is also produced from nitrogen in the coal during gasification and is recovered as a product. Sulfur, which occurs in essentially all coals, is released during gasification as byproduct hydrogen sulfide used to make sulfuric acid or disposed with the carbon dioxide byproduct. The CO_2 is separated from the gas and pumped under high pressure into mineral formations at depths up to around 2000 m. If these formations are oil-bearing, the carbon dioxide enables petroleum recovery. Byproduct heat from the plant can be used for district heating. Particularly when it is integrated with byproduct recovery, chemical synthesis of NH_3 and H_2SO_4, and district heating, an integrated plant of this kind is an excellent example of a system of industrial ecology.

Fuel from Carbon Dioxide

An interesting potential use of carbon dioxide is to use it as a source of carbon for the synthesis of hydrocarbon fuels and other organic compounds including alcohols. The requirement for so doing is an abundant and inexpensive source of elemental hydrogen, H_2, which can be reacted with CO_2 through the reverse water-gas shift reaction:[3]

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{15.9.4}$$

The CO produced can be reacted with additional H_2 to produce methane gas (methanation), hydrocarbon liquids (Fischer-Tropsch synthesis), or alcohols. The overall process is the reverse of the energy-yielding combustion of hydrocarbon fuels, so it consumes a lot of energy and requires a cheap source of energy in order to be practical. The most likely energy source is “free” wind power generating electricity that can produce H_2 gas by electrolysis of water (see Reaction 15.11.1). In this application the intermittent characteristic of wind power is not an issue and hydrogen produced in abundance during times of strong wind can be pumped underground to be withdrawn for subsequent reaction with CO_2 and CO.

15.10: Nuclear Energy

Nuclear energy is generated by the neutron-induced fissioning of heavy atomic nuclei, most commonly those of the uranium isotope with a mass number of 235 or plutonium with a mass number of 239, to produce radioactive fission products, an average of 2.5 more neutrons and an astounding amount of energy compared to an ordinary chemical reaction. A typical example of such a fission reaction is the following:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{133}_{51}\mathrm{Sb} + {}^{99}_{41}\mathrm{Nb} + 4\,{}^{1}_{0}\mathrm{n} \tag{15.10.1}$$

A nuclear reactor operating at a constant power level is controlled such that on average 1 neutron from each fission reaction is absorbed to cause another fission reaction, thus sustaining a **chain reaction**. The excess neutrons are absorbed by nonfissionable material. In order to cause the desired fission, the neutrons, initially released as rapidly moving, high energy particles must be slowed down, which is done by a **moderator**, such as water, in the reactor.

The basic function of a nuclear power reactor is to serve as a heat source to produce steam used to generate mechanical energy. The basic components of a nuclear power reactor are shown in Figure 15.13. Pressurized superheated water circulates through the hot reactor core in an enclosed loop (to prevent escape of radioactive contaminants). Heat from this water is used to convert water to steam in a heat exchanger. The rest of the power plant is like a conventional fossil-fueled plant with a steam turbine coupled to a generator and the steam from the steam turbine being condensed to provide liquid water for the heat exchanger.

Although only 0.71% of natural uranium is fissionable uranium-235, and uranium to be used for fission must be enriched in this isotope, there is an adequate global supply of uranium. In principle, the remaining 99.28% of uranium that consists of uranium-238 could be converted to fissionable plutonium by absorption of neutrons in **breeder reactors**. Plutonium is actually generated by uranium-238 absorbing neutrons in a conventional nuclear power reactor, and after the reactor has operated for a few months after refueling, a large fraction of its energy output comes from plutonium generated in the reactor.

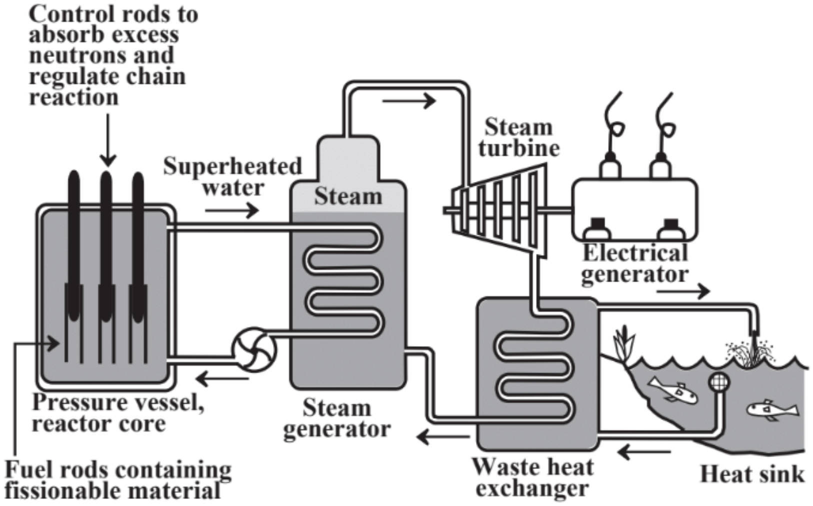


Figure 15.13. Nuclear fission reactor for electrical power generation.

An interesting possibility for breeder reactors is the liquid-sodium-cooled **travelling wave reactor** in which a relatively small segment at the end of a mass of uranium held in an array of fuel rods is enriched in fissionable uranium-235. The fission process is initiated in this portion of the fuel and neutrons from it migrate to the adjacent non-enriched segment where they are absorbed by uranium-238 to produce fissionable plutonium-239. This builds up a sector containing enough plutonium to sustain fission and the nuclear fission process very slowly and continuously migrates into the area with the newly fissionable material. With proper design such a reactor can function for decades before the “wave” reaches the end of the mass of uranium and no more fissionable material is produced to sustain fission.

A major issue with nuclear power reactors is posed by the **high-level nuclear wastes** consisting of radioactive fission products generated when the uranium nucleus splits apart and the radioactive transuranic elements produced when uranium nuclei absorb neutrons. Some of the radioactive fission products may last for several centuries and some of the transuranic isotopes remain lethal for thousands of years. At the present time, spent fuel elements are being stored under water at the reactor sites. This is actually a good thing because the short-lived fission products that are responsible for most of the radioactivity in nuclear fuel freshly removed from a reactor decay rapidly, and after a few years of storage only a small fraction of the original activity is present. Under current regulations in most countries, the wastes from this fuel will eventually have to be buried. A better alternative is to process the material in the spent fuel elements to remove radioactive products from uranium fuel. The relatively short-lived fission products decay spontaneously within several hundred years and can be stored in a secure location for several centuries. The longer-lived nuclear transuranic wastes can be bombarded with neutrons in nuclear reactors, a process of **transmutation** in which the elements are converted to other elements or fission products with shorter half lives resulting in relatively rapid production of stable isotopes. Radioactive waste elements for which transmutation is feasible include plutonium, americium, neptunium, curium, technetium-99, and iodine-129. Plutonium, americium, neptunium, and curium are heavy actinide elements that are fissionable and add fuel value in a nuclear reactor.

Another problem with nuclear reactors is their decommissioning. One option is to dismantle the reactor soon after it is shut down using apparatus operated by remote control. The radioactive reactor parts are then disposed. Another approach is to allow the reactor to stand for 30–100 years before dismantling, by which time most of the radioactivity has decayed (and most of the people responsible for the reactor initially have died). A third option is to entomb the reactor in a concrete structure.

Two accidents have dealt a strong blow to the future of nuclear energy. The first, and much lesser of these, occurred on March 28, 1979, when Metropolitan Edison Company’s nuclear reactor located on Three Mile Island in the Susquehanna River, 28 miles outside of Harrisburg, Pennsylvania, lost much of its coolant resulting in overheating, and partial disintegration of the reactor core. Some radioactive xenon and krypton gases were released to the atmosphere and some radioactive water entered the river. The problem was remediated and the reactor building sealed. Then in April of 1986 a reactor of inherently dangerous Soviet design blew up in Chernobyl, which is now part of Ukraine. Officially, 31 people were killed, but the death toll was probably many more, especially when delayed effects of exposure to radioactive materials are considered. Food, including reindeer meat in Lapland, was contaminated as far away as Scandinavia, thousands of people were evacuated, and the entire reactor building was entombed in a massive concrete structure. The reactor that blew up was one of four units, the last of which was not shut down permanently until the end of 2000!

Given the horrors described above, why would reputable scientists even advocate development of nuclear energy? The answer is, simply, carbon dioxide. With massive world resources of coal and other non petroleum fossil fuels, the world has at least enough readily available fossil fuel to last for a century. But evidence is mounting that the carbon dioxide from fossil fuel combustion is leading to global warming accompanied by effects such as rising sea levels that will inundate many coastal cities. Humans do know how to design and operate nuclear reactors safely and reliably; indeed, France has done so for years and gets most of its electricity from nuclear fission, and the U.S. Navy has had an exemplary safety record with reactors on submarines and aircraft carriers. So, it may be that nuclear energy is far from dead and that humankind, reluctantly and with great care, will have to rely on it as the major source of energy in the future. A new generation of nuclear power plants is waiting to be built that have the desirable characteristics of **passive stability**. This means that measures such as gravity feeding of coolant, evaporation of water, or convection flow of fluids operating automatically provide for safe operation of the reactor and automatic shutdown of the reactor if something goes wrong. New designs are also much more reliable with only about half as many pumps, pipes, and heat exchangers as are contained in older power reactors.

Nuclear Fusion

The fusion of a deuterium nucleus and a tritium nucleus releases a lot of energy as shown below, where Mev stands for million electron volts, a unit of energy:

$$ {}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} + 17 \cdot 6\ \mathrm{MeV}\ (\text{energy released per fusion}) \tag{15.10.2}$$

This reaction is responsible for the enormous explosive power of the “hydrogen bomb.” So far it has eluded efforts at containment for a practical continuous source of energy. And since physicists have been trying to make it work on a practical basis for the last approximately 60 years, it will probably never be done. (Within about 15 years after the discovery of the phenomenon of nuclear fission, it was being used in a power reactor to propel a nuclear submarine.) However, the tantalizing possibility of using the essentially limitless supply of deuterium, an isotope of hydrogen, from Earth’s oceans for nuclear fusion still give some investigators hope of a practical nuclear fusion reactor.

Nuclear fusion was the subject of one of the greatest scientific embarrassments of modern times when investigators at the University of Utah in 1989 announced that they had accomplished so-called cold fusion of deuterium during the electrolysis of deuterium oxide (heavy water). The announced “discovery” of cold fusion resulted in an astonishing flurry of activity as scientists throughout the world sought to repeat the results, whereas others ridiculed the idea. Unfortunately, for the attainment of a cheap and abundant source of energy, the skeptics were right, and the whole story of cold fusion stands as a lesson in the (temporary) triumph of wishful technological thinking over scientific good sense.

15.11: Renewable Energy Sources - Solar Energy

Ideal energy sources are those that do not pollute and never run out. Such sources are commonly called renewable energy resources. There are several practical renewable energy resources that are discussed briefly in this section. The sun is the ultimate renewable energy source and solar energy is discussed first.

Solar Energy is The Best — When The Sun Shines

Sunshine comes close to meeting the criteria of an ideal energy source, including widespread availability, an unlimited supply, and zero cost up to the point of collection. The utilization of solar energy does not cause air, heat, or water pollution. Sunshine is intense and widely available in many parts of the world. If it were possible to collect solar energy with a collection efficiency of 10%, approximately one-tenth of the area of Arizona would suffice to meet U.S. energy needs, and at 30% collection efficiency, only about one-thirtieth of the area of that generally sunny state would suffice. But, keep in mind that such an area is still enormous and the implications of covering it with solar collectors would be profound.

There are several ways in which solar energy can be utilized. The simplest of these is for heating, and solar-heated houses and solar water heaters have been developed and used successfully. At a somewhat more sophisticated level, solar boilers have been developed that are located on towers and receive concentrated sunlight from an array of parabolic mirrors, thus generating steam to make electricity (see Figure 15.5). Some years ago a serious proposal was even made to use solar collectors in Earth orbit and convert the energy to a beam of microwave radiation focused on a receiver on Earth’s surface. Visions of this beam straying from its aiming point or hapless birds or even aircraft straying into it and being instantly cooked by an extraterrestrial microwave oven have prevented this plan from coming to fruition. Photosynthetic generation of biomass is another way of utilizing solar energy as discussed in a later section of this chapter.

Other than low-grade building and water heating, the most promising way to utilize solar energy is by its direct conversion to electricity in photovoltaic cells (see Figure 15.14). Originally just a laboratory curiosity, these devices became practical sources of electricity for satellites and space vehicles where their high cost was of little concern. But over the years they have become more efficient and cheaper, and it is now common to see arrays of these cells used to power data processors and signaling devices in remote locations. And some houses even have banks of photovoltaic cells.

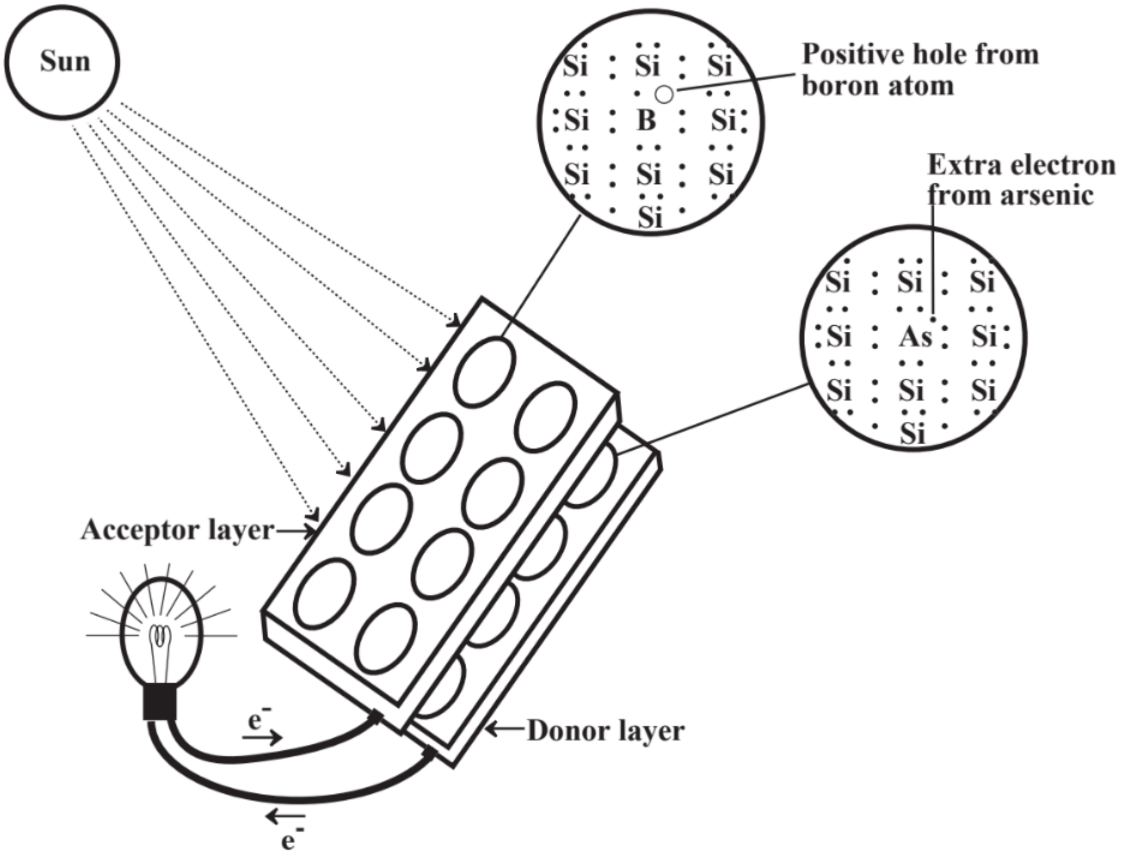
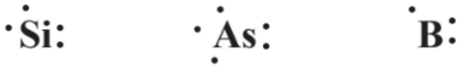


Figure 15.14. Photovoltaic cell

Photovoltaic cells depend upon the special electronic properties of silicon atoms containing low levels of other elements. The cell consists of two layers of silicon, a donor layer that is doped with about 1 part per million of arsenic atoms and an acceptor layer doped with about 1 part per million of boron. Examination of the Lewis symbols of these three elements,



shows that substitution of an arsenic atom with its 5 valence electrons for a silicon atom with its 4 valence electrons in the donor layer gives a site with an excess of 1 electron whereas substitution of a boron atom with only 3 electrons for a silicon atom in the acceptor layer gives a site “hole” that is deficient in one electron. The surface of a donor layer in contact with an acceptor layer contains electrons that are attracted to the acceptor layer. When light shines on this area, the energy of the photons of light can push these electrons back onto the donor layer, from which they can go through an external circuit back to the acceptor layer. This flow of electrons constitutes an electrical current that can be used for energy.

Current photovoltaic cells are around 12–15% efficient in converting radiant solar energy to electricity at a cost significantly higher than that of electricity generated in fossil fuel powerplants. However, advances are continually being made in solar cell technology and it can be anticipated that efficiencies will continue to increase as costs decrease. The obvious major disadvantage of solar energy is that it does not work in darkness, and variable atmospheric conditions affect its output. Flexibility in electrical power grids allows such intermittent sources for up to 15% of power without using special devices for energy storage. Furthermore, there are means of storing energy, such as by extremely high-temperature/high-pressure supercritical water stored deep underground or mechanical energy stored in the extremely rapid rotation of flywheels.

A very attractive energy storage option for solar energy given the growing use of fuel cells is hydrogen gas. Electrolysis of water containing a solution of electrolyte (commonly KOH)

$$2\,H_2O + electricalenergy \rightarrow 2\,H_2(g) + O_2(g) \tag{15.11.1}$$

with solar-generated electricity provides elemental hydrogen and oxygen, which are exactly the fuels used by fuel cells. Commercially available electrolyzers are 55-75% efficient in converting electricity to hydrogen and oxygen. The overall efficiency of this process can be increased significantly by the development of direct means for splitting water molecules into hydrogen and oxygen using the energy of light photons.

15.12: Energy from Wind and Water

Moving fluids are rich sources of energy that can be tapped, usually by turbines linked to electrical generators. Moving water and blowing winds are energy-rich fluids that have some similarities as energy sources so they are considered together in this section. Both are renewable and both are indirect means of harnessing solar energy — winds produced by the uneven heating of air masses and water carried by the solar-powered hydrologic cycle. Both are among the oldest sources of energy, such as wind used to propel sailing ships and waterwheels used for centuries to grind grain. And both are among the newest sources of energy — winds with technologically advanced wind turbines and water through ingenious devices such as those used to capture the energy of moving water in ocean tides.

Favorable Winds

As the sun heats air masses unevenly, winds are generated that can be tapped as an indirect form of solar energy. Wind power is undergoing rapid growth in a number of countries and has become competitive in cost with more conventional sources in some areas. In parts of Europe, California, Wyoming, and other locations, the sight of wind-powered generators mounted on towers has become common (Figure 15.15). In 2009 world wind power capacity increased by 31%reaching a capacity of 158 gigawatts. During 2009 China’s wind power capacity doubled from 12GW to 25 GW and the U.S. capacity grew by 10 GW to 35 GW total capacity. This gave the U.S.the largest wind power capacity of any nation in the world, though rapidly being overtaken by China.

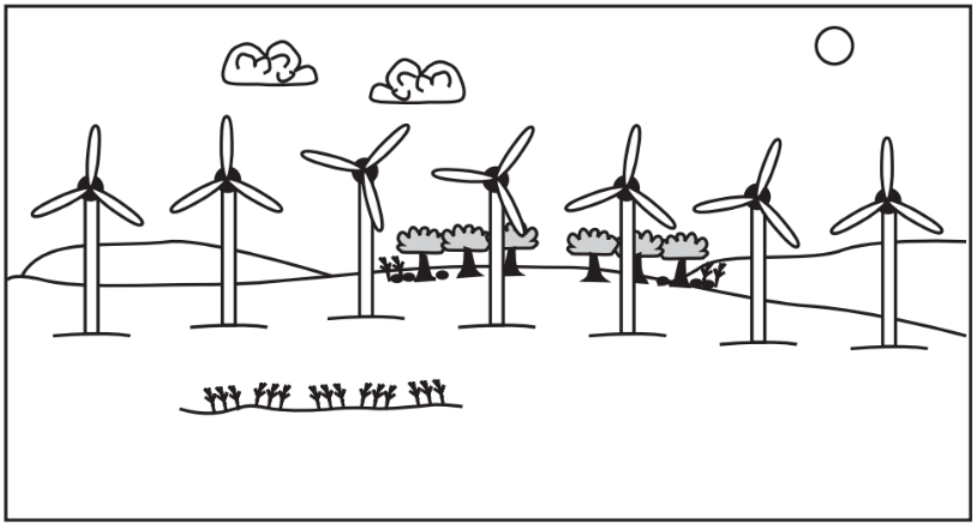


Figure 15.15. Wind-powered electrical generators mounted on towers are becoming increasingly common sights in the world in areas where consistent wind makes this nonpolluting source of renewable energy practical.

Modern wind turbines are generally large and sophisticated machines with diameters of 40 to 50 meters and rated between 0.5 to 2 megawatts. The largest turbines available as of 2010 were rated at 7 MW. Wind turbines are designed to operate consistently at varying wind speeds, to respond to changing wind direction, and to operate over a wide range of temperatures. Provision is made for electrical resistance heating of turbine blades in cold climates where ice accumulation is likely.

Offshore locations with turbines firmly anchored to the sea bed offer several advantages for production of wind power including generally consistent winds in coastal areas and lack of conflict with uses of land. The largest offshore wind power project to date began operation off the coast of southeast England in September 2010. This facility operated by Vattenfall, a Swedish energy company, has 100 turbines each 115 meters tall, and produces up to 300 megawatts of electricity, enough to power 200,000 homes

Energy from Moving Water

Various means of harnessing the energy of moving water have been used since ancient times with water-powered sailing vessels and waterwheels driven by flowing water for grinding grain known in ancient Greece and Rome. Waterwheels up to 50 horsepower were developed in the Middle Ages and were widely applied to grist mills, sawmills, and leather, textile, and machine shop operations in Colonial America. These sources suffered from problems due to irregular water flow and freezing during winter so that many of these facilities were abandoned when steam engines became widely available in the early 1800s.

A renaissance in waterpower occurred in the late 1800s when it became practical to drive electrical generators with water. Starting with the first hydroelectric plant in the U.S. on the Fox River near Appleton, Wisconsin, in 1882, hydroelectric power driven by sophisticated power turbines grew rapidly in the U.S. and throughout the world. By 1980 hydroelectric power composed 25% of world electricity production and 5% of total world energy generation. Norway generates essentially all of its electric power and about 50% of its total energy from hydroelectric sources.

The morphology of the geosphere has a strong influence on the potential for hydroelectric power generation, which is favored by mountainous terrain and large river valleys. Abundant rainfall and snowmelt are also important factors. China has about 1/10 of the world's potential for hydroelectric energy and its enormous Tree Gorges installation on the Yangtze River is the world's largest. The reservoir for this power source has been impounded with a 185-meter high, 1,300-m long dam located at the end of a number of steep canyons holding a body of water that extends for 630 km with an average width of 1.2 km. When fully operational, this massive installation will have 32 generating units and a capacity of 22.5 gigawatts, equivalent to 22 large coal-fired powerplants.

With the hydrologic cycle continuously pumping water into it, hydroelectric power is certainly sustainable, and prevents release of greenhouse gases. Bodies of water impounded to provide power can serve as water supplies for agriculture, municipalities, and industries. The potential exists to practice aquaculture in reservoirs by raising fish and freshwater shrimp(prawns). On the negative side, the development of hydroelectric power can present some serious environmental problems. In the modern era construction of a large power reservoir displaces significant numbers of people (more than 1 million for China's Three Gorges project), alters river flow, changes aquatic ecology, and fills once scenic valleys with water. In several significant cases dams have been removed from rivers to restore their valleys to their former state.

Water Energy without Dams

Hydrokinetic and **wave energy conversion** devices are being developed to harvest the kinetic energy of moving water in natural streams, tidal estuaries, ocean currents, and constructed waterways free of dams. A typical such device consists of a turbine with relatively large and widely spaced blades coupled directly to a generator that is fixed in a river or other water current. Such a device can be anchored directly to a river bed or attached to bridge supports.

Another source of energy from moving water is that from tides, changing levels of seawater resulting from the gravitational pull of the sun and moon. Tidal energy is feasible as demonstrated by the 240 megawatt tidal power station that has operated reliably in the Rance estuary region of France since it was constructed in 1966. This facility has about 1/4 the capacity of a standard 1,000MW coal-fired or nuclear plant. Several other small installations have been built including an 18MW experimental unit at Annapolis Royal, Canada. Tidal electricity generating stations suffer from the disadvantage that sufficient water flows to generate electricity only about 10 hours per day. Nevertheless, the amount of energy potentially available from tides is enormous and it is completely renewable.

An interesting way of harnessing water energy is **pressure-retarded osmosis** in which saline ocean water and fresh water are separated by a water-permeable membrane and the flow of water through the membrane from the fresh water to the saline water side builds pressure in the latter that can be harnessed to produce electricity. Pressure-retarded osmosis is illustrated in Figure15.16. Although the process operates on a continuous basis it is shown as a stepwise process in Figure 15.16 to illustrate the operating principle. The world's first osmotic plant, a demonstration unit with a minuscule capacity, went into operation in Tofte, Norway, in November, 2009. Pressure-retarded osmosis plants can be located in almost any of the huge number of locations worldwide where fresh water flows into the sea.

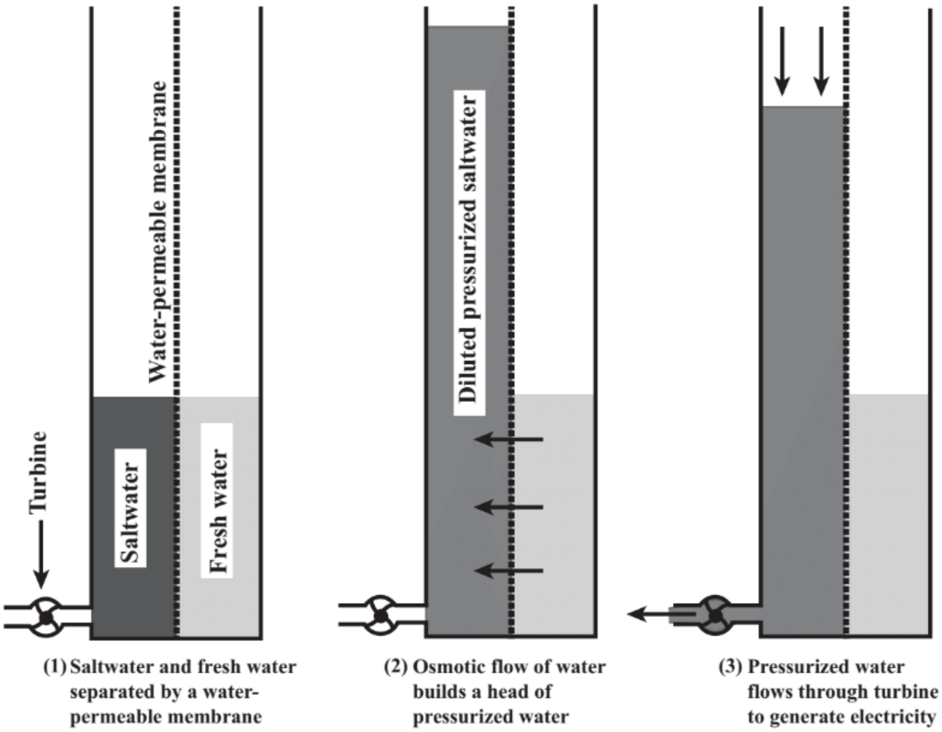


Figure 15.16. Illustration of the principle of pressure-retarded osmosis power generation that is based on the difference in osmotic pressure between saltwater and fresh water. Although it is shown here as a stepwise process, this mode of power generation operates on a continuous basis.

15.13: Biomass Energy

Biomass and liquid and gaseous fuels made by processing it are the most promising sources of renewable energy for transportation.4As noted earlier in this chapter, photosynthesis,

$$6\,\mathrm{CO_2} + 6\,\mathrm{H_2O}(\text{solar energy}, h\nu) \rightarrow \mathrm{C_6H_{12}O_6}(\text{glucose carbohydrate}) + 6\,\mathrm{O_2} \tag{15.13.1}$$

enables the conversion of solar energy to chemical energy in the form of biomass. Photosynthetically generated biomass supplies the food energy for essentially all organisms and,until about 200 years ago, was the source of most fuel. In addition to fuelwood and charcoal, **biofuels**, include forestry residues; agricultural byproducts; rapidly-growing grasses such as switchgrass; livestock manure; methane gas produced by anoxic fermentation of biomass; bioethanol from fermentation of sugar made from sugarcane, sugar beets, and cornstarch; and biodiesel synthesized from plant oils. As shown in Figure 15.6, photosynthesis suffers from the disadvantage of having less than 0.5% efficiency in the conversion of solar energy to chemical energy (although some plants, most notably sugarcane, convert solar energy to biomass energy with an efficiency of around 0.6%). Despite the limitations of photosynthesis in capturing energy, biomass is the predominant energy source in many developing regions of the world where approximately two billion people rely on wood for their primary household energy sources, especially for cooking. Today, more than 14% of the world's primary energy comes from biofuels, especially fuelwood and charcoal from wood. Finland gets a significant portion of its energy from burning the black liquor byproduct from pulp and paper manufacture, which uses wood as a raw material.

Properly utilized, biomass is a largely nonpolluting source of energy. Since it is produced by photosynthesis, there is no net addition to global atmospheric carbon dioxide. Although the heating value of dried biomass is only about half that of coal, biomass combustion produces very little sulfur dioxide, and the ash residue containing mineral nutrients can be returned to soil without adding harmful heavy metals, which can be a problem with coal ash.

The kinds of biomass that can be used for fuel fall into the four categories of (1) lignocellulosic materials from perennial plants, crop residues, wood, and biowastes; (2) starch from corn and other grains; (3) sugars from sugarcane and sugarbeets; and (4) oils from soybeans, rapeseed, and palm oil. These potential sources are addressed here.

As shown in Reaction 15.13.1, carbohydrates, such as glucose, $C_6H_{12}O_6$, are produced by photosynthesis. They can be burned directly, converted chemically to other fuels, or fermented to produce ethyl alcohol fuel. Hydrocarbons are more desirable as fuels, and some plants produce them directly. One example is the Philippine plant, *Pittsosporum reiniferum*, the fruits of which contain such a high content of hydrocarbon terpenes, primarily α-pinene and myrcene, that they can be burned to provide illumination. Rubber trees and other plants, such as *Euphorbia lathyrus* (gopher plant), a small bush growing wild in California, produce hydrocarbon emulsions. Seed oils, such as those produced by sunflowers and peanuts, and more exotic sources including buffalo gourd, cucurbits, and Chinese tallow tree, can be used for fuel, especially in diesel engines.

Despite concerns that not enough biomass can be grown to produce fuel and that it detracts from food supplies, it should be noted that about 150 billion metric tons of biomass are produced in the world each year by photosynthesis, mostly from uncontrolled plant growth. Corn, the most productive common field crop produces about 4 metric tons per acre of dry biomass annually(including stalks, leaves, husks, and corncobs). Switchgrass, a prolific producer of biomass, typically generates 11-12 tons of biomass per acre per year (there are 640 acres in a square mile of land). About 6% of the biomass generated globally each year would be equivalent to the world's demand for fossil fuels. Cultivation for fuel biomass of 6-8% of the land area of the 48 contiguous states would provide energy equivalent to annual U.S. consumption of petroleum and natural gas. Furthermore, only a small fraction of widely grown grain crops goes into grain; the rest is plant biomass, much of which could be used for energy production. And the U.S. has vast areas of underutilized land that could be devoted to the cultivation of energy-yielding plants. Much of this neglected, erosion-prone land would benefit from the cultivation of perennial plants that could be harvested for energy and regrow from roots left in the ground, thus lowering water and wind erosion.

A potentially important aspect of biomass fuel production that could improve its economics and environmental acceptability is coproduction of protein that can be used to feed animals. Now most protein used for feed comes from grain, particularly soybeans and corn. However, legumes(especially alfalfa) and perennial and annual grasses generate significant amounts of **leaf protein**. This material can be isolated by squeezing protein-rich juice from freshly ground plant leaves and heating the juice to precipitate the protein. The remaining fibrous material can then be used as a feedstock for the synthesis of biofuels.

Prolific Production of Biomass from Algae

Microscopic single-cell algae (microalgae) and photosynthetically-capable bacteria(cyanobacteria) growing in water can readily produce 10 times more biomass per unit area than terrestrial plants. In addition to their prolific productivity, microalgae offer several potential advantages for the generation of biofuels. These advantages include high production of oils and lipids (30-60% of dry algae mass), ability to grow in areas not suitable for terrestrial plants, ability to grow in saline water including seawater, growth in nutrient-rich sewage, and ability to grow in water enriched in dissolved carbon dioxide, such as from combustion sources. Concentrated by centrifugation and suspended in water or other liquid, microalgae can be introduced as a fluid emulsion into biorefineries offering processing advantages over soli.d biomass sources. Because of these advantages, microalgae are likely to become the predominant source of biofuels in the future.

Fuels from Fermentation of Biomass

Biological fermentation can be used to produce fuels from biomass. Yeasts act upon carbohydrates,

$$C_6H_{12}O_6 \rightarrow 2\,C_2H_5OH + 2\,CO_2 \tag{15.13.2}$$

to produce ethanol, C_2H_5OH. This liquid alcohol can be used alone as a fuel, but is usually added to gasoline at levels of about 10% to produce **gasohol**, which burns more cleanly and with less CO output than ordinary gasoline. The source of carbohydrate for ethanol production is usually corn grain or sugar produced by sugarcane. Grain-based ethanol has seen strong growth in the U.S. and some other countries in recent years, much of it due to legislative initiatives. However, the net energy yield from this source is very low and its production competes with food crops, so it is nota very sustainable means of producing fuel. Ethanol from sugarcane sugars is significantly more competitive in Brazil, a prolific producer of sugarcane.

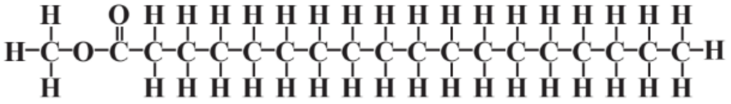
Another biomass fermentation occurs with methane-forming bacteria,

$$C_6H_{12}O_6 \rightarrow 3\,CH_4 + 3\,CO_2 \tag{15.13.3}$$

to produce methane gas, CH_4. The gas mixture produced by this biochemical process can be burned directly, or the carbon dioxide can be removed to produce pure methane gas. Anoxic(oxygen-free) methane digesters used to degrade the biomass in sewage sludge, the residue from biological treatment of wastewater, can generate enough power to provide for the pumping and electrical needs of a large sewage treatment plant. Small methane digesters running on crop and food residues and human and animal wastes are used in rural areas of China to provide methane for cooking and lighting.

Biodiesel Fuel

Biodiesel fuel is a combustible liquid synthesized from lipids, primarily those from plant oil seeds such as soybeans. Diesel fuel from petroleum consists of high-molecular-mass hydrocarbons containing 10-20 C atoms generally in a straight chain. Most lipids from plants are fatty acid esters of glycerol, such as triglyceride of stearic acid shown in Chapter 7, Figure 7.5. Examination of this formula shows that the fatty acid entities in it are predominantly straight-chain hydrocarbons except for the oxygen-containing carboxylate groups through which they are attached to the glycerol alcohol. Hydrolysis of the triglyceride and esterification with methanol yields liquid esters such as methyl stearate,



Methyl stearate, an ester in biodiesel fuel

that have the combustion characteristics needed for diesel fuel. In addition to methyl stearate, biodiesel fuel contains methyl esters of other fatty acids including linoleic acid, oleic acid, lauric acid, and behenic acid. Unlike ethanol, which cannot be transported through existing pipeline systems because it absorbs water, is therefore corrosive, and must be blended with gasoline at the point of distribution, biodiesel can be handled through existing facilities.

Biodiesel fuel can be synthesized from oils extracted from rapeseed (the major source in Europe), soybean (predominant in the U.S.), sunflower, palm, coconut, and jatropha. Both rapeseed and soybeans leave a protein-rich byproduct after the oil has been removed that is a good food source for animals. Palm oil, coconut oil and jatropha (from *Jatropha curcus*, planted for hedges) are attractive oil sources for biodiesel production because they come from perennials that thrive in the tropics. Unfortunately, the explosive growth of palm oil tree plantations in Malaysia and Indonesia has resulted in high levels of rain forest destruction.

As noted above, microalgae are prolific producers of biomass and these organisms may have oil contents exceeding 50% making algae attractive for the production of biodiesel fuel. Whereas the annual production of biodiesel from soybeans may reach 200 liters per acre and from palm oil 2,500 liters per acre, optimistic projections for biodiesel production from algae are as much as 40,000 liters per acre annually. Furthermore, as noted above, algae can be produced on desert lands and in saltwater, thus not competing with food crops.

15.14: Geothermal Energy

The final form of renewable energy to be considered here is **geothermal energy** in the form of steam, hot water, or hot rock that produce steam used in steam turbines. First harnessed for the generation of electricity at Larderello, Italy, in 1904, geothermal power has since been developed in Japan, Russia, New Zealand, the Phillipines, at the Geysers in northern California and especially in Iceland, an island nation that essentially rests upon a bed of steaming hot rock.

The best source of geothermal energy is subterranean dry steam which, unfortunately, is rather rare. Steam mixed with superheated water is much more common, with the byproduct water varying from very high purity to water laden with corrosive, scale-forming salts. Badly contaminated water is normally injected back into the hot rock formation from which it came to prevent contamination of surface water.

Hot, dry rocks can be used to produce steam from water injected into fractured rock formations. This source of geothermal energy is potentially ten times that of steam and hot water sources, but has been hindered largely over concerns raised by miniscule earthquakes that have resulted from fracturing the rocks. Development of this source continues on an experimental basis.

An interesting possibility that has yet to be demonstrated is the use of supercritical carbon dioxide as a working fluid for the extraction of energy from hot rocks (Figure 15.16).

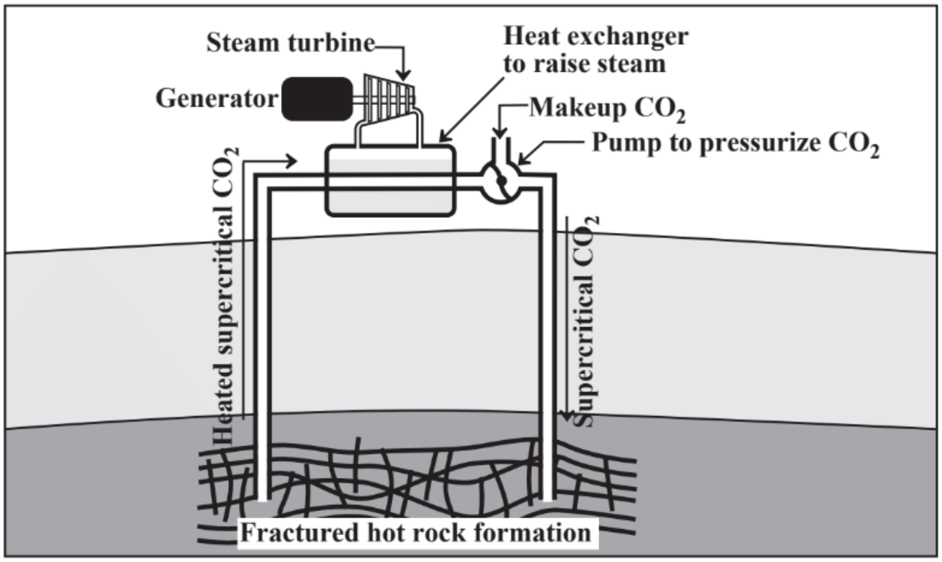


Figure 15.16. A system for extracting heat from hot dry rock formations using supercritical or dense phase carbon dioxide. The carbon dioxide is pumped into a fractured hot rock formation through an injection well and is removed through a production well. The hot carbon dioxide is run through a heat exchanger to raise steam to run a turbine that is coupled to an electrical generator and through which water and steam are recycled. Makeup carbon dioxide is added to the carbon dioxide line downstream from the heat exchanger and the carbon dioxide is repressurized and recycled through the hot rock formation.

15.15: Hydrogen for Energy Storage and Utilization

Hydrogen gas, H_2, can serve as a pollution-free means to store and utilize energy. Elemental hydrogen is the least polluting of fuels because it produces only water. Electricity that is generated on an intermittent basis from solar, wind, and even tidal flow processes can be used to electrolyze water,

$$2\,H_2O + \text{electrical energy} \rightarrow 2\,H_2(g) + O_2(g) \tag{15.15.1}$$

and the hydrogen piped some distance and combusted in an engine, used in a fuel cell (Figure 15.5(5)), or stored by pumping it underground. Although not yet practical, direct photochemical processes that can split water molecules to H_2 and O_2 are attractive from the viewpoint of sustainability.

Hydrogen is employed to a limited extent to power vehicles. Such vehicles using internal combustion engines fueled with hydrogen are especially well adapted to Iceland where abundant geothermal and hydroelectric power provide ample supplies of electrolytically generated hydrogen. Furthermore, in Iceland it is not possible to drive long distances so that one is unlikely to be stranded far from a refueling station. Honda has made a very limited number of fuel-cell-powered automobiles available for lease in southern California where the company has established hydrogen fueling stations.

The idea of a “hydrogen economy” in which H_2 gas is the predominant medium of energy transfer, storage, and utilization may be too optimistic because of factors such as hydrogen’s low heating value per unit volume and the wide range of explosive mixtures it forms with air. One of the greatest barriers to the widespread adoption of hydrogen-fueled vehicles has been their inability to carry sufficient hydrogen for an acceptable range. Several solutions to this problem are now being investigated. One possibility is the storage of hydrogen in high-strength containers at up to almost 700 times atmospheric pressure reputed to contain sufficient hydrogen to propel an automobile 300 miles. Solids with very high sorptive capacities for H_2 (“super activated carbons”)are being investigated for hydrogen storage. Liquid fuels including gasoline and methanol can be broken down catalytically to generate hydrogen, but in so doing release greenhouse gas carbon dioxide.

Unlike fossil fuels such as methane, elemental hydrogen is not a primary source of energy and must be produced from other energy sources. In addition to generation by the electrolysis of water, most hydrogen now is produced by steam reforming of methane from natural gas

$$CH_4 + H_2O \rightarrow 3\,H_2 + CO \tag{15.15.2}$$

The carbon monoxide product can be reacted with steam,

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{15.15.3}$$

to produce additional H_2 and the CO_2. Such a process is counterproductive in providing fuel especially in that methane gas is easier to store and transport than elemental hydrogen and the modern internal combustion engine with associated emissions controls running on methane is virtually pollution-free. So the intermediate step to produce elemental hydrogen is not a very sustainable approach. Although production of elemental hydrogen by electrolysis of water using electricity from renewable sources as discussed above is essentially non-polluting, electrolysis is a relatively inefficient means of using electrical energy, which might more sustainably be used for example in charging batteries in plugin hybrid vehicles.

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Questions and Problems

Access to and use of the internet is assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be "right."

1. The tail of a firefly glows, although it is not hot. Explain the kind of energy transformation that is most likely involved in the firefly's producing light.

2. What is the standard unit of energy? What unit did it replace? What is the relationship between these two units?

3. Which law states that energy is neither created nor destroyed.

4. What is the special significance of 1,340 watts?

5. What is the reaction in nature by which solar energy is converted to chemical energy?

6. In what respects is wind both one of the oldest, as well as one of the newest, sources of energy?

7. What are two major problems with reliance upon coal and petroleum for energy?

8. Why does natural gas contribute less to greenhouse warming than does petroleum and much less than coal?

9. How might coal be utilized for energy without producing greenhouse gas carbon

10. What is a large limiting factor in growing biomass for fuel, and in what respect does this limit hold hope for the eventual use of biomass fuel?

11. What relationship describes the limit to which heat energy can be converted to mechanical energy?

12. Why does a diesel-powered vehicle have significantly better fuel economy than a gasoline-powered vehicle of similar size?

13. Why is a nuclear power plant less efficient in converting heat energy to electricity than is a fossil-fueled power plant?

14. Instead of having a sparkplug that ignites the fuel, a diesel engine has a glow plug that operates only during engine startup. Explain the operation of the glow plug

15. Cite two examples of vastly increased efficiency of energy utilization that took place during the 1900s.

16. Describe a combined power cycle. How may it be tied with district heating?

17. Describe a direct and an indirect way to produce electricity from solar energy.

18. What is the distinction between donor and acceptor layers in photovoltaic cells?

19. Using internet resources for information list some possible means for storing energy generated from solar radiation?

20. What are the advantages of *Pittsosporum reiniferum*and*Euphorbia lathyrus* for the production of biomass energy?

21. Corn produces biomass in large quantities during its growing season. What are two potential sources of biomass fuel from corn, one that depends upon the corn grain and the other that does not?

22. Does the use of biomass for fuel contribute to greenhouse gas carbon dioxide? Explain.

23. What fermentation process is used to generate a fuel from wastes, such as animal wastes?

24. What are two potential pollution problems that accompany the use of geothermal energy to generate electricity?

25. What basic phenomenon is responsible for nuclear energy? What keeps the process going?

26. What is the biggest problem with nuclear energy? Why is it not such a bad idea to store spent nuclear fuel at a reactor site for a number of years before moving it?

27. What is meant by passive stability in nuclear reactor design?

28. What is the status of thermonuclear fusion for power production?

29. Arrange the following energy conversion processes in order from the least to the most efficient:(a) electric hot water heater, (b) photosynthesis, (c) solar cell, (d) electric generator, (e) aircraft jet engine.

30. Considering the Carnot equation and common means for energy conversion, what might be the role of improved materials (metal alloys, ceramics) in increasing energy conversion efficiency?

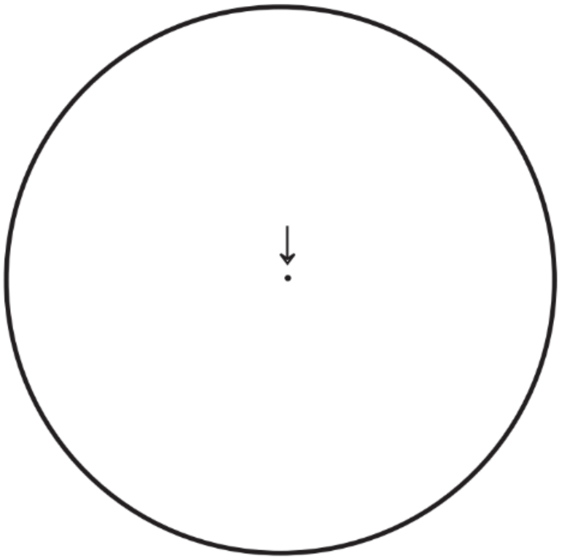
31. Justify describing the sun as “an ideal energy source.” What are two big disadvantages of solar energy?

32. What are some of the greater implications of the use of biomass for energy? How might such widespread use affect greenhouse warming? How might it affect agricultural production of food?

CHAPTER OVERVIEW

16: Terrorism, Toxicity, and Vulnerability- Green Chemistry and Technology in Defense of Human Welfare

“If the area of the large circle below represents a fatal dose of the once-popular organophosphate insecticide parathion, now banned because of its toxicity, the area of the barely perceptible dot indicated by the arrow represents a fatal dose of organophosphate Sarin a nerve gas military prison of concern for its potential use in terrorist attacks.”



16.1: Vulnerability to Terrorist Attack
16.2: Protecting the Anthrosphere
16.3: Substances That Explode, Burn, or React Violently
16.4: Toxic Substances and Toxicology
16.5: Toxic Chemical Attack
16.6: Protecting Water, Food, and Air
16.7: Detecting Hazards
16.8: Green Chemistry to Combat Terrorism
16.9: Green Chemistry for Sustainable Prosperity and a Safer World
16.10: Green Chemistry to Combat Terrorism
16.11: Green Chemistry for Sustainable Prosperity and and a Safer World
Literature Cited
Questions and Problems

16.1: Vulnerability to Terrorist Attack

Terrorist attacks upon human targets have become a constant fear in modern times. In the United States, vulnerability to such attacks were illustrated in horrifying detail by the suicide attacks by hijacked commercial aircraft on the New York World Trade Center on September 11, 2001. Other nations have long lived in the shadow of threats from groups that would cause them harm. Throughout the world, the possibility of deliberate attacks upon people, their support systems, and the anthrospheric infrastructure have come to be the greatest concern facing large numbers of people.

Chemicals and chemistry figure prominently in considerations of terrorist actions. The sudden release of a huge amount of chemical energy from a mixture of ammonium nitrate (a common agricultural fertilizer) and diesel fuel brought down the Alfred P. Murrah Oklahoma City Federal Building in 1995 with the loss of dozens of lives. Powerful explosives strapped to the bodies of suicide bombers have killed 20 or more people at a time in attacks in Afghanistan, Iraq, Pakistan, and Israel. The extreme toxicity of military poison nerve gases is a constant concern in subways and other locations where large numbers of people are packed into small spaces. Biochemistryapplied to recombinant DNA science may enable production of particularly virulent disease pathogens, such as vaccine-resistant smallpox. The accidental release of methyl isocyanate in an industrial chemical accident in Bhopal, India, in 1984 killed more people than even the 2001 attack on the World Trade Center. At least 243 people died from hydrogen sulfide contained in natural gas released from a pressurized deposit of this lethal mixture penetrated by a drilling operation in the Chuandongbei natural gas field of southwestern China in December, 2003. Hundreds of people were made ill and thousands were evacuated. A massive fire resulted when the escaping gas was ignited to convert the hydrogen sulfide (H_2S) to toxic, but much less lethal sulfur dioxide, SO_2.

Terrorist activities are not confined to direct attacks upon humans. The environment is susceptible to terrorist activities and may be severely damaged by them. For example, a major nuclear war — arguably the ultimate form of terrorism — could contaminate large areas of land and other parts of the environment with radioactive materials and, in the worst case scenario, could do substantial harm to the global climate resulting in a “nuclear winter.”

So, what can green chemistry do to prevent terrorist attacks and mitigate their effects? Actually, green chemistry is a key discipline in such endeavors. For example, one of the basic tenets of green chemistry is to use the safest possible chemicals as safely as possible. When particularly dangerous chemicals are not made or used, they are not available to cause mischief. The practice of green chemical manufacturing calls for minimizing the accumulation of hazardous chemicals and seeks to eliminate hazardous chemical wastes. Safer materials made under the practice of green chemical technology minimize hazards from more dangerous substances. Highly sensitive analytical techniques developed by chemical science can be used to detect minuscule quantities of explosives or toxic substances slated for use in terrorist attacks. Biochemistry and recombinant DNA science have the potential to enable the development of better vaccines against pathogenic biological warfare agents and antidotes to chemical and biological toxins. More subtly, the use of green chemistry and chemical technology to produce effective substitute materials can reduce potential for “resource blackmail” that can lead to vulnerability to terrorist activity. A prime example is the substitution of biomass alternatives for petroleum feedstocks that to a certain extent many nations must obtain from potentially unfriendly nations.

This chapter addresses potential terrorist threats with emphasis upon those that employ chemical and biological agents. Having identified threats that may occur, it then discusses ways in which chemistry, especially the proper practice of green chemistry, can minimize such threats.

16.2: Protecting the Anthrosphere

The anthrosphere constructed with a high degree of human ingenuity has provided a generally safe and comfortable environment for human beings. The underpinning of this entire support system is the **infrastructure**, which includes systems to purify and deliver water, electricity generation and distribution systems, communications, fuel distribution networks, highways, and railroads. The sophistication and complexity of the infrastructure is what makes it work so smoothly (for the most part), but also makes it vulnerable to attack. A key aspect of this susceptibility to attack is **vulnerability due to interconnectivity**, which arises from the high degree to which various parts of the infrastructure are interconnected and mutually dependent. No part of the infrastructure illustrates vulnerability due to interconnectivity more so than modern electrical grids, which can stretch across vast geographical regions and across national borders. A reminder of this vulnerability occurred on August 14, 2003, when a failure of the electrical grid in the northeastern U.S. and southeastern Canada resulted in a power outage for tens of millions of people in New York City, Detroit, Cleveland, and Toronto. In this incident a total of 68,100 megawatts of generating capacity — equivalent to 68 very large, modern power generating facilities — was lost as dozens of high-voltage transmission lines shut down. This occurred within about 5 minutes, and the event that caused it probably took only about 10 seconds. The precipitating event was not terrorism — although it well could have been — and probably resulted from nothing more dramatic than tree limbs interfering with transmission lines.

The electrical power failure described above illustrates a phenomenon called **cascading failures** on complex networks discussed in a 2009 article in *Scientific American*.1An electrical power distribution system is a complex network of hundreds of electrical power plants interconnected by electrical transmission lines. Such a system enables very efficient generation, distribution, and utilization of electrical power in that a surge in demand on one part of the system can be compensated by redistribution of power from the network to that segment of the system. Therefore, local generating facilities do not have to maintain the capacity to meet temporary demand, and this results in high efficiency and much lower costs. Other parts of the infrastructure have similar networks. Routers on the Internet are designed to route Internet traffic around bottlenecks or other routers that are temporarily out of commission. Modern manufacturing operations using “just-in-time” deliveries of components make it unnecessary to stockpile large quantities of parts, thereby minimizing the need for production capacity and maximizing efficiency. The downside is that these systems operate “close to the edge” so that a relatively small failure, such as one brought about by human mischief, can rapidly cascade into a major failure.

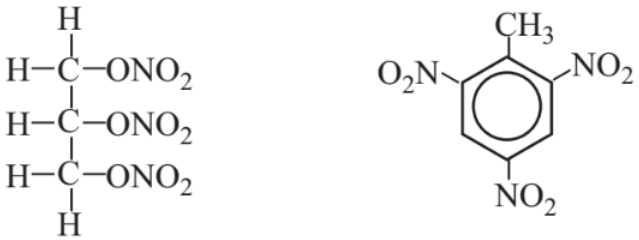
Arguably the part of the infrastructure most vulnerable due to interconnectivity and subject to cascading failures resulting from terrorist attack is the vast, intricately interconnected computer network that is now part of all modern systems of communication, commerce, and military operations.[2] These systems are vulnerable to so-called cyber crime in which key components can be disrupted leading in worst cases to total system breakdown. Much of the effort in homeland security in the U.S. and similar efforts in other countries is devoted to combatting cyber crime.

Chemistry can be applied to infrastructure protection. One area in which this is true is the production of materials that resist heat and flame. Such materials used in buildings can provide substantial protection from fire. Processes that are consistent with the practice of green chemistry also provide protection from attack. For example, green chemistry attempts to reduce the production and use of hazardous materials. Sophisticated analytical chemistry and analytical instrumentation can be used to detect agents of attack before damage is done.

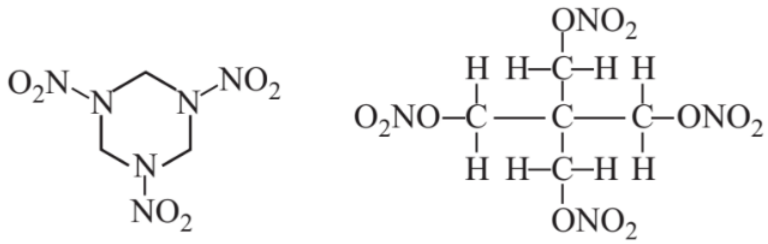
16.3: Substances That Explode, Burn, or React Violently

Substances that react violently and rapidly enough to cause fires, explosions, or corrosive destruction of materials are those that have been used most commonly in terrorist attacks and that have the most potential for future use. Reactive substances, such as explosives used to quarry rock, have many commercial uses and are therefore widespread and potentially readily available, both to legitimate users and terrorists.

Explosives are the most common materials used in terrorist attacks. The devastating effects of explosives have been illustrated by a number of incidents including the 1995 bombing of the Murrah Federal Building in Oklahoma City, the 2003 bombing of the British consulate in Turkey,and frequent bombings of various sites in Iraq in 2003/2004. Explosives can be made from readily available materials; the Murrah Federal Building was brought down by a mixture of ammonium nitrate fertilizer and diesel fuel. Gunpowder has long been prepared from charcoal, sulfur, and nitrate salts. Nitroglycerin, the explosive in dynamite, is made from glycerin, a byproduct of soap preparation, reacted with nitric and sulfuric acids (most amateurs who attempt this synthesis succeed in blowing their heads off). More sophisticated explosives consist of organic compounds containing nitrogen and oxygen, such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), and pentaerythritol tetranitrate (PETN). Figure 16.1 gives structural formulas of several explosives that could be used by terrorists.



Nitroglycerin **2,4,6-Trinitrotoluene (TNT)**



1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX) **Pentaerythritol tetranitrate (PETN)**

Figure 16.1. Structural formulas of four explosive compounds that have the potential for use in terrorist attacks. Note that all contain an abundance of oxygen bound with nitrogen.

The potential of flammable substances to cause death and destruction was shown by the jet-fuel-fed fires that brought down both towers of the New York World Trade Center in the 9/11/01 attack. Fires set on ruptured petroleum pipelines have caused significant destruction in Iraq in 2003/2004. When mixed with air, vapors of flammable liquids can cause massive explosions. Adding to the hazard of flammable substances are oxidants that release oxygen to react with combustible materials. In 1997, oxidant sodium chlorate, $NaClO_3$, an ingredient of emergency oxygen generators in aircraft that were being transported contrary to regulations in the cargo hold of a Valujet airplane, caused a devastating fire of aircraft tires that brought the aircraft down in the Florida Everglades.

By their nature, fuels are flammable substances, as are some common industrial solvents. Flammable fuels and solvents are used throughout almost all societies and are readily available to those who would use them for malevolent ends. Adding to their availability is their transport by truck, rail, and pipeline. The hazard of flammable substances is increased by the ease by which they and their vapors can be distributed through sewers, elevator shafts, subway tunnels, and other conduits.

Corrosive substances that destroy materials and flesh have been used in attacks on equipment and people. Concentrated sulfuric acid, which dehydrates and destroys flesh, has been used by criminals to blind people. Corrosive materials can be used to damage relays and other devices in communications equipment as a means of sabotage.

A major concern with respect to flammable, reactive, and explosive substances is their widespread industrial use. Actually, such materials are relatively safe inside of manufacturing plants and properly secured storage areas. The greater threat comes from their transport. This is illustrated by very frequent transportation accidents involving rail cars, trucks, barges, and pipelines that result in explosions, fires, and release of corrosive materials. Hijacking of trucks transporting hazardous materials and even trucks driven by terrorists are a particular concern. The practice of industrial ecology and green chemistry can help minimize such threats by, for example, promoting the production of hazardous substances in minimal quantities where needed and as needed. “Just-in-time” production minimizes storage of hazardous substances.

16.4: Toxic Substances and Toxicology

One of the greater concerns that the general public has with chemistry is the potential toxic effects of various substances including those that could be used for terrorist attacks. **Poisons**, or **toxicants**, are substances that can adversely affect biological tissue leading to harmful responses including, in the severest cases, even death. The study of such substances and their effects is the science of **toxicology**. The science that relates the chemical properties of toxic substances to their toxic effects is **toxicological chemistry**. Because poisons are among the leading terrorist threats, it is appropriate to consider toxic substances and toxicological chemistry here.

Any kind of tissue and all organs can be the subject of attack by toxic substances. The major human organ systems that are potentially adversely affected by toxic substances are given in Table 16.4.1.

Table 16.4.1

Table 16.4.1	Typical Toxic Responses
Respiratory system	Emphysema from cigarette smoke, lung cancer from asbestos
Skin responses	Allergic contact dermatitis, such as from exposure to dichromate; chloracne from exposure to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (“dioxin”); skin cancer from exposure to coal tar constituent
Hepatotoxicity (toxic effects)	Steatosis (fatty liver), such as from exposure to carbon tetrachloride cirrhosis; (deposition and build up of fibrous collagen tissue) from excessive ingestion of ethanol; haemangiosarcoma, a type of liver cancer observed in workers heavily exposed to vinyl chloride in PVC plastic manufacture
Reproductive system	Interference with sperm development by some industrial chemicals, interference with cells involved with egg formation by chemicals such as cyclophosphamide
Blood	Carboxyhemoglobin formation from binding of carbon monoxide to blood hemoglobin, methemoglobinemia consisting of conversion of iron(II) to iron(III) in hemoglobin from exposure to substances such as aniline or nitrobenzene, aplastic anemia from exposure to benzene
Immune system effects	Immunosuppression from exposure to radiation, hypersensitivity from exposure to beryllium
Endocrine system effects	Disruption of endocrine function by endocrine disruptors such as bisphenol-A
Nervous system	Encephelopathy (brain disorder), such as from exposure to lead; peripheral neuropathy from exposure to organic solvents; inhibition of acetylcholinesterase enzyme in nerve function by exposure to organophosphate military poisons
Kidney and urinary tract system	Nephrotoxicity to the kidney by heavy metal cadmium

Toxicities

The toxicities of substances vary over a wide range, and those that are toxic at lowest doses are of most concern for deliberate poisoning. This is illustrated in Figure 16.1 which gives the toxicities of several substances. It is important to note that the dosage scale in this figure is logarithmic; that is for each division *decrease* on the scale, a substance is *ten times* as toxic. The two circles in Table 16.4.1 illustrate the enormous differences between toxicities of different substances. If the area of the large circle represents the size of a fatal dose of parathion, a once widely used insecticide that has killed a number of people and has now been banned because of its toxicity, a fatal dose of military poison nerve gas Sarin is represented by the minuscule dot below the circle!

Toxicities are normally expressed as LD50 values, the dose in units of mass of poison per unit mass of test subject. Rats are usually used for tests, and toxicities to humans are inferred from these test values.

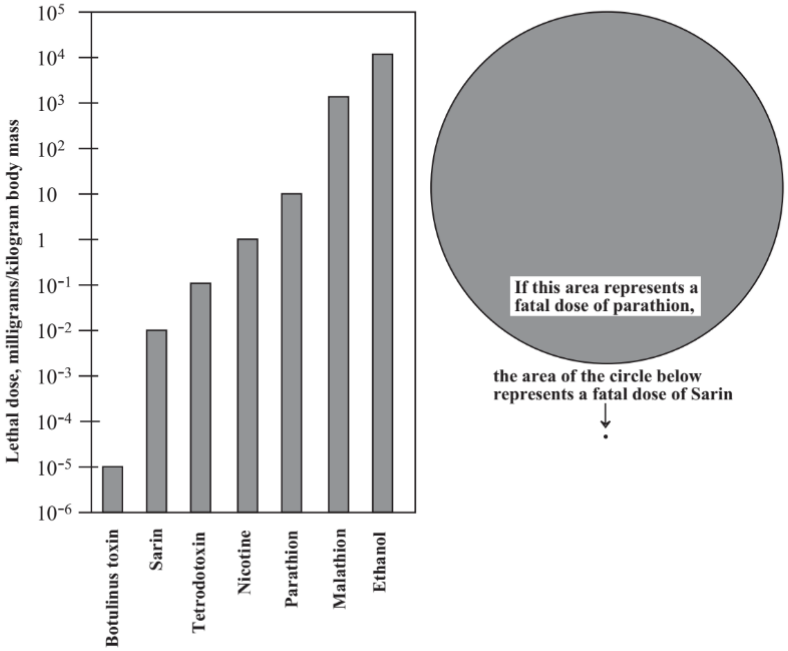
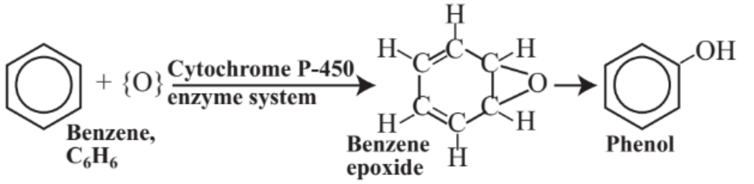


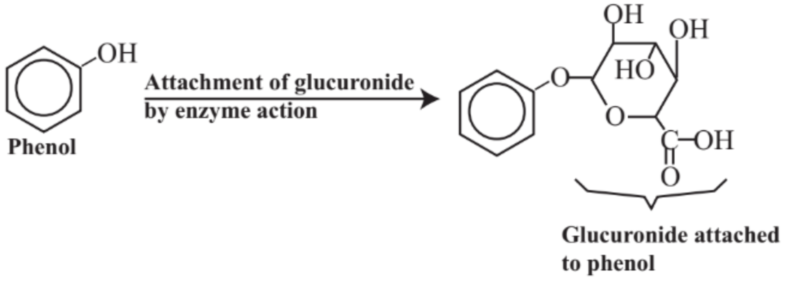
Table 16.4.1: Relative toxicities of various substances in units of milligrams dose per kilogram of body mass required to kill 50% of test subjects (LD50). Note that the estimated lethal dose is plotted on a log scale. Also shown are the relative toxicities of parathion, a once commonly used insecticide that has been discontinued because of its toxicity to humans, and Sarin, an extremely toxic military poison.

Metabolism of Toxic Substances

Toxic substances that enter the body and that are foreign to it, commonly called **xenobiotic substances**, are subject to metabolic processes that may activate them or make them less toxic(detoxification). The metabolism of toxic substances may be divided into two phases. Phase I reactions normally consist of attachment of a functional group, usually accompanied by oxidation. For example, benzene, C_6H_6, (see Chapter 6, Section 6.2) is oxidized in the body by the action of the cytochrome P-450 enzyme system as shown in Reaction 16.4.1. The Phase I oxidation product is phenol, a toxic substance. A reactive intermediate in the process is benzene epoxide, which interacts with biomolecules to cause toxic effects. The phenol Phase I oxidation product of benzene may undergo a second reaction, a Phase II reaction in which it is bound with a conjugating agent that is endogenous to (produced naturally by) the body, such as glucuronide as illustrated in Reaction 16.4.2



(16.4.1)



(16.4.2)

Although Phase I and Phase II reactions generally act to make xenobiotic substances more water soluble, more readily eliminated from the body, and less toxic, in some cases, the opposite occurs and metabolic processes make substances more toxic. Most known human carcinogens (cancer-causing agents) are actually produced by biochemical processes in the body from noncarcinogenic precursor substances.

The Action of Toxic Substances

Toxic substances, which, as noted above, are often produced by metabolic processes from nontoxic precursors, produce a toxic response by acting upon a **receptor** in the body. Typically, a receptor is an enzyme that is essential for some function in the body. As a consequence of the binding of the receptor to the toxicant there is a **biochemical effect**. A common example of a biochemical effect occurs when a toxicant binds to an enzyme such that the bound enzyme may be inhibited from carrying out its normal function. As a result of a biochemical effect, there is a response, such as a behavioral or physiological response, which constitutes the actual observed toxic effect. Acetylcholinesterase enzyme inhibited by binding to nerve gas Sarin may fail to stop nerve impulses in breathing processes, leading to asphyxiation. The phenomena just described occur in the **dynamic phase** of toxicant action as summarized in Figure 16.3.

16.5: Toxic Chemical Attack

Other than nuclear weapons, chemical and biological agents (pathogenic microorganisms) have more potential than any other mode of attack to debilitate and kill victims. Not the least of these effects is their ability to spread fear and terror among potential victims. Most of what is known of the potential of chemical and biological agents to harm and terrorize people has been learned from their use and preparation for use in warfare as summarized in a book on the history of weapons of terror.[3]

Chemical and biological agents have been used for centuries by civilizations around the world that have poisoned water supplies and employed diseased animals and human bodies, incendiary materials, poison-tipped arrows, and even venomous snakes to attack their enemies. Modern chemical warfare normally is considered to date from the use of toxic chlorine gas by the German army in an attack at Ypres, Belgium, during World War I in 1915 causing 7,000 to 15,000 casualties. The British used chlorine five months later in the Battle of Loos, but suffered 2,000 casualties when a change of wind blew the gas back over their own lines. The use of chemical agents continued throughout the war and, in addition to physical damage that was done, contributed to psychological stress and the need to implement cumbersome protective measures and logistics. The Geneva Protocol of 1925 banned the use of chemical and biological agents in warfare, although before, during, and after World War II nations continued development of these means of attack.

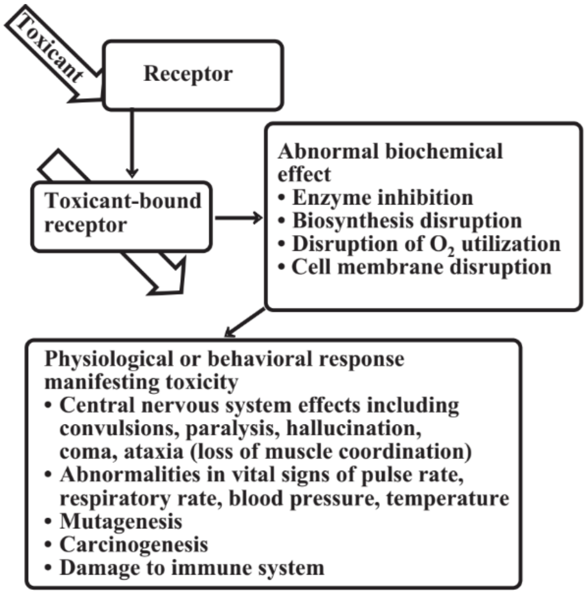


Figure 16.5.1: The dynamic phase of toxicity in which a toxicant interacts with a receptor in the body to cause a biochemical alteration that is manifested in a toxic response

The next large scale use of chemical weapons took place in the 1980-1988 war between Iraq and Iran in which Iraq employed approximately 1,800 tons of blistering agent mustard gas and 140 and 600 tons respectively of nerve gas sarin and Tabun causing an estimated 30,000 casualties. Toward the end of this conflict Iraq killed and injured thousands of people with chemical agents in quelling a Kurdish rebellion. Fear of missile-launched chemical attack by Iraq was a major concern during the war that followed Iraq's 1990 invasion of Kuwait. Suspected possession by Iraq of such "weapons of mass destruction" was cited as justification for the 2003 invasion of Iraq by the U.S.

Biological warfare agents are regarded as having significantly more potential than chemical agents for inflicting casualties. This is because of the ability of pathogens to propagate and afflict far more people than those exposed in the initial attack.

Chemical and biological agents are probably more effective for terrorist attacks against civilians than they are for warfare. Civilian targets are generally less likely to have protective measures in place, are more subject to surprise attack, and can be attacked in enclosed areas with relatively unsophisticated means. As exemplified by the October 2001 anthrax bacteria attack on several targets carried out through the U.S. Postal Service, which caused 22 cases of the disease and killed 5 people, panic fueled in part by intense media attention can cause widespread panic and disruption, always the goal of a terrorist attack.

16.6: Protecting Water, Food, and Air

The tragedy that arguably illustrates most vividly the potential of chemicals to cause major loss of life was the accidental release of methyl isocyanate from a chemical manufacturing operation in Bhopal, India. This disaster occurred during the night of December 2/3, 1984, exposing many victims as they slept in their homes. A total of about 40 tons of this chemical was released during the incident exposing thousands of residents in the surrounding area. Of those exposed, more than 3000 died, primarily from pulmonary edema (fluid accumulation in the lung). Immunological, neurological, ophthalmic (eye), and hematological effects were also observed. Because of its high vapor pressure and toxicity to multiple organs,

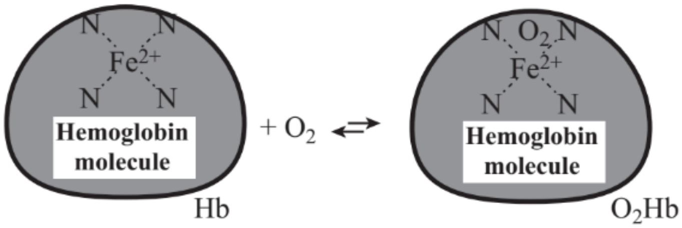
$H_3C{-}N{=}C{=}O$

methyl isocyanate is the most toxic of the isocyanates. An interesting aspect of methyl isocyanate toxicity is its ability to cross cell membranes and reach organs far from the site of exposure, despite its very high reactivity.

It is unlikely that methyl isocyanate or of any other substance with similar toxicity could be obtained and delivered to potential victims in large enough quantities and with sufficiently effective delivery to cause widespread death and illness in a deliberate attack. Nevertheless, the magnitude of the Bhopal catastrophe vividly illustrates the potential of toxic substances to cause harm and the incident serves as a grim reminder of the potential of toxic chemicals, especially those that may be airborne, to be used in attacks. And the Bhopal incident, which occurred as the result of a tragic accident, serves as a grim warning of the potential of terrorist attacks upon chemical plants to cause widespread harm.

Potential Chemical Agents

Although an unlikely “weapon of mass destruction,” **carbon monoxide**, **CO**, can certainly cause fatal poisonings. It has killed thousands of people accidentally and through suicide. Given the fact that carbon monoxide is odorless and provides essentially no warning of exposure, it should be regarded as a potential weapon. To understand the action of carbon monoxide, it is important to realize that oxygen in blood is carried from the lungs to tissue by **hemoglobin**, a large-molecule protein in red blood cells that contains iron(II) (the Fe^{2+} ion) bound with nitrogen. This functionality exchanges oxygen



converting hemoglobin, Hb, into oxyhemoglobin, O_2Hb, which carries oxygen to tissues where it is released to be used for metabolic processes. When carbon monoxide is present in inhaled air, the oxygen bound to hemoglobin is displaced,

$$O_2Hb + CO \rightleftharpoons COHb + O_2 \tag{16.6.1}$$

producing **carboxyhemoglobin**, COHb. This species is not only useless for carrying oxygen, it is much more stable than oxyhemoglobin, O_2Hb, so that a relatively low concentration of carbon monoxide will convert enough of the hemoglobin to carboxyhemoglobin to cause a serious oxygen deficiency. Rapid death ensues from inhalation of air containing 1,000 parts per million (ppm) carbon monoxide, and unconsciousness results from inhaling 250 ppm CO. Dizziness, headache, and fatigue result from inhalation of 100 ppm CO and levels as low as 10 ppm can impair visual perception and judgment.

Chlorine (Cl_2) gas could potentially be used in terrorist attacks because of its wide availability for water disinfection and other uses. Illustrative of this potential is the fact that chlorine was the first substance used as a military “poison gas” in World War I. Chlorine is a strong oxidizer that reacts with water, including water in tissue, to produce an oxidizing, acidic solution that is especially damaging to respiratory (lung) tissue. Air containing only 10–20 ppm chlorine causes acute discomfort to the respiratory tract and brief exposure to 1,000 ppm of Cl_2 can be fatal. Because of its widespread use and transport as the liquid in railway tank cars, chlorine is regarded as having a high potential as a terrorist weapon.

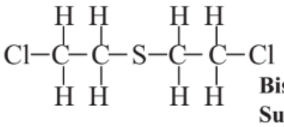
Hydrogen cyanide, HCN, is a potentially devastating gaseous pollutant. It has been used to carry out death sentences in gas chambers, causing death very rapidly when inhaled. Another toxic form of cyanide is **cyanide ion**, CN^-, in salts such as KCN. Only about 60 mg of KCN will kill a human. Glass ampules containing KCN or liquid HCN were used by some doomed Nazi leaders to commit suicide near the end of World War II. There is concern that potassium cyanide or other soluble cyanide salts may be put into water supplies as toxic agents.

The metabolic action of cyanide depends upon its strong binding for iron in the +3 oxidation state. In the essential utilization of molecular oxygen in the body (the respiration process called oxidative phosphorylation) iron cycles between iron(III) in ferricytochrome oxidase enzyme andiron(II) in the chemically reduced form, ferrous cytochrome oxidase. By stabilizing ferricytochrome oxidase, cyanide stops this cycle, preventing utilization of oxygen and causing metabolic processes to cease. It is interesting to note that an antidote to cyanide poisoning — in those rare instances where the victim survives long enough for antidotes to be administered — is to have the victim inhale a volatile nitrite ester. The nitrite converts a fraction of the iron(II) in hemoglobin to iron(III), generating methemoglobin. This form of hemoglobin cannot carry oxygen, but it can bind with cyanide, preventing it from tying up ferricytochrome oxidase enzyme.

Hydrogen sulfide, H_2S, is a colorless gas with a foul, rotten-egg odor that is as toxic as hydrogen cyanide and may kill even more rapidly. Inhalation of 1000 ppm hydrogen sulfide causes rapid death from respiratory system paralysis. Nonfatal doses of this gas can cause excitement due to damage to the central nervous system; headache and dizziness may be symptoms of exposure.

Military Poisons and Nerve Gas Agents

Beginning with the use of toxic chlorine gas in World War I, nations have developed a variety of diabolical toxic agents to disable and kill opposing troops in war. One such agent is **sulfur mustard**, a class of chemical compounds, the most common of which is bis(2-chloroethyl)sulfide



$$\mathrm{Cl-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-S-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Cl}$$

Bis(2-chloroethyl)sulfide,
Sulfur Mustard

The vapors of this substance penetrate rapidly and deeply into tissue causing tissue damage and destruction well below the point of entry. Because of its penetrating ability, efforts to remove sulfur mustard from exposed tissue are futile after about 30 minutes. Sulfur mustard is classified as a vesicant (“blistering gas”) producing severely inflamed lesions that are susceptible to infection. Such lesions in the lungs are likely to be fatal. (An internet search for pictures of sulfur mustard lesions will bring up some horrifying images of the wounds that this material can inflict.) Sulfur mustard causes mutations because it forms a reactive intermediate that binds with DNA and is thought to be a primary carcinogen that does not require metabolic activation to produce cancer.

The chemical agents of greatest concern for their potential use in terrorist attacks are the organophosphorus “nerve gases.” The first of these deadly agents was reported in 1937 by Gerhard Schrader of the German concern Farbenfabriken Bayer AG. Work continued on these compounds in Germany during World War II and by other nations after the war and during the cold war between Western and Communist bloc nations until around 1990. The possibility that Iraq possessed large stores of military nerve gas “weapons of mass destruction” was part of the rationale for the U.S./Iraq war in 2003. Among the common nerve gases are Sarin, Soman, Tabun, CMPF, VX, and diisopropylphosphofluoridate (fluorodiisopropyl phosphate)Structural formulas of three of these compounds are shown in Figure 16.4.

Sarin is perhaps the best known organophosphorus military poison because of its use in a 1995 attack by a terrorist group on the Tokyo subway system that killed several people and caused illness in a number of others. It is estimated that a dose of only about 0.01 milligrams of Sarin per kilogram of body mass is fatal; absorption of a single drop of liquid Sarin through the skin can kill a human. Sarin and other organophosphate military poisons act on the nervous

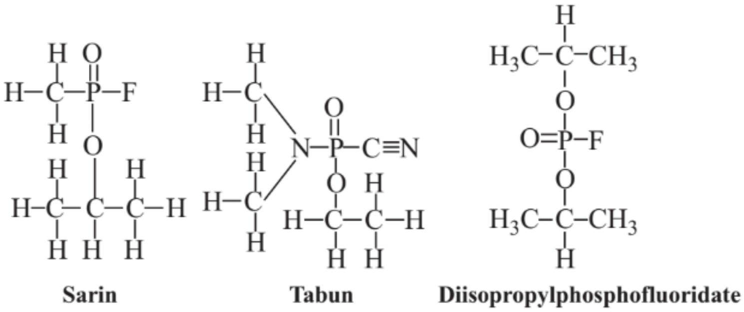
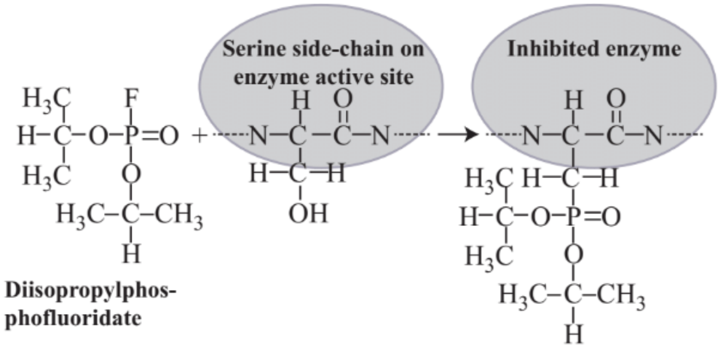


Figure 16.4. Three common nerve gas organophosphate military poisons

system by binding with and inhibiting acetylcholinesterase enzyme, which is required to hydrolyze acetylcholine and stop nerve impulses once their function has been completed. The failure of the hydrolysis of acetylcholinesterase typically causes failure of the respiratory system. The binding of diisopropylphosphofluoridate to a serine side-chain on the active site of acetylcholinesterase enzyme is shown by the reaction below:



(16.6.2)

Biotoxins

Some of the most toxic substances known are produced by organisms and some of these have been used to attack humans.*Clostridium botulinum* bacteria growing in the absence of oxygen produce **botulinum** toxin, which has killed many people who have eaten improperly canned food (heating to 80–100°C for a sufficient time deactivates the toxin). Consisting of several proteins, botulinum toxin binds irreversibly to nerve terminals preventing the release of acetylcholine, an enzyme required for proper nerve function. Neurologic symptoms are followed by paralysis of the respiratory muscles and death. From the LD50 of about 1×10^{-5} mg/kg for botulinum toxin shown in Figure 16.1, it may be inferred that a 70 kg person could die from absorbing 70 kg 1×10^{-5}mg/kg = 0.0007 mg of botulinum toxin, or only about 1 microgram of this extraordinarily deadly substance. A simple calculation would show that literally millions of people could be killed by the amount of this toxin that could be carried in a terrorist's pocket if some efficient means could be found to deliver it.

Another highly toxic natural product is **ricin**, a very stable proteinaceous material extracted from castor beans (*Ricinus communis*). Only about 1/2 milligram of ricin (about the size of a pinhead) can be fatal when injected resulting in failure of kidneys, liver, and spleen along with massive blood loss from the digestive tract. Ricin gained notoriety in the 1978 assassination in London of the Bulgarian writer and journalist Georgi Markov injected with ricin from the tip of an umbrella. Although it is mentioned as a potential terrorist tool, ricin has its greatest toxicity by injection, which tends to limit its use as a weapon.

16.7: Detecting Hazards

In the future, disease-causing agents are more likely to be used than are chemicals for terrorist attack. Because of the ability of pathogens to multiply in the human body and to spread among people, they are much more effective than chemical agents per unit mass. A 1993 report from theU.S. Office of Technology Assessment estimated that as many as 3 million people could be killed by the airborne release of 100 kg of anthrax spores in a highly populated area such as Washington, DC. The magnitude of the collateral damage from a biological attack can be appreciated from the chaos that ensued from the October 2001 anthrax incident in which the spores for this deadly agent were spread by letters received in Washington, DC, New York, Connecticut, and Florida that resulted in 22 cases of anthrax, five of which were fatal. Congress and the U.S. Supreme Court were among the facilities closed for some time and decontamination costs came to $300 million.

In modern times the most devastating biological warfare was carried out by Japan in its biological attacks on Manchuria and China in the 1930s and during World War II. Among the pathogenic agents studied by the Japanese army were anthrax, cholera, dysentery, typhoid, paratyphoid, bubonic plague, and tularamia. In 1940 and 1941 at least three Japanese air raids against Chinese cities using bombs laden with live human fleas infected by bubonic plague killed almost 150 people. During a retreat by the Japanese army in the Chekiang Province of China in1942 water sources and houses were deliberately contaminated by cholera, plague, and dysentery agents causing many casualties among the populace and Chinese troops who occupied the area. This strategy backfired however when Japanese troops re-occupied the region suffering about 10,000 casualties of which about 1,700 were fatal due to the disease agents previously spread in the area. The release of plague agents by Japanese troop retreating from invading Soviet forces in Manchuria at the end of World War II caused plague epidemics in 1946 and 1947.

Although pathogenic organisms are the oldest form of terrorist attack, modern recombinant DNA biotechnology threatens much higher potential for devastation with these agents. The potential exists to modify known pathogens to strains that are more robust, more virulent, and resistant to antibiotics. As one particularly deadly example, Soviet scientists used recombinant DNA technology to add genes for the production of myelin toxin to *Yersinia pseudotuberculosis* bacteria so that targets infected with this pathogen would be afflicted by both tuberculosis lung symptoms and the paralysis caused by the myelin toxin.

16.8: Green Chemistry to Combat Terrorism

Water to drink, food to eat, and air to breathe — the most basic of human needs — are likely targets for terrorist attack. The finding of a single cow with mad cow disease in Washington State in December, 2003, caused a major upheaval in cattle markets, loss of exports, and a final cost of perhaps hundreds of millions of dollars. Earlier outbreaks of mad cow disease and hoof and mouth disease in England had caused staggering economic loss. Mad cow disease is caused by a protein agent called a prion and can infect humans through contaminated meat causing fatal Creutzfeldt-Jakob disease characterized by devastating brain and nervous system effects. Over 200 cases ofthis malady linked to mad cow disease have been reported including a victim in Italy in 2010. Reported incidents of mad cow disease were the result of accident and poor agricultural and food production practices, not terrorism, but they illustrate the vulnerabilities of the food supply to potential terrorist attack.

A chemical attack on food supplies, though plausible, would be very difficult to carry out on a scale that would cause great damage. Spraying of food crops with toxic substances before harvest could cause some adverse effects and great anxiety, but would be relatively easy to detect and probably would not cause widespread harm.

Direct contamination of food with disease-causing agents is a possible terrorist action. An incident has been described in which 12 laboratory staff were infected by acute diarrheal illness that hospitalized 4 due to ingestion of *Shigella dysenteriae* bacteria taken from a culture in the laboratory and deliberately placed on doughnuts or muffins in the facility break room.4Mostpeople have experienced the abdominal pain, vomiting, diarrhea and fever of “food poisoning” caused by *Salmonella* bacteria in contaminated food. Hundreds of millions of eggs infected by *Salmonella* in the U.S. during the summer of 2010 caused illness in several hundred people. Although rarely fatal, *Salmonella* on food have the potential to cause temporary disability.

Because of their central distribution to large numbers of people, water supplies are susceptible to both chemical and biological attack. There are reports of terrorist groups trying to obtain deadly cyanide salts with the objective of contaminating water supplies. The tragic arsenic contamination of water from tube wells unknowingly drilled into arsenic-bearing aquifers that may have afflicted as many as 77 million people in Bangladesh is a reminder of the potential for ill effects from chemical contamination of drinking water. Astoundingly toxic botulinus toxin from *Botulinus* bacteria (see Figure 16.2) is a potential chemical agent that could be put in water supplies. Though possible, it would be rather difficult to deliberately contaminate a municipal water supply with toxic chemicals.

Throughout history, drinking water contaminated by microorganisms that cause amebic, bacterial, and viral diarrhea; cholera; typhoid; and other maladies have killed millions and still cause disease and fatalities. The World Health Organization estimates that approximately 1.8million people die each year from diarrhea and dysentery, much of which results from drinking contaminated water. In 1993, more than 400,000 people in Milwaukee were sickened and over 50 died from waterborne protozoal *Cryptosporidium parvum*. In May, 2000, approximately 3000 people were made ill and seven died in Walkerton, Ontario, Canada, from drinking water contaminated with *Escherichia coli* bacteria. Although usually *E. coli* bacteria are harmless and normal residents of human intestinal systems, they may develop strains with DNA transferred from *Shigella dysenteriae* bacteria that produce shiga toxin, the cause of potentially fatal dysentery, which is what happened in the Ontario incident. Bacteria that could be added deliberately to drinking water include *Shigella dysenteriae*, *Vibrio cholerae*, and *Yersinia pestis*.

Air is a possible medium for both chemical and biological attack. A means is required to deliver agents through the air, which makes it difficult to expose people through this medium. Although a low-flying crop-spraying plane would be an effective means of spreading either chemical or biological agents through the air, it would rapidly alert authorities leading to corrective action. Spores of bacteria that cause anthrax, *Bacillus anthracis*, are of particular concern for bioterror attack through air. Other microbial agents of concern for their potential for airborne attack include *Variola major*, which causes smallpox;*Francisella tularensis*, which causes tularemia, and viruses that cause viral hemorrhagic fevers, including Ebola, Marburg, Lassa, and Machupo.

Historically, the disease that has caused devastation most closely resembling the harm that could result from a massive attack by bio-agents is “plague,” which killed tens of millions of people in Europe during the Middle Ages. This malady is caused by infection with *Yersinia pestis* bacteria. This disease takes several forms, the most common of which is bubonic plague characterized by swollen, tender lymph glands called buboes. Readily cured by antibiotics in its early stages, it is transferred from infected rodents to humans by fleas, and several cases are reported each year in the Southwestern U.S. Pneumonic plague is readily spread through air between humans and is the form of most concern for terrorist attack. Initial symptoms similar to those of influenza progress to a fatal form of pneumonia.

16.9: Green Chemistry for Sustainable Prosperity and a Safer World

A key to protection from terrorist threats is their detection before damage can be done. The detection of explosives immediately comes to mind. Another priority area is detection of disease-causing pathogenic organisms.

Hazardous substances are not readily detected by standard metal detectors and X-ray imagers used to find weapons and bombs on air travelers and in their luggage. Residues of TNT, RDX, and PETN explosives (see Figure 16.1) can be detected by sophisticated instruments including ion mobility spectrometers and chemiluminescence sensors. Such instruments normally detect residues of explosives on swabs from swabbing luggage; they can be circumvented by careful cleaning of luggage. Nuclear quadrupole resonance (NQR) may develop as an especially promising detection technique for explosives. One reason for this is its specificity for nitrogen, which is abundantly present in all common explosives. Secondly, NQR has the potential to detect explosives in containers and even land mines. It works by generating a pulse of radio frequency radiation which excites nitrogen atoms to higher quantized energy levels. By following the signals given off as the atoms return to their ground energy levels the kinds and abundances of nitrogen functional groups in explosives molecules can be determined.

“Canine olfactory detection,” which uses the sniffing abilities of dogs, is widely used to detect explosives, illicit drugs, and other potentially hazardous materials. A dog has approximately 220 million mucus-coated olfactory receptors, about 40 times the number possessed by a human, making the canine nose an extraordinarily sensitive detector. In order for canine olfactory detection to work, a rewards system must be used. This can lead to unpredictable, temperamental behavior in dogs of the type commonly attributed to humans and computers. As a result, dogs are not completely reliable and, according to an authority on the subject, “Dogs lie. We know they do.”[5]

16.10: Green Chemistry to Combat Terrorism

As *safe* and *sustainable* chemistry, green chemistry has an important role to play in the war on terrorism. When safe chemistry is practiced, hazards and hazardous substances that might be stolen or diverted for use in attacks are not made or used in large quantities. The successful practice of green chemistry means that chemical products do what they are supposed to do and are used in minimum quantities. With green chemistry, materials and processes that are likely to result in violent reactions, fires, high pressures, and other extreme conditions are avoided and auxiliary substances and flammable materials are not used.

Green chemistry minimizes energy consumption, thereby reducing energetic, high-temperature processes that might be susceptible to sabotage. With its emphasis on biological processes, where applicable, green chemical processes are carried out under the mild, low temperature, toxic-substance-free, inherently less hazardous conditions conducive to biochemical reactions. By reducing demand for energy and raw materials, green chemistry reduces reliance on uncertain sources that are controlled by potentially hostile populations and therefore are inherently subject to disruption and blackmail.

The practice of green chemistry requires exacting process control combined with real-time,in-process monitoring techniques. These are conditions that resist sabotage. In addition, green chemistry uses passive safety systems that function by default in the event of failure of or deliberate damage to intricate control systems. An example of such a system is gravity-fed cooling water for nuclear reactors that will continue to flow even if the pumps for the cooling system pumps fail.

The chemical industry and related enterprises continue to implement green chemistry practices to reduce hazards and vulnerabilities to attack. For example, a DuPont chemical facility in Texas now makes methyl isocyanate, the agent of the catastrophic 1984 Bhopal, India, disaster, on site so that it does not have to store large quantities of this dangerous chemical.

As noted in Section 16.6, liquified and pressurized elemental chlorine, the first “poison gas” to be employed in warfare, has a high potential for terrorist attack because of its toxicity, volatility, and widespread shipping and storage. Alkaline aqueous solutions of hypochlorite ion, OCl^-, are widely used for bleaching and disinfection. Because liquified Cl_2 is the most economical form in which to ship chlorine, the common practice has been to react the elemental substance with base to produce hypochlorite:

$$\mathrm{Cl_2 + 2\,Na^+ + 2\,OH^- \leftrightarrows 2\,Na^+ + OCl^- + Cl^- + H_2O} \tag{16.10.1}$$

Maintained in a basic state, the equilibrium of this reaction lies to the right so that the equilibrium concentration of Cl_2 in solution remains very low. Both Cl_2 and NaOH are made by passing a direct electrical current through a solution of NaCl where the reaction at the cathode is

$$\mathrm{2\,Na^+ + 2\,H_2O + 2\,e^- \leftrightarrows 2\,Na^+ + 2\,OH^- + H_2(g)} \tag{16.10.2}$$

and that at the anode is the following (where e^- represents the electron)

$$\mathrm{2\,Cl^- \leftrightarrows Cl_2(g) + 2\,e^-} \tag{16.10.3}$$

The chlorine gas produced at the anode can be reacted with the basic NaOH solution generated at the cathode to produce sodium hypochlorite (Reaction 16.8.1), which is produced, stored, and used as aqueous solutions. Many water treatment plants have started using relatively safe sodium hypochlorite solutions in place of toxic, reactive liquid chlorine formerly stored in large pressurized tanks on site. A potential problem in storing sodium hypochlorite solutions is their decomposition to produce elemental oxygen,

$$\mathrm{2\,Na^+ + 2\,OCl^- \rightarrow O_2(g) + 2\,Na^+ + 2\,Cl^-} \tag{16.10.4}$$

a process catalyzed by traces of transition metal ions such as Cu^{2+}. This results in a loss of product and a potentially hazardous buildup of oxygen and pressure.

By 2010 the Clorox company, a major world supplier of chlorine-based bleach announced that it would no longer be using liquid chlorine to make sodium hypochlorite, but would be shipping relatively concentrated aqueous solutions of sodium hypochlorite and diluting them to the strength required for bleaching. A reasonable alternative to using liquid chlorine or solutions of sodium hypochlorite for larger installations, such as major metropolitan water treatment plants, would be to have relatively small installations for the electrolysis of sodium chloride solutions which would make sodium hypochlorite directly on site. Such a facility might fit well with an industrial ecosystem in which several users of sodium hypochlorite would be clustered in close proximity.

16.11: Green Chemistry for Sustainable Prosperity and and a Safer World

Poverty, human misery, and hopelessness are conditions that feed terrorism. Although eliminating these conditions would not guarantee a safe world, reducing them would go far toward ensuring safe societies. People with satisfied material needs able to lead comfortable and fulfilling lives are relatively less likely to commit violent acts. To the extent that the practice of green chemistry fulfills human needs and makes life more comfortable, it can play a significant role in reducing terrorism.

Prosperity, narrowly defined, has resulted in consumption of increasingly scarce resources and environmental degradation. But, as stated by Elsa Reichmanis, a former President of the American Chemical Society, “We are past the days when we can trade environmental contamination for economic prosperity; that is only a temporary bargain, and the cost of pollution both economically and on human health is too high.”[6] Green chemistry and the practice of industrial ecology can go far in providing high living standards without ruining the environment or recklessly exploiting resources.

The key to material prosperity consists of sources of abundant, inexpensive energy that can be tapped sustainably without major environmental harm; with such energy sources, all else is possible. Energy sources tend to be contentious and competition for them has precipitated past wars. Some of the most abundant producers of petroleum, currently the key energy source for industrialized nations, are regions that are breeding grounds for terrorists. The provision of adequate energy independent of such sources would substantially reduce terrorist threats.

Figure 16.5 shows how abundant, sustainable energy is the foundation of the kind of prosperity that can lead to less terror-prone societies. Abundant energy can be used to produce food through synthesis of fertilizers (particularly by synthetic fixation of atmospheric nitrogen)and for irrigation, cultivation, and reclamation of farmland. Energy can be used to fabricate materials for housing and to provide the heating, cooling, and lighting required to make dwellings comfortable. Energy is required to pump water, in some cases over great distances from abundant sources to more arid regions. Energy can be used to purify water of marginal quality and to reclaim water after use. With an abundant source of energy, seawater can be desalinated for domestic, industrial, and agricultural use. Safe, comfortable, non-polluting transportation systems require an abundance of energy. These and other amenities based upon abundant, sustainable energy can go far toward building peaceful, productive societies with high living standards. They do not guarantee tranquility and prosperity because reasonable social systems, functional democratic governments, and sensible religions are needed as well, but material well being based upon a foundation of abundant, sustainable energy can go far in eliminating conditions that breed terrorism.

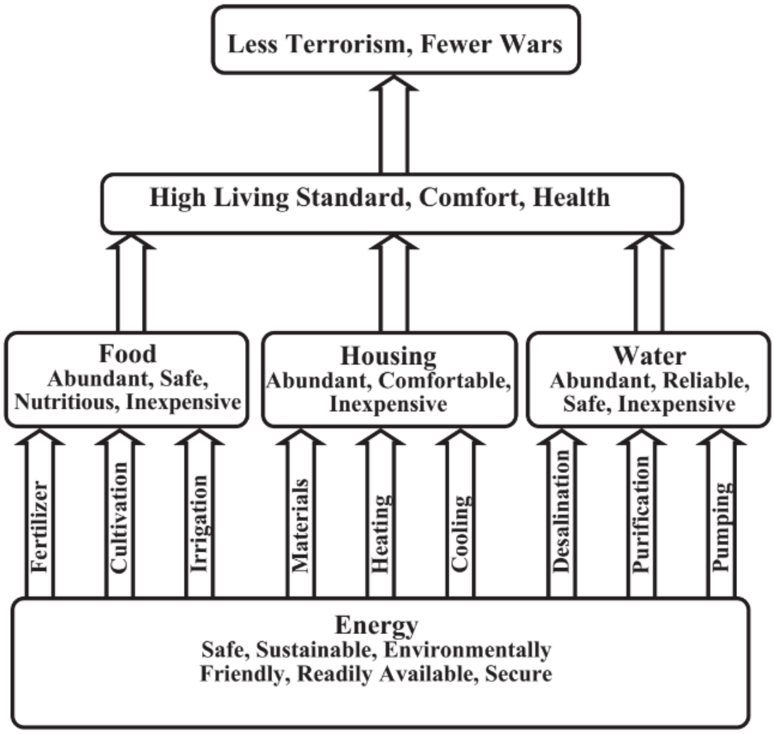


Figure 16.5. Abundant, sustainable energy is the base of a pyramid through which greater human well-being combined with suitable political and social systems leads to less conflict and terrorism

The provision of abundant, sustainable energy in the future requires the best practice of green chemistry, green engineering, and industrial ecology. Increased efficiency of energy utilization is a key aspect of providing more usable energy. Solar, wind, and biomass energy are leading contenders for renewable energy sources. Another essentially inexhaustible energy source is thermonuclear fusion, the stuff of hydrogen bombs and the sun’s energy, but despite significant investments, a practical controlled system of energy production from this source has proven elusive. Fossil fuels will play an interim role, especially if sequestration of greenhouse gas carbon dioxide byproduct can be achieved. Despite its bad reputation in some quarters, nuclear fission with uranium and perhaps thorium fuel can provide abundant energy safely with new-generation nuclear reactors and with reprocessing of nuclear fuel.

A key challenge in providing abundant renewable energy is its storage and transport. Wind and solar sources are by nature intermittent and dispersed, and they often produce electricity in locations far from where it is used, so the energy that they generate must be moved over long distances and stored for later use. For example, solar collectors function only in daytime and, aside from rooftop installations, are often located in remote desert locations. Wind-powered electrical generators, which require at least some wind, are not usually welcome in urban areas where the energy is required, and some of the prime locations for them are the remote plains of Kansas orTexas or offshore. Superconductor or quantum conductor power cables are candidates for transport of electrical energy from source to use. Various means are available for energy storage, such as pumped water hydroelectric storage or high-speed flywheels coupled with electric motor/generators. In the future, elemental hydrogen, H2, will be widely used for energy storage and transport as well as for fuel. Hydrogen can be produced by electrolysis of water and direct photoconversion of water to hydrogen and oxygen may eventually become practical. Hydrogen can be moved by pipeline and used to produce electricity directly in fuel cells.

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5. Derr, Mark, “With Dog Detectives, Mistakes Can Happen,” *New York Times*, Dec. 24, 2002, p.D1.

6. As quoted in “Green Solutions to Global *Problems*,” Stephen K. Ritter, *Chemical and Engineering News*,81, 31–33 (2003).

Questions and Problems

Access to and use of the internet is assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be "right."

1. At the beginning of this chapter, it was noted that the Alfred P. Murrah Oklahoma City Federal Building was destroyed in 1995 by the explosion of a mixture of ammonium nitrate (chemical formula NH_4NO_3) and diesel fuel ($C_{16}H_{34}$). An explosion occurs when chemicals react very rapidly to produce much more stable chemical species, gases, and heat. Consider that H_2O, CO_2, and N_2 are very stable forms of the elements present in a mixture of ammonium nitrate and diesel fuel, that CO_2, and N_2 are gases, and that at the temperature of an explosion H_2O is a gas as well. Attempt to write a chemical reaction that occurs when a mixture of ammonium nitrate and diesel fuel explodes.

2. Nitroglycerin explodes by itself without having to react with any other chemical. Look up its formula and, from the information given in the preceding question, give a possible chemical reaction for a nitroglycerin explosion.

3. Consider the infrastructure of your home. Suggest how it might be vulnerable because of the interconnectivity in it. Suggest how cascading failures might do great damage to your homelife.

4. For a 75-kg person, estimate the lethal dose in grams, milligrams, or micrograms of each of the toxic substances shown in Figure 16.2.

5. Exposure of a person to toxic benzene can be estimated by measuring phenol in blood. Explain the rationale for such an analysis. Why is benzene epoxide not commonly determined to estimate benzene exposure?

6. Consider the toxicity of inhaled carbon monoxide in the context of Figure 16.3. Identify for carbon monoxide the receptor, the abnormal biochemical effect, and the physiological response manifesting toxicity.

7. Compare carbon monoxide to chlorine as agents of terrorist attack. What characteristic of carbon monoxide might make it a favored weapon. Why might chlorine be favored by terrorists? What characteristic would make it less attractive than carbon monoxide to terrorists?

8. Match each toxic substance and potential terrorist agent from the list on the left below with its characteristic from the list on the right.

A. Botulinus toxin 1. A disease-causing agent (pathogen)

B. Sarin 2. Inhibits acetylcholinesterase enzyme

C. Methyl isocyanate 3. Most toxic of those listed

D. Shigella dysenteriae 4. Toxic in gaseous, solid, or solution form

E. Cyanide 5. An industrial chemical that has killed thousands in a single incident

9. Figure 16.5 illustrating how abundant, sustainable sources of energy can lead to a high living standard emphasizes food, housing, and water. Suggest areas other than these three that depend upon abundant, sustainable energy and that can lead to a high living standard.

10. Natural gas pipelines are sometimes cited as elements of the infrastructure that are vulnerable targets for terrorist attack. Look up and describe an incident from 2010 that illustrates this vulnerability.

11. The compound sodium chlorate, $NaClO_3$, is mentioned in this chapter as an oxidant. Suggest with a chemical reaction what happens to this compound when it is heated. How might it actas an agent to accelerate fire or even cause an explosion?

12. What is meant by "just-in-time" chemical production and how may it minimize hazards in chemical production? In what sense is it consistent with the practice of green chemistry? In what sense does it potentially contribute to vulnerability in the chemical manufacture process?

13. Native American populations in what is now the U.S. were drastically reduced by a disease-causing agent after European explorers and settlers arrived on the continent. What was this agent and why were the Native Americans particularly vulnerable to its effects? Were there any cases in which it was deliberately spread?

14. There are two major ways in which biological agents (including microorganisms) can be used to harm humans. Explain.

15. At least two different water disinfecting agents can be made with electricity using raw materials so abundant that they may be regarded as renewable. What are these agents and how could they be synthesized as needed on site at a water treatment plant? How might such systems reduce the danger of terrorist attack?

CHAPTER OVERVIEW

17: The Ten Commandments of Sustainability and Sensible Measure

“On August 14, 2010, a massive traffic jam began building on one of the main highways into Bejing, China, that would eventually extend for 60 miles and last for weeks, on some days moving less than a mile. Nothing better illustrates the futility of continued reliance on individual vehicles for basic transportation needs in an increasingly crowded world.”

17.1: We Cannot Go on Like This
17.2: The First Commandment
17.3: The Second Commandment
17.4: The Third Commandment
17.5: The Fourth Commandment
17.6: The Fifth Commandment
17.7: The Sixth Commandment
17.8: The Seventh Commandment
17.10: The Ninth Commandment
17.11: The Tenth Commandment
17.12: Some Sensible Measures for Sustainability
17.9: The Eighth Commandment
Literature Cited
Questions and Problems
Supplementary References

17.1: We Cannot Go on Like This

In 1968 the Stanford University biologist Paul Ehrlich published a book entitled *The Population Bomb*,[1] a pessimistic work that warned Earth had reached its population carrying capacity sometime in the past and that catastrophe loomed. Ehrlich predicted rapid resource depletion, species extinction, grinding poverty, starvation, and a massive dying of human populations in the relatively near future. “Not so,” retorted Julian Simon a University of Maryland economist writing in a number of books, the most recent of which, finished just before his death in 1998, is titled *Hoodwinking the Nation*.[2] Ehrlich hedged his views by stating that he might be wrong and that “some miraculous change in human behavior” or a “totally unanticipated miracle” might “save the day.” Simon expressed the view that Ehrlich’s doom and gloom views were nonsense and that human ingenuity would overcome the problems foreseen by him.

The debate between Ehrlich and Simon led to a famous wager by Simon in 1980 that $200 worth of each of five raw materials chosen by Ehrlich—copper, chromium, nickel, tin and tungsten—would actually decrease in price over the next 10 years in 1980 dollars. Each did in fact decrease in price and Ehrlich paid. Simon then offered to raise the ante to $20,000, a proposition that Ehrlich declined. (After 1990 there were some spectacular price increases in these and other mineral commodities.

The Ehrlich/Simon wager is often cited by anti-environmentalists as evidence that we will never run out of essential resources and that a way will always be found to overcome shortages. However, common sense dictates that Earth’s resources are finite. Whereas unexpected discoveries, ingenious methods for extracting resources, and uses of substitute materials will certainly extend resources, a point will inevitably be reached at which no more remains and modern civilization will be in real trouble.

Unfortunately, the conventional economic view of resources often fails to consider the environmental harm done in exploiting additional resources. Fossil fuels provide an excellent example. As of 2005, there was ample evidence that world petroleum resources were strained as prices for petroleum reached painfully high levels. This has resulted in a flurry of exploration activities including even drilling in some cemeteries! Natural gas supplies have been extended by measures such as tapping coal seams for their gas content, often requiring pumping of large quantities of alkaline water from the seams and release of the polluted water to surface waters. There is no doubt that liquid and gaseous fossil fuel supplies could be extended by decades using coal liquefaction and gasification and extraction of liquid hydrocarbons from oil shale. But these measures would cause major environmental disruption from coal mining and processing, production of salt-laden oil shale ash, and release of greenhouse gases.

The sad fact is that on its present course humankind will deplete Earth’s resources and damage its environment to an extent that conditions for human existence on the planet will be seriously compromised or even become impossible. There is ample evidence that in the past civilizations have declined and entire populations have died out because key environmental support systems were degraded.3A commonly cited example is that of the Easter Islands where civilizations once thrived and the people erected massive stone statues that stand today. The populations of these islands vanished and it is surmised that the cause was denuding the islands of once abundant forests. A similar thing happened to pre-Columbian Viking civilizations in Greenland, where 3 centuries of unusually cold weather and the Vikings’ refusal to adopt the ways of their resourceful Inuit neighbors were contributing factors to their demise. Iceland almost suffered a similar fate, but the people learned to preserve their support systems so that Iceland is now a viable country.

There is much truth in the expression that, “The only thing we have to do to ensure a planet uninhabitable by our descendants is to continue what we are doing now.”Fortunately, modern civilizations have the capacity to avoid the fates of the ancient Easter Islanders and GreenlandVikings—if they can muster the will and the institutional framework to do so. The key is sustainability, which simply means living in ways that do not deplete Earth’s vital support systems. The great challenges to sustainability are (1) population growth beyond Earth’s carrying capacity, (2) potentially disruptive changes in global climate, (3) provision of adequate food, (4)depletion of Earth’s resources, (5) supply of adequate energy, and (6) contamination of Earth’senvironment with toxic and persistent substances. It won’t be easy to overcome these challenges and achieve sustainability and it is by no means certain that humankind will ultimately succeed or even survive on Earth. But we have to try; the alternative of a world population reduced to just a few million people surviving in poverty and misery on a sadly depleted planet under conditions hostile to higher life forms is too grim to contemplate.

The achievement of sustainability will require adherence to some important principles. These can be condensed into ten commandments of sustainability, which are listed below:

1. Human welfare must be measured in terms of quality of life, not just acquisition of material possessions, which demands that economics, governmental systems, creeds,and personal life-styles must consider environment and sustainability.

2. Since the burden upon Earth's support system is given by the relationship Burden = (number of people)×(demand per person) it is essential to address both numbers of people on Earth and the demand that each puts on Earth's resources.

3. Given that even at the risk of global catastrophe, *technology will be used* in attempts to meet human needs, it is essential to acknowledge the anthrosphere as one of the five basic spheres of the environment and to design and operate it with a goal of zero environmental impact and maximum sustainability.

4. Given that energy is a key to sustainability, the development of efficiently-used, abundant sources of energy that have little or no environmental impact is essential

5. Climate conducive to life on Earth must be maintained and acceptable means must be found to deal with climate changes that inevitably occur.

6. Earth's capacity for biological and food productivity must be maintained and enhanced, considering all five environmental spheres.

7. Material demand must be drastically reduced; materials must come from renewable sources, be recyclable and, if discarded to the environment, be degradable

8. The production and use of toxic, dangerous, persistent substances should be minimized and such substances should not be released to the environment; any wastes disposed to disposal sites should be converted to nonhazardous forms.

9. It must be acknowledged that there are risks in taking no risks.

10. Education in sustainability is essential; it must extend to all ages and strata of society, it must be promulgated through all media, and it is the responsibility of all who have expertise in sustainability.

Each of the ten commandments of sustainability is discussed in the remaining sections of this Chapter.

17.2: The First Commandment

HUMAN WELFARE MUST BE MEASURED IN TERMS OF QUALITY OF LIFE, NOT JUST ACQUISITION OF MATERIAL POSSESSIONS, WHICH DEMANDS THAT ECONOMICS, GOVERNMENTAL SYSTEMS, CREEDS, AND PERSONAL LIFE-STYLES MUST CONSIDER ENVIRONMENT AND SUSTAINABILITY.

This commandment goes to the core question of, “What is happiness?” Many people have come to measure their happiness in terms of material possessions—the larger sport utility vehicle, the bigger house on a more spacious lot farther from the city, more and richer food. But such measures of human welfare based upon the accumulation of more stuff has come at a high cost to Earth as a whole and even to the people who acquire the most stuff. The sport utility vehicle guzzles fuel from steadily decreasing petroleum supplies, commodious houses require more energy to heat and cool, large lots remove increasingly scarce farm land from food production, dwellings far from the workplace mean long commutes that consume time and fuel, and too many of the current generation of humans have consumed food to a state of unhealthy obesity.

The things that really count for happiness—good health, good nutrition, physical comfort, satisfying jobs, good interpersonal relations, interesting cultural activities—can be had with much less consumption of materials and energy than is now the case in wealthier societies. In order for sustainability to be achieved, it is essential for societies to recognize that happiness and well-being are possible with much less consumption of materials and energy.

Environmental and Sustainability Economics

Conventional neoclassical (Newtonian) market economics have not adequately considered resource and environmental factors in the overall scheme of economics. Since about 1970, however, environmental and natural resource economics has developed as a viable discipline.[4] This discipline, commonly called environmental economics addresses the failure of a strictly market economy to deal with scarcity and to address environmental problems. Much more complex than neoclassical economics, environmental economics addresses sustainability issues, resource economics, pollution costs, costs and benefits of pollution control, and the value of natural capital. Economic instruments can be powerful influences in reducing pollution and extending resources. The conventional market economy does act to extend resources. For example, as petroleum prices increase to painfully high levels, the rate at which consumption increases is diminished. Artificial market intervention can act to thwart such a desirable outcome. For example, U.S. government subsidies of biomass-based ethanol and biodiesel fuels contribute to increased stress on agricultural resources requiring increased amounts of fertilizers and fuel to grow the extra grain required to produce grain-based fuels.

Economic measures can be used to reduce pollution and demand on resources. Carbon and energy taxes can be imposed to reduce emissions of greenhouse gas carbon. Pollution trading has evolved as an effective pollution control measure. In the case of greenhouse gas carbon dioxide, for example, a utility installing a new coal-fired power plant may pay another concern to do reforestation projects that take an equivalent amount of carbon dioxide from the atmosphere.

More difficult to quantify, but no less real, are environmental amenities. There are certainly costs associated with impaired air quality in terms of increased respiratory disease and damage to buildings. In principle, such costs are quantifiable. Much more difficult to quantify are the value of a beautiful scenic view or the costs of eyesore billboard clutter.

A major issue with environmental economics is that of expenditures in the public sector versus those in the private sector. Free market capitalism is a powerful force in providing goods and services and in promoting innovation. Dismal past failures of planned economies and subsequent growth of these economies after they were converted to free market systems—China is probably the most striking example—illustrate the power of market forces. However, much of what is needed for sustainable development requires investment in the public sector, especially in infrastructure. The central challenge for economic systems in the future will be to integrate essential development in the public sector with free market forces. Both are essential in order for sustainable economic systems to flourish.

The Role of Governments

Sustainability will require the strong involvement of governments at all levels and extending across international boundaries. At local levels ordinances and regulations that promote sustainability are essential. For example, there are many cases in which local governments have set up recycling programs for paper, plastic, glass, and metals to reduce the need to dispose of solid wastes. In many cases only national governments have the power and authority to undertake massive projects and to promote changes required for sustainability. Since sustainability is a global concern, ways must be found to enable governmental action and cooperation among nations.

An essential part of the role of government in sustainability is the quality of government and the people involved in it as well as the public perception of government. “Government bashing” is fashionable in many circles, and in some cases is even richly deserved. However, in order for sustainability to succeed, the finest minds that societies have must be willing to enter government service and their contributions must be respected by the public.

Personal Life Styles and Value Systems

The achievement of sustainability will require an unprecedented commitment from individuals. This may well be the most difficult of all objectives to achieve. Many people seem to have an insatiable appetite for possessions and activities that consume large amounts of materials and energy. Nothing illustrates this better than the private automobile; most teenagers find the wait to get their driver’s licenses excruciatingly long and senior citizens dread the day when they are no longer able to drive.

Although people in developed countries are commonly accused of being too materialistic, populations in less developed countries have the same desires for material possessions. Some of the greatest environmental and resource impacts occur when the economies of less developed nations improve to the point that large numbers of their citizens can afford more of the things and services that prosperity, conventionally defined, offers. For example, as of 2010, the fastestgrowing market for automobiles was in China as its economy grew.

The achievement of sustainability will require that individuals adopt sustainability as part of their belief systems. Indeed, it would be very helpful if environmental protection and the preservation of Mother Earth and her limited resources were to become virtually a religion or to be incorporated into existing religions. In this respect, some of the more primitive of Earth’s tribes had belief systems that were much more consistent with sustainability than the predominant religions of today. In some pre-Columbian Native American cultures, Earth and nature were worshipped, a belief system that could well serve as an example to current denizens of the globe. There is some evidence that modern religions are beginning to consider sustainability as a moral issue. One example is the movement, “What would Jesus drive?,” that preaches that pollution from vehicles significantly impacts human health, peace and security are threatened by reliance on imported oil from politically unstable regions, and, therefore, Jesus would not likely drive a fuel guzzling sport utility vehicle!

17.3: The Second Commandment

GIVEN THAT THE BURDEN UPON EARTH'SSUPPORT SYSTEM IS THE PRODUCT OF NUMBER OF PEOPLE TIMES DEMAND PER PERSON, IT IS ESSENTIAL TO ADDRESS BOTH NUMBERS OF PEOPLE ON EARTH AND THE DEMAND THAT EACH PUTS ON EARTH'S RESOURCES

The burden placed upon Earth's support systems can be expressed by the equation

$$\text{Burden} = (\text{Number of people}) \times (\text{Demand per person}) \tag{17.3.1}$$

This equation shows that both the number of people and the demand that each puts on Earth'sresources must be considered in reducing the impact of humans on Earth. Both must be addressed to achieve sustainability.

As of 2010, Earth's human population approached 7 billion people and that of the U.S. stood at approximately 308 million people. Numbers of people on Earth will be controlled eventually by one way or another. Studies of natural ecosystems show that increases in population beyond an ecosystem's carrying capacity are always followed by a population crash; the same principle applies to human populations. Although improved food crop productivity and other measures have so far averted the catastrophic starvation that some experts were predicting in the 1960s, these humane practices have simply delayed the massive population crash that inevitably will occur if population continues to grow.

There is some good news (or perhaps less bad news) regarding population in that the population increase is significantly below that suggested by projections made 40 or 50 years earlier. Even in developing countries, birth rates have fallen to significantly lower levels than expected earlier. Particularly in Italy, Spain, France, and other nations in Europe, birth rates have fallen to appreciably below the replacement level and there is concern over depopulation. Even in the U.S., the birth rate has fallen below replacement levels and population growth that is taking place is the result of immigration. The increase in world population that has occurred over the last half century has been more due to decreasing death rates than to increasing birth rates. One U.N.official opined that, "It is not so much that people started reproducing like rabbits that they stopped dying like flies!" Although these trends do not justify complacency—population growth rates globally and in the world as a whole are still too high—they provide room for some encouragement and give hope that the first factor in Equation 17.3.1 may be controlled.

Reduction of demand per person for materials, energy, and other natural capital supplied by Earth through the application of sustainability science and technology must be accomplished to help mitigate the demands of high population. The second factor in the above equation, demand per person, may prove to be more intractable. A reasonable indicator of demand is reflected in the amount of carbon emitted per person each year, which reflects fossil fuel consumption as shown for several major countries in Figure 17.1. This figure shows that the more industrially developed countries emit the most per capita. However, the two countries with the largest populations, Chinaand India, have much lower carbon emissions per person. As the economies of these two giants grow, demand for material goods and energy-consuming services will grow as well. For example,if the average living standard of the citizens of China were to reach the modest level of those of Mexico, world petroleum consumption would have to double under conventional economic systems. Were the average person in China to live like the average person in the U.S., an impossible burden would be placed on Earth's carrying capacity. Obviously, ways must be found to meet the basic resource demands per person in more developed countries and means found to deliver a high quality of life to residents of less developed countries without placing unsupportable demands on Earth's resources.

Figure 17.1 illustrates another point regarding the relationship of population and consumption per capita, that the addition of population to more developed countries has a much greater impact on resources than it does on less developed nations. Taking per capita carbon emissions as a measure of impact, the addition of one person to the U.S. population has *at least 10 times* the impact as adding one person to India's population. It may be inferred that immigration into the U.S. and other developed countries from less highly developed nations has an inordinate impact upon resources as the immigrants attain the living standards of their new countries.

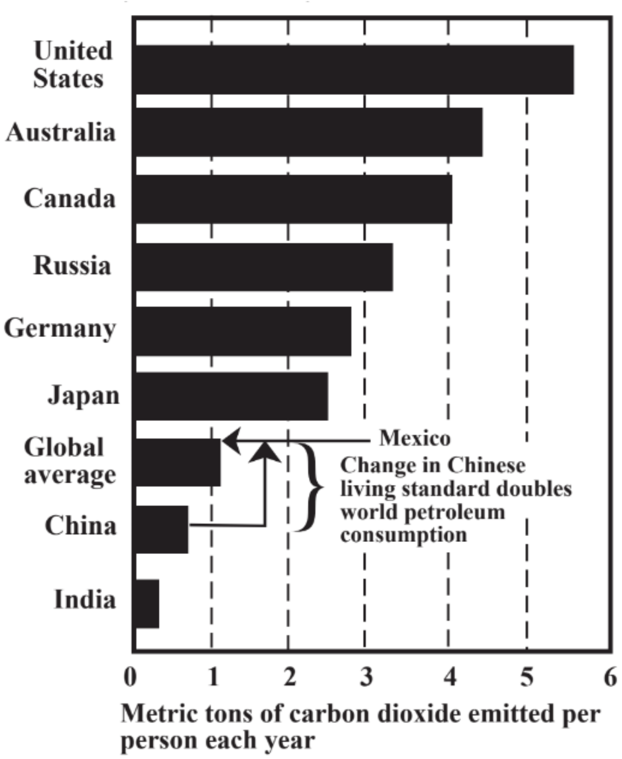

Figure 17.1. Per capita emissions of carbon dioxide per year in some major countries. The data shown are from 2004.

17.4: The Third Commandment

GIVEN THAT EVEN AT THE RISK OF GLOBAL CATASTROPHE, ***TECHNOLOGY WILL BE USED*** IN ATTEMPTS TO MEET HUMAN NEEDS, IT IS ESSENTIAL TO ACKNOWLEDGE THE ANTHROSPHERE AS ONE OF THE FIVE BASIC SPHERES OF THE ENVIRONMENT AND TO DESIGN AND OPERATE IT WITH A GOAL OF ZERO ENVIRONMENTAL IMPACT AND MAXIMUM SUSTAINABILITY

One of the most counterproductive attitudes of some environmentalists is a hostility to technology and to technological solutions to environmental problems. Humans are simply not going to go back to living in caves and teepees. Technology is here to stay. And even recognizing that the misuse of technology could result in catastrophe, *it will be used* to attempt to fulfill human needs. To deny that is unrealistic and foolish.

So a challenge for modern humankind is to use technology in ways that do not irreparably damage the environment and deplete Earth’s resources. In so doing it is essential to recognize the anthrosphere—structures and systems in the environment designed, constructed, and modified by humans—as one of the five main spheres of the environment (see Chapter 8, Section 8.6). Some of the major parts of the anthrosphere are shown in Figure 17.2

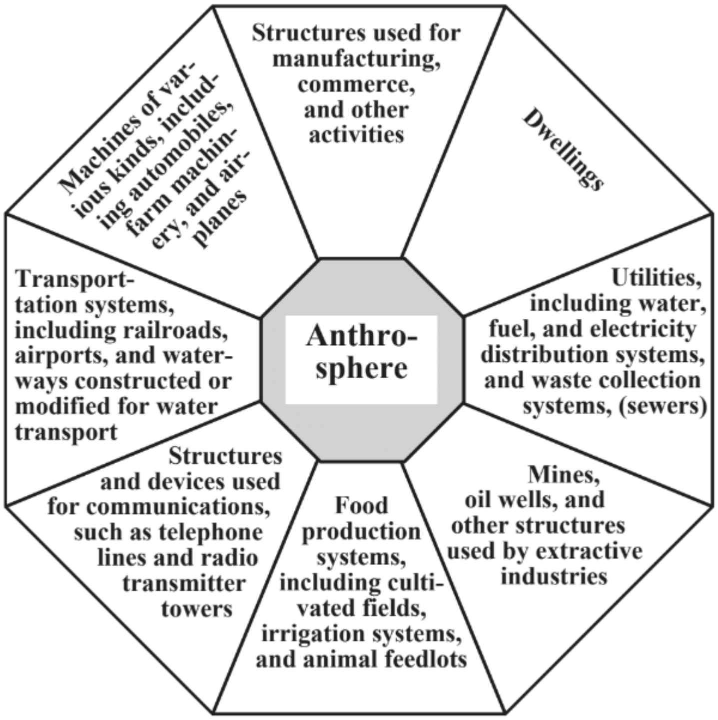

Figure 17.2. The anthrosphere is a multifaceted system designed and constructed by humans.

A key to sustainability is reorientation of the anthrosphere so that (1) it does not detract from sustainability and (2) it makes a contribution to sustainability. There is enormous potential for improvement in both of these areas.

Much is already known about designing and operating the anthrosphere so that it does not detract from sustainability. This goal can be accomplished through applications of the principles of industrial ecology discussed in Chapter 13. Basically, the anthrosphere must be operated so that maximum recycling of materials occurs, the least possible amount of wastes are generated, the environment is not polluted, and energy is used most efficiently. Furthermore, to the maximum extent possible, materials and energy must come from renewable sources.

The anthrosphere can be designed and operated in a positive way to improve and enhance the other environmental spheres. For example, modern earth-moving equipment with its capacity to move enormous amounts of material, though largely used in the past in ways that harmed the environment, can be employed positively to modify the geosphere surface in ways that will enhance the biosphere. Some specific examples of things that can be done are the following:

- Restoration of topsoil in areas depleted of this resource by poor farming practices or by contamination by wastes and pollutants
- Terracing land to prevent water erosion of soil

- Removal of obsolete and abandoned anthrospheric structures, such as old steel mills, and decontamination and restoration of the sites upon which they are located
- Construction of wetlands that can serve to restore wastewater to a quality enabling its release to the environment
- Pumping water underground to restore depleted aquifers
- Addition of “meanders” to streams, some of which have been unwisely straightened in the past, to reduce erosion and flooding
- Dredging of sediments from bodies of water and sediments to restore conditions conducive to aquatic life
- Construction and operation of reverse osmosis plants to remove excess salt from irrigation waters
- Construction of electrified railroads to replace inefficient, resource intensive, environmentally damaging truck transport

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17.5: The Fourth Commandment

GIVEN THAT ENERGY IS A KEY TO SUSTAINABILITY, THE DEVELOPMENT OF EFFICIENTLY-USED, ABUNDANT SOURCES OF ENERGY THAT HAVE LITTLE OR NO ENVIRONMENTAL IMPACT IS ESSENTIAL

As discussed in Chapter 15, “Sustainable Energy: The Essential Basis of Green Systems,” abundant, sustainable energy that can be used without harming the environment is arguably the most important facet of sustainability. Several aspects of energy in sustainability are discussed here. Examples of what can be accomplished with sufficient sustainable energy include the following: Toxic organic matter in hazardous waste substances can be totally destroyed and any remaining elements can be reclaimed or put into a form in which they cannot pose any hazards, wastewater from sewage can be purified to a form in which it can be reused as drinking water, pollutants can be removed from stack gas, and essential infrastructure can be constructed.

The accomplishment of sustainability is impossible without the development of efficient, sustainable, nonpolluting sources of energy. Here lies the greatest challenge to sustainability because the major fossil-fuel-based energy sources used today are inefficient, unsustainable, and, because of the threat to world climate from greenhouse gases, threaten Earth with a devastating form of pollution. Other means to provide energy that are friendly to the environment and sustainable must be developed.

Fortunately, as discussed in Chapter 15, alternatives are available to fossil fuels, given the will to develop them. Most renewable energy sources are powered ultimately by the sun. The most direct use of solar energy is solar heating. Solar heating of buildings and of water has been practiced increasingly in recent decades and should be employed wherever possible. The conversion of solar energy to electrical energy with photovoltaic cells is feasible and also practiced on an increasing scale. At present, electricity from this source is more expensive than that from fossil fuel sources, but solar electricity is gradually coming down in price and is already competitive in some remote locations far from power distribution grids.

Wind energy has emerged as a somewhat surprising alternative to fossil fuels and is now competitive in price in many areas. There are numerous geographical locations that are suitable for installation of large aerogenerators, which are to be found increasingly on the European landscape, particularly in Denmark and Germany. In the U.S., areas of California, Kansas, and West Texas are particularly well adapted to the installation of wind generating facilities. Some people regard the tall, graceful aerogenerators as ugly (others see them as graceful and picturesque), but they are certainly not as ugly as the landscape will become if massive climate warming occurs.

There is one big problem common to solar and wind energy—their intermittent nature. Solar energy works poorly when the sun does not shine and wind energy fails when the wind does not blow (although modern aerogenerators function at remarkably low wind speeds). Therefore, it is necessary to have reliable means of energy storage to provide for an even energy flow. Batteries for storage in major electrical systems would be too large and expensive. Possible alternatives include pumped water storage, kinetic energy in rapidly spinning flywheels, and production of hydrogen and oxygen by electrolysis of water with these two gases later recombined in fuel cells to produce electricity.

For some applications, most notably aircraft fuels, there are no realistic substitutes for carbon-based fuels. The challenge is to utilize such fuels with minimal addition of greenhouse gas carbon dioxide to the atmosphere. The best sustainable alternative for producing such fuels is to make them from biomass. It is possible to synthesize and utilize biomass fuels in a manner that is greenhouse-gas-neutral, that is, the carbon in the carbon dioxide released by their combustion came originally from the atmosphere by photosynthesis (as did the carbon in fossil fuels, but over a vastly longer time frame). Biomass is now used for liquid fuels in two major forms. One of these is ethanol made from the fermentation of sugar from grain starch or sugar from sugarcane. The other alternative is diesel fuel made by esterifying plant oils, particularly soybean oil. But these sources require a high-value raw material that is in demand for food and are economic only because of substantial government subsidies. Efforts to extract sugars for fermentation to alcohol from wood and crop byproduct sources including stalks, leaves, and straw have proven difficult and uneconomical.

The best alternative for preparing liquid fuels from biomass sources is thermochemical gasification, which produces a synthesis gas consisting of a mixture of carbon monoxide, CO, and elemental hydrogen, H_2. The proportion of H_2 can be increased by reacting CO with steam (H_2O). The CO and H_2 can be combined in various proportions to produce a wide range of fuels including methane, gasoline, jet fuel, and diesel fuel. The fraction of biomass that is consumed to generate the H_2 required to make synthetic fuels, a process that generates one molecule of greenhouse gas CO_2 for each molecule of H_2 produced, can be greatly reduced by using hydrogen gas made by the electrolysis of water using renewable wind energy.

Other alternatives for energy production, conservation, and utilization are presented in Chapter 15. The most promising of these are summarized below:

- Use of water power without dams by means including turbines anchored in flowing river water and tidal energy sources.
- Generation of geothermal energy, especially from dry hot rock sources.
- Use of fossil fuels with underground carbon dioxide sequestration.
- Increased use of nuclear power with breeder reactors that produce more fissionable matter than they consume and destruction of long-lived fissionable radioactive transuranic elements such as plutonium by their use as reactor fuel.
- Conversion of rail systems from diesel-powered locomotives to electricity generated from renewable sources.
- Increased use of methane (synthetic natural gas) made from biomass sources as fuel for motor vehicles
- Storage of energy from intermittent renewable sources by means such as pumping hydrogen gas made by electrolysis of water into underground storage sites

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17.6: The Fifth Commandment

CLIMATE CONDUCIVE TO LIFE ON EARTH MUST BE MAINTAINED AND ACCEPTABLE MEANS MUST BE FOUND TO DEAL WITH CLIMATE CHANGES THAT INEVITABLY OCCUR

The most plausible way that humans can ruin the global environment is by modifying the atmosphere such that global warming on a massive scale occurs. The most likely cause of such a greenhouse effect is release of carbon dioxide into the atmosphere from fossil fuel combustion as discussed in Section 10.6. Human activities are definitely increasing atmospheric carbon dioxide levels and there is credible scientific evidence that global warming is taking place. These phenomena and the climate changes that will result pose perhaps the greatest challenge for human existence, at least in a reasonably comfortable state, on the planet.

The Fifth Commandment is very much connected with the Fourth Commandment because so much of the increased atmospheric carbon dioxide levels are tied with energy and fossil fuel use. Other factors are involved as well. Destruction of forests (see the Sixth Commandment below)removes the carbon dioxide-fixing capacity of trees, and the decay of biomass residues from forests releases additional carbon dioxide to the atmosphere. Methane is also a greenhouse gas. Itis released to the atmosphere by flatulent emissions of ruminant animals (cows, sheep, moose), from the digestive tracts of termites attacking wood, and from anoxic bacteria growing in flooded rice paddies. Some synthetic gases, particularly virtually indestructible fluorocarbons, are potent greenhouse gases as well. The achievement of sustainability requires minimization of those practices that result in greenhouse gas emissions, particularly the burning of fossil fuels

Unfortunately, if predictions of greenhouse gas warming of Earth’s climate are accurate, some climate change inevitably will occur. Therefore, it will be necessary to adapt to warming and the climate variations that it will cause. Some of the measures that will have to be taken are listed below:

- Relocation of agricultural production from drought-plagued areas to those mademore hospitable to crops by global warming (in the Northern Hemisphereagricultural areas are likely to shift northward)
- Massive irrigation projects to compensate for drought
- Development of heat-resistant, drought-tolerant crops
- Relocation of populations from low-lying coastal areas flooded by rising sea levels caused by melted ice and expansion due to warming of ocean water
- Construction of sea walls and other structures to compensate for rising sea levels
- Water desalination plants using sea water and brackish groundwater to make up for reduced precipitation in some areas
- Increased utilization of saline water such as growing algae for biomass energy production in salt water instead of fresh water

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17.7: The Sixth Commandment

The loss of Earth’s biological productivity would certainly adversely affect sustainability and, in the worst case, could lead to massive starvation of human populations. A number of human activities have been tending to adversely affect biological productivity, but these effects have been largely masked by remarkable advances in agriculture such as by increased use of fertilizer, development of highly productive hybrid crops, and widespread irrigation. Some of the factors reducing productivity are the following:

- Loss of topsoil through destructive agricultural practices
- Urbanization of land and paving of large amounts of land area
- Desertification in which once productive land is degraded to desert
- Deforestation
- Air pollution that adversely affects plant growth

Biological productivity is far more than a matter of proper soil conditions. In order to preserve and enhance biological productivity, all five environmental spheres must be considered. Obviously, in the geosphere, topsoil must be preserved; once it is lost, the capacity of land to produce biomass is almost impossible to restore. Deforestation must be reversed and reforestation of areas no longer suitable for crop production promoted. (This is happening in parts of New England where rocky, hilly farmland is no longer economical to use for crop production.) In more arid regions where trees grow poorly, prairie lands should be preserved, desertification from overgrazing and other abuse prevented, and marginal crop lands restored to grass.

The hydrosphere may be managed in a way to enhance biological productivity. Measures such as terracing of land to minimize destructive rapid runoff of rainfall and to maximize water infiltration into groundwater aquifers may be taken. Watersheds, areas of land that collect rainwater and which may be areas of high biological productivity should be preserved and enhanced.

It is especially important that the atmosphere be maintained in a condition of climate conducive to high bioproductivity by minimization of global warming.

Management of the biosphere, itself, may enhance biological productivity. This has long been done with highly productive crops. The production of wood and wood pulp on forest lands can be increased—sometimes dramatically—with high-yielding trees, such as some hybrid poplars. Hybrid poplars from the same genus as cottonwoods or aspen trees grow faster than any other tree variety in northern temperate regions, so much so that for some applications they may be harvested annually. They have the additional advantage of spontaneous regrowth from stumps left from harvesting.

Proper management of the anthrosphere is essential to maintaining biological productivity. The practice of paving large areas of productive land should be checked. Factories in the anthrosphere can be used to produce fertilizers for increased biological productivity.

17.8: The Seventh Commandment

MATERIAL DEMAND MUST BE DRASTICALLY REDUCED; MATERIALS MUST COME FROM RENEWABLE SOURCES, BE RECYCLABLE AND, IF DISCARDED TO THE ENVIRONMENT, BE DEGRADABLE

Reduced material demand is essential to sustainability. Fortunately, much is being done to reduce material demand and the potential exists for much greater reductions. Nowhere is this more obvious than in the communications and electronics industries. Old photos of rail lines from the early 1900s show them lined with poles holding 10 or 20 heavy copper wires, each for carrying telephone and telegraph communications. Now far more information can be carried by a single thread-sized strand of fiber optic material. The circuitry of a bulky 1948-vintage radio with its heavy transformers and glowing vacuum tubes has been replaced by circuit chips smaller than a fingernail. These are examples of dematerialization and also illustrate material substitution. For example, fiber optic cables are made from silica extracted from limitless supplies of sand whereas the conducting wires that they replace are made from scarce copper.

Wherever possible, materials should come from renewable sources. This favors wood, for example, over petroleum-based plastics for material. Wood and other biomass sources can be converted to plastics and other materials. From a materials sustainability viewpoint natural rubber is superior to petroleum-based synthetic rubber, and it is entirely possible that advances in genetic engineering will enable growth of rubber-producing plants in areas where natural rubber cannot now be produced.

Materials should be recyclable insofar as possible. Much of the recyclability of materials has to do with how they are used. For example, binding metal components strongly to plastics makes it relatively more difficult to recycle metals. Therefore, it is useful to design apparatus, such as automobiles or electronic devices, in a manner that facilitates recycling.

Some materials, by the nature of their uses, have to be discarded to the environment. An example of such a material is household detergent, which ends up in wastewater. Such materials should be readily degradable, usually by the action of microorganisms. Detergents provide an excellent example of a success story with respect to degradability. The household detergents that came into widespread use after World War II contained ABS surfactant (which makes the water “wetter”) that was poorly biodegradable such that sewage treatment plants and receiving waters were plagued with huge beds of foam. The ABS surfactant was replaced by LAS surfactant which is readily broken down by bacteria and the problem with undegradable surfactant in water was solved.

17.10: The Ninth Commandment

IT MUST BE ACKNOWLEDGED THAT THERE ARE RISKS IN TAKING NO RISKS

Some things for which there are no suitable substitutes are inherently dangerous. We must avoid becoming so risk adverse that we do not allow dangerous, but necessary activities (some would put sex in this category) to occur. A prime example is nuclear energy. The idea of using a“controlled atom bomb” to generate energy is a very serious one. But the alternative of continuing to burn large amounts of greenhouse-gas-generating fossil fuels, with the climate changes that almost certainly will result, or of severely curtailing energy use, with the poverty and other ill effects that would almost certainly ensue, indicates that the nuclear option is a good one.

So it is necessary to manage risk and to use risky technologies in a safe way. As discussed in Chapter 15, with proper design and operation, nuclear power plants can be operated safely and spent nuclear fuel can be processed safely. Modern technology and applications of computers can be powerful tools in reducing risks. Computerized design of devices and systems can enable designers to foresee risks and plan safer alternatives. Computerized control can enable safe operation of processes such as those in chemical manufacture. Redundancy can be built into computerized systems to compensate for failures that may occur. The attention of computers does not wander, they do not do drugs, become psychotic, or do malicious things (although people who use them are not so sure). Furthermore, as computerized robotics advance, it is increasingly possible for expendable robots to do dangerous things in dangerous areas where in the past humans would have been called upon to take risks.

Although the goal of risk avoidance in green chemistry and green technology as a whole is a laudable one, it should be kept in mind that without a willingness to take some risks, many useful things would never get done. Without risk-takers in the early days of aviation, we would not have the generally safe and reliable commercial aviation systems that exist today. Without the risks involved in testing experimental pharmaceuticals, many life-saving drugs would never make it to the market. Although risks must be taken judiciously, a total unwillingness to take risks will result in stagnation and a lack of progress in important areas required for sustainability.

17.11: The Tenth Commandment

EDUCATION IN SUSTAINABILITY IS ESSENTIAL; IT MUST EXTEND TO ALL AGES AND STRATA OF SOCIETY, IT MUST BE PROMULGATED THROUGH ALL MEDIA, AND IT IS THE RESPONSIBILITY OF ALL WHO HAVE EXPERTISE IN SUSTAINABILITY

Although the achievement of sustainability is the central challenge facing humanity, most people know pathetically little about it. The reader of this chapter belongs to a small fraction of the populace who have been exposed to the idea of sustainability. If asked, a distressingly large number of people would probably say that they know little about sustainability (and some would say that they do not even care or that they are even hostile to the concept!). Therefore, education is essential and a key to achieving sustainability.

Education in sustainability must begin early with children in primary school and should be integrated into curricula from kindergarten through graduate school. By providing containers for recyclables in grade schools, there is some small benefit from the waste paper, plastics, and aluminum cans collected, but a much greater benefit in the lessons of sustainability that those containers illustrate. Green chemistry should be part of the background of every student graduating with a university degree in chemistry and the principles of green engineering should be part of the knowledge base of every engineering graduate. But of equal —often greater—importance is the education of people in nontechnical areas in the principles of sustainability. Lawyers, political scientists, economists, and medical professionals should all graduate with education in sustainability.

A particular challenge is that of informing the general public of the principles of sustainability and of its importance. The general public has more choice in its sources of information than does the captive audience of a student body, so the challenge of informing them about sustainability is greater. In this respect the media and the internet have key roles to play. Unfortunately, relative to the large amounts of media time devoted to the salacious antics of some attention-seeking fools—matters that have virtually no relevance to the lives of everyday citizens—almost no air time is devoted to sustainability, which is highly relevant to the lives of all. Therefore, those who have an interest in, and knowledge of sustainability have an obligation to get the message out through the media and the internet.

17.12: Some Sensible Measures for Sustainability

Some ideas for measures to enhance sustainability are discussed here. Some of these are simple and readily implemented. Others are grandiose and even “far out.” Most have probably been suggested in one form or another by others or have been implemented in some places. Few require the invention of anything new. They are presented here with the idea of stimulating thought and discussion. Probably the reader can suggest other ideas for sustainability. Although most of these ideas are presented from the viewpoint of their potential implementation in the United States, most of them, or closely related measures, could be implemented in other countries as well.

The Methane Energy Economy

The basic idea of the methane energy economy is to greatly increase the role of natural gas as a fuel, particularly for transportation. Methane, CH_4, is the cleanest burning of the fossil fuels and produces the least greenhouse gas per unit energy generated. Significantly more energy can be stored in a pressurized tank of methane than is the case for elemental hydrogen. Largely regarded as a rapidly depleting source of fuel as recently as the turn of the century (2000), natural gas has emerged as an abundant energy source. There are two major reasons for this abundance. One is a revolutionary development of methods for gas extraction from hydraulically-fractured tight shale formations. These formations, previously inaccessible for natural gas extraction, are widely distributed in many countries including in the U. S. wide areas of Pennsylvania, Arkansas, Louisiana, and Texas (one of the richest deposits lies beneath the city of Fort Worth, Texas). A second factor is the construction of large depots for the export of liquified natural gas from countries that formerly burned it in flares as a waste byproduct of crude oil production. As of 2010it was projected that the U.S. had 100 years of natural gas reserves and might become an exporter of this fuel.

As depletable underground sources of methane become exhausted, methane can be made by gasification of coal and biomass and the byproduct carbon dioxide from solids gasification converted to methane by reacting CO_2 with hydrogen made from water electrolysis using electricity from renewable sources such as wind. Methane is readily distributed by pipeline, and a system for so doing is already in place in the U.S. and many other nations. Once properly installed underground, a pipeline is a less disruptive, highly reliable, means of transporting energy than is a high-voltage electrical line or transport of liquid fuels by train or barge. An important consideration is that the pipeline infrastructure must be very well designed, constructed, and maintained to avoid destructive blowouts. A very bad natural gas pipeline failure happened on September 9, 2010, with the rupture of a 30-inch natural gas pipeline in San Bruno, California. This devastating incident resulted in an explosion and massive fire that killed 8 people, destroyed 38 houses, damaged many more homes, and left a crater 12 meters deep, 51 m long, and 8 m wide.

Conversion to Highly Efficient Hybrid Vehicles

As noted above, methane is a very sustainable energy source that can replace most existing applications of fossil fuels. One of the most attractive options is to use methane to power locomotives, trucks, and other vehicles. The Clean Air Power Company has designed highly energy-efficient truck engines that get 90% of their energy from methane fed into the engine with intake air and that are ignited by a small amount of diesel fuel injected at the peak of the compression stroke.[5] This is an application of the stratified-charge ignition concept that enables internal combustion engines to run on a fuel/air mixture that is too lean (fuel-deficient) to ignite with a spark but can be ignited by a small fuel-rich ignition zone created by injecting fuel directly into a small region of the combustion chamber (in a spark-ignited engine directly onto the spark plug).

The ultimate in automobile fuel economy would be a plug-in hybrid vehicle with a natural gas fueled stratified-charge ignition engine (see above). The battery on such a vehicle could be charged by plugging into a source of electricity and with a full charge could be driven several tens of miles distance before the internal combustion engine would need to be engaged. When needed to charge the battery, the internal combustion engine could be run at optimum speeds for comparatively long periods of time for maximum efficiency and minimum pollution. One problem with hybrid vehicles is the need for the internal combustion engine to start immediately in cold weather to provide heat for the vehicle heater. This problem may be overcome with a phase-change material held as a heated liquid in an insulated container and that releases latent heat as it solidifies.[6]

Diverting the Mississippi

In Chapter 8 a scheme was presented to utilize the vast resource of the Mississippi River by diverting part of its flow from the Gulf of Mexico to water-deficient regions of the southwesternU.S. and northern Mexico. The scheme would impound a fraction of the river discharge into a contained wetlands area at the mouth of the river, allow natural processes to purify the water, and use wind energy to pump the purified water as much as 2000 miles as far as southern California for municipal water supply and irrigation. Major sustainability aspects of this scheme are the following:

- Plant growth in the constructed wetlands impoundment would remove nutrients from the water thereby reducing their discharge into the Gulf of Mexico where they cause a eutrophied “dead zone.”
- Plant biomass harvested from the constructed wetlands could be used for synthetic fuels production.
- River sediment collected in the impoundment would aid in coastal restoration.
- Water transported to arid regions would reduce current excessive demand for water from the Colorado and Rio Grande rivers.
- Fish and freshwater shrimp grown in the waterway and impoundments along its course could provide a significant source of protein

Three Day Per Week Mail Delivery

In the modern electronic age, communication by conventional mail is relatively less important than it was in the pre-computer age. Significant cost and energy savings could be achieved by reducing mail delivery to three days per week, Monday, Wednesday, Friday on some routes and Tuesday, Thursday, Saturday on alternate routes. Such a system would need to be implemented gradually to avoid layoffs of personnel.

Rail Connections to and within All Major Airports

Ground transportation systems to many major airports are cumbersome, slow, and wasteful oftime and energy. Each large airport should have an integrated rail system linking terminals to the rail system serving the city and, within the airport area itself, parking areas, car rental locations,hotels and other facilities. Such a totally integrated system would save energy and time and significantly reduce pollution in the airport complex.

Fertilization of Algae Beds with Exhaust Carbon Dioxide

This proposal is to use combustion exhaust gas from powerplant furnaces to enrich algae cultures with carbon dioxide. The efficiency of algal media to sequester carbon dioxide is enhanced by the ability of algae to make media basic in the production of biomass ({CH_2O}) by the following photosynthesis reaction

$$\mathrm{HCO_3^-} + \mathrm{H_2O} + h\nu \rightarrow (\mathrm{CH_2O}) + \mathrm{O_2} + \mathrm{OH^-} \tag{17.12.1}$$

Such a system would further purify the exhaust gas by sequestering acid gas, particularly SO_2, and particulate matter

Nuclear Fuel Reprocessing

Burying spent nuclear fuel in a permanent disposal repository is a wasteful practice inconsistent with the principles of sustainability and green chemistry. A much better practice is to reprocess the spent fuel as explained in the discussion of nuclear energy in Section 15.10. The relatively short-lived fission products can be isolated for burial and will decay to harmless levels within a few centuries. The longer-lived transuranic elements, several of which are useful fissionable fuels can be treated by neutron bombardment, a process called transmutation. As an interim solution, relatively long term storage of spent fuel elements at reactor sites (up to 100 years, for example) enables decay of a very large fraction of the initial radioactivity making it easier to reprocess the fuels. Such long term storage also allows time for the development of improved recycling technologies and breeder reactors that can use spent fuels.

Extraction of Heat from Wastewater

Wastewater is a significant source of heat that can be extracted with a heat pump for heating homes and commercial buildings. The concept involves collecting filtered sewage in a storage tank and pumping heat from the water with a heat pump. Subsequently, the water, cooled by several degrees, can be discharged to the sewer. The same system can be used for cooling in which case heat can be pumped into the water before it is discharged

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17.9: The Eighth Commandment

THE PRODUCTION AND USE OF TOXIC, DANGEROUS, PERSISTENT SUBSTANCES SHOULD BE MINIMIZED AND SUCH SUBSTANCES SHOULD NOT BE RELEASED TO THE ENVIRONMENT; ANY WASTES DISPOSED TO DISPOSAL SITES SHOULD BE CONVERTED TO NONHAZARDOUS FORM

The most fundamental tenet of green chemistry is to avoid the production and use of toxic, dangerous, persistent substances and to prevent their release to the environment. With the caveat that it is not always possible to totally avoid such substances (see the Ninth Commandment below)significant progress has been made in this aspect of green chemistry. Much research is ongoing in the field of chemical synthesis to minimize toxic and dangerous substances. In cases where such substances must be used because no substitutes are available, it is often possible to make minimum amounts of the materials on demand so that large stocks of dangerous materials need not be maintained.

Many of the environmental problems of recent decades have been the result of improperly disposed hazardous wastes. Current practice calls for placing hazardous waste materials in secure chemical landfills. There are two problems with this approach. One is that, without inordinate expenditures, landfills are not truly “secure” and the second is that, unlike radioactive materials that do eventually decay to nonradioactive substances, some refractory chemical wastes never truly degrade to nonhazardous substances. Part of the solution is to install monitoring facilities around hazardous waste disposal facilities and watch for leakage and emissions. But problems may show up hundreds of years later, not a good legacy to leave to future generations.

Therefore, any wastes that are disposed should first be converted to nonhazardous forms. This means destruction of organics and conversion of any hazardous elements to forms that will not leach into water or evaporate. A good approach toward this goal is to co-fire hazardous wastes with fuel in cement kilns; the organics are destroyed and the alkaline cement sequesters acid gas emissions and heavy metals. Ideally, hazardous elements, such as lead, can be reclaimed and recycled for useful purposes. Conversion of hazardous wastes to nonhazardous forms may require expenditure of large amounts of energy (see the fourth commandment, above)

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Questions and Problems

Access to and use of the internet is assumed in answering all questions including general information, statistics, constants, and mathematical formulas required to solve problems. These questions are designed to promote inquiry and thought rather than just finding material in the text. So in some cases there may be several "right" answers. Therefore, if your answer reflects intellectual effort and a search for information from available sources, your answer can be considered to be "right.

1. The U.S. Geological Survey posts prices in metals corrected for inflation from 1959 through 1998 athttp://minerals.usgs.gov/minerals/.../metal_prices/. Other internet sources give current prices of metals. Using these resources, look up past and current prices of copper, chromium, nickel, tin and tungsten, the metals in the historic Ehrlich/Simon wager to see how the wager would have turned out in recent years. Explain your observations and suggest future trends.

2. At the beginning of the chapter were stated six "great challenges to sustainability." Using adiagram, if appropriate, suggest how these challenges are very much interrelated.

3. Much of Earth's population is dependent upon seafood for its protein. Suggest how provisionof adequate food by this route might be affected by the challenges of adequate energy supply as related to contamination of Earth's environment with toxic and persistent substances.

4. Suggest scenarios by which the people of your country might be adversely affected and its population might even decline because of declines in key environmental support systems. Suggest how these problems might be avoided in the future by actions taken now.

5. Look up telecommuting on the internet and explain how it might fit with the ten commandments of sustainability.

6. In a quote attributed to the British sociologist Martin Albrow, sociospheres consist of "distinct patterns of social activities belonging to networks of social relations of very different intensity, spanning widely different territorial extents, from a few to many thousands of miles." Suggest how sociospheres relate to the anthrosphere. What is your sociosphere? How might sociospheres be important in sustainability.

7. It has been estimated that U.S. coal resources can provide for up to three centuries of U.S.energy needs and could provide energy for much of the world. Is this a sustainable source ofenergy? Explain.

8. Explain how unsustainability may be the result of depletion of resources, environmentalpollution, or a combination. Give an example in which environmental pollution reducesresource availability.

9. From news events of the last five years, cite evidence that global climate change is in factoccurring. Cite evidence to the contrary.10. Currently, population growth tends to occur in coastal areas. Suggest how global warmingmight reverse that trend.11. Prior to European settlement, vast areas of the U.S. Great Plains supported huge herds of bisonthat provided the base for a viable Native American population. Given the erratic climate ofthat region, depleted groundwater for irrigation, and the aversion of many people to dwell onthe "lone prairie," some authorities have suggested that these areas revert to a bison-basedsystem, sometimes called the "buffalo commons." Suggest how such a system might be viableand sustainable and give arguments against it.12. Is the term "secure chemical landfill" an oxymoron? What are the alternatives to suchlandfills?13. Among the ideas for sustainability discussed in Section 17.12, might be added a suggestion forgreatly increasing the numbers of telecommuters. What are telecommuters? How mightincreasing their numbers enhance sustainability?14. Some countries in Asia have constructed new airports with exemplary rail connections. Citeand discuss several examples.

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Index

A

agriculture
12.11: Production of Food and Fiber by the Biosphere - Agriculture

anthrosphere
8.6: The Anthrosphere

aquifer
8.2: The Hydrosphere

B

biochar
11.11: Soil Loss - Desertification and Deforestation

biochemical effect
16.4: Toxic Substances and Toxicology

biodegradation
12.10: Biodegradation

biosphere
8.5: The Biosphere
12.2: The Biosphere

bond energy
4.5: Covalent Bonds in Compounds

botulinum
16.6: Protecting Water, Food, and Air

breeder reactor
15.10: Nuclear Energy

C

carbon sequestration
10.6: The Enormous Importance of Climate

cellulose
14.7: Cellulose

chain reaction
15.10: Nuclear Energy

climate
10.6: The Enormous Importance of Climate

climate change
10.6: The Enormous Importance of Climate

clod
11.8: Have You Thanked a Clod Today?

cometabolism
12.10: Biodegradation

conservation tillage
11.11: Soil Loss - Desertification and Deforestation
12.11: Production of Food and Fiber by the Biosphere - Agriculture

D

deforestation
11.11: Soil Loss - Desertification and Deforestation

desertification
11.11: Soil Loss - Desertification and Deforestation

detoxication
12.10: Biodegradation

G

geosphere
8.4: The Geosphere
11.2: The Nature of the Geosphere

glyphosate
12.1: Pigweed’s Revenge

green products
1.10: Green Products and Services- Design for Sustainability

H

humification
11.8: Have You Thanked a Clod Today?

hydrogen
3.2: Hydrogen - The Simplest Atom

hydrologic cycle
8.2: The Hydrosphere

L

Lattice Energy
4.3: Sodium Chloride and Ionic Bonds

lignin
14.9: Lignin

M

microcrystalline cellulose
14.7: Cellulose

micronutrients
11.9: Plant Nutrients and Fertilizers in Soil

mineralization
12.10: Biodegradation

moderator
15.10: Nuclear Energy

municipal refuse
11.7: The Geosphere as a Waste Repository

N

nuclear waste
15.10: Nuclear Energy

O

octet
3.6: The Magic Octet of 8 Outer-Shell Electrons

octet rule
3.6: The Magic Octet of 8 Outer-Shell Electrons

P

passive stability
15.10: Nuclear Energy

pic
Questions and Problems

R

rhizosphere
11.8: Have You Thanked a Clod Today?

ricin
16.6: Protecting Water, Food, and Air

S

sanitary landfills
11.7: The Geosphere as a Waste Repository

sarin
16.6: Protecting Water, Food, and Air

soil conservation
11.11: Soil Loss - Desertification and Deforestation

soil erosion
11.11: Soil Loss - Desertification and Deforestation

surface albedo
11.2: The Nature of the Geosphere

sustainability
1.3: Seeing Green

T

transmutation
15.10: Nuclear Energy

travelling wave reactor
15.10: Nuclear Energy

X

xenobiotic substances
16.4: Toxic Substances and Toxicology

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        - 1.1: Sustainability - *CC BY-NC-SA 4.0*
        - 1.2: The Environment and the Five Environmental Sphere - *CC BY-NC-SA 4.0*
        - 1.3: Seeing Green - *CC BY-NC-SA 4.0*
        - 1.4: Natural Capital of the Earth - *CC BY-NC-SA 4.0*
        - 1.5: Sustainability as a Group Effort- It Takes a (Very Big) Village - *CC BY-NC-SA 4.0*
        - 1.6: Sustainable Energy- Away from the Sun and Back Again - *CC BY-NC-SA 4.0*
        - 1.7: Green Science - *CC BY-NC-SA 4.0*
        - 1.8: Green Technology - *CC BY-NC-SA 4.0*
        - 1.9: Sustainability and the Eco-Economy - *CC BY-NC-SA 4.0*
        - 1.10: Green Products and Services- Design for Sustainability - *CC BY-NC-SA 4.0*
        - Questions and Problems - *CC BY-NC-SA 4.0*
    - 2: The Key Role of Chemistry and Making Chemistry Green - *CC BY-NC-SA 4.0*
        - 2.1: Chemistry is Good (and Unavoidable) - *CC BY-NC-SA 4.0*
        - 2.2: The Environment and its Chemistry - *CC BY-NC-SA 4.0*
        - 2.3: What is Environmental Chemistry? - *CC BY-NC-SA 4.0*
        - 2.4: Environmental Pollution - *CC BY-NC-SA 4.0*
        - 2.5: Practice of Green Chemistry - *CC BY-NC-SA 4.0*
        - 2.6: Green Chemistry and Synthetic Chemistry - *CC BY-NC-SA 4.0*
        - 2.7: Reduction of Risk- Hazard and Exposure - *CC BY-NC-SA 4.0*
        - 2.8: The Risks of No Risks - *CC BY-NC-SA 4.0*
        - 2.9: Waste Prevention - *CC BY-NC-SA 4.0*
        - 2.10: Basic Principles of Green Chemistry - *CC BY-NC-SA 4.0*
        - 2.11: Some Things to Know About Chemistry before You Even Start - *CC BY-NC-SA 4.0*
        - 2.12: Combining Atoms to Make Molecules and Compounds - *CC BY-NC-SA 4.0*
        - 2.13: The process of making and breaking chemical bonds- chemical reactions - *CC BY-NC-SA 4.0*
        - 2.14: The Nature of Matter and States of Matter - *CC BY-NC-SA 4.0*
        - References and Questions - *CC BY-NC-SA 4.0*
    - 3: The Elements - Basic Building Blocks of Green Chemicals - *CC BY-NC-SA 4.0*
        - 3.1: Elements, Atoms, and Atomic Theory - *CC BY-NC-SA 4.0*
        - 3.2: Hydrogen - The Simplest Atom - *CC BY-NC-SA 4.0*
        - 3.3: Helium - The First Noble Gas - *CC BY-NC-SA 4.0*
        - 3.4: Lithium, The First Metal - *CC BY-NC-SA 4.0*
        - 3.5: The Second Period of the Periodic Table - *CC BY-NC-SA 4.0*
        - 3.6: The Magic Octet of 8 Outer-Shell Electrons - *CC BY-NC-SA 4.0*
        - 3.7: Completing the 20-Element Periodic Table - *CC BY-NC-SA 4.0*
        - 3.8: The Brief Periodic Table is Complete - *CC BY-NC-SA 4.0*
        - 3.E: The Elements - Basic Building Blocks of Green Chemicals (Exercises) - *CC BY-NC-SA 4.0*
        - 3.R: References - *CC BY-NC-SA 4.0*
    - 4: Compounds- Safer Materials for a Safer World - *CC BY-NC-SA 4.0*

  - 4.1: Chemical Bonds and Compound Formation - *CC BY-NC-SA 4.0*
  - 4.2: Electrons Involved in Chemical Bonds and Octets of Electrons - *CC BY-NC-SA 4.0*
  - 4.3: Sodium Chloride and Ionic Bonds - *CC BY-NC-SA 4.0*
  - 4.4: Covalent Bonds in H2 and Other Molecules - *CC BY-NC-SA 4.0*
  - 4.5: Covalent Bonds in Compounds - *CC BY-NC-SA 4.0*
  - 4.6: Covalent Bonds and Green Chemistry - *CC BY-NC-SA 4.0*
  - 4.7: Predicting Formulas of Covalently Bound Compounds - *CC BY-NC-SA 4.0*
  - 4.8: Chemical Formulas, the Mole, and Percentage Composition - *CC BY-NC-SA 4.0*
  - 4.9: What Are Chemical Compounds Called? - *CC BY-NC-SA 4.0*
  - 4.10: Acids, Bases and Salts - *CC BY-NC-SA 4.0*
  - Questions and Problems - *CC BY-NC-SA 4.0*
- 5: Chemical Reactions- Making Materials Safely and Sustainable - *CC BY-NC-SA 4.0*
  - 5.1: Describing What Happens with Chemical Equations - *CC BY-NC-SA 4.0*
  - 5.2: Balancing Chemical Equations - *CC BY-NC-SA 4.0*
  - 5.3: Just Because You Can Write It Doesn't Mean That It Will Happen - *CC BY-NC-SA 4.0*
  - 5.4: Yield And Atom Economy in Chemical Reactions - *CC BY-NC-SA 4.0*
  - 5.5: Catalysts That Make Reactions Go - *CC BY-NC-SA 4.0*
  - 5.6: Kinds of Chemical Reactions - *CC BY-NC-SA 4.0*
  - 5.7: Oxidation-Reduction Reactions and Green Chemistry - *CC BY-NC-SA 4.0*
  - 5.8: Quantitative Information from Chemical Reactions - *CC BY-NC-SA 4.0*
  - 5.9: Energy in Chemical Reactions - *CC BY-NC-SA 4.0*
  - 5.10: Stoichiometry by the Mole Ratio Method - *CC BY-NC-SA 4.0*
  - 5.11: Limiting Reactant and Percent Yield - *CC BY-NC-SA 4.0*
  - 5.12: Titrations - Measuring Moles by Volume of Solution - *CC BY-NC-SA 4.0*
  - 5.13: Industrial Chemical Reactions - The Solvay Process - *CC BY-NC-SA 4.0*
  - Questions and Problems - *CC BY-NC-SA 4.0*
- 6: The Wonderful World of Carbon - Organic Chemistry and Biochemicals - *CC BY-NC-SA 4.0*
  - 6.1: Rings and Chains of Carbon Atoms - *CC BY-NC-SA 4.0*
  - 6.2: Compounds of Carbon and Hydrogen - Hydrocarbons - *CC BY-NC-SA 4.0*
  - 6.3: Using Lines To Show Organic Structural Formulas - *CC BY-NC-SA 4.0*
  - 6.4: Functional Groups - *CC BY-NC-SA 4.0*
  - 6.5: Giant Molecules from Small Organic Molecules - *CC BY-NC-SA 4.0*
  - Questions and Problems - *CC BY-NC-SA 4.0*
  - Supplementary References - *CC BY-NC-SA 4.0*
- 7: Chemistry of Life and Green Chemistry - *CC BY-NC-SA 4.0*
  - 7.1: Green Biochemistry - *CC BY-NC-SA 4.0*
  - 7.2: Biochemistry and the Cells - *CC BY-NC-SA 4.0*
  - 7.3: Carbohydrates - *CC BY-NC-SA 4.0*
  - 7.4: Proteins - *CC BY-NC-SA 4.0*
  - 7.5: Lipids - Fats, Oils, and Hormones - *CC BY-NC-SA 4.0*
  - 7.6: Nucleic Acids - *CC BY-NC-SA 4.0*
  - 7.7: Enzymes - *CC BY-NC-SA 4.0*
  - 7.8: Biochemical Processes in Metabolism - *CC BY-NC-SA 4.0*
  - 7.9: Biochemistry of Toxic Substances and Toxicological Chemistry - *CC BY-NC-SA 4.0*
  - Literature Cited - *CC BY-NC-SA 4.0*
  - Questions and Problems - *CC BY-NC-SA 4.0*
  - Supplementary References - *CC BY-NC-SA 4.0*
- 8: The Five Environmental Spheres and Biogeochemical Cycle - *CC BY-NC-SA 4.0*
  - 8.1: Five Environmental Spheres - *CC BY-NC-SA 4.0*
  - 8.2: The Hydrosphere - *CC BY-NC-SA 4.0*
  - 8.3: The Atmosphere - *CC BY-NC-SA 4.0*
  - 8.4: The Geosphere - *CC BY-NC-SA 4.0*
  - 8.5: The Biosphere - *CC BY-NC-SA 4.0*
  - 8.6: The Anthrosphere - *CC BY-NC-SA 4.0*
  - 8.7: Cycles of Matter - *CC BY-NC-SA 4.0*
  - Questions and Problems - *CC BY-NC-SA 4.0*
  - Supplementary References - *CC BY-NC-SA 4.0*
- 9: Water - the Ultimate Green Substance - *CC BY-NC-SA 4.0*
  - 9.1: H_2O - Simple Formula, Remarkable Molecule - *CC BY-NC-SA 4.0*
  - 9.2: Occurrence, Availability , and Utilization of Water on Earth - *CC BY-NC-SA 4.0*
  - 9.3: Water Chemistry - *CC BY-NC-SA 4.0*
  - 9.4: Water Pollution - *CC BY-NC-SA 4.0*
  - 9.5: Greening of Water - Purification Before Use - *CC BY-NC-SA 4.0*
  - 9.6: Wastewater Treatment - *CC BY-NC-SA 4.0*
  - 9.7: Advanced Wastewater Treatment and Recycling - *CC BY-NC-SA 4.0*
  - 9.8: The Many Uses of Water - *CC BY-NC-SA 4.0*

  - 9.9: Hot Water - Pressurized Subcritical Water - *CC BY-NC-SA 4.0*
  - 9.10: Supercritical Water - *CC BY-NC-SA 4.0*
  - Literature Cited - *CC BY-NC-SA 4.0*
  - Questions and Problems - *CC BY-NC-SA 4.0*
  - Supplementary References - *CC BY-NC-SA 4.0*
- 10: Blue Skies for a Green Environment - *CC BY-NC-SA 4.0*
  - 10.1: More Than Just Air to Breathe - *CC BY-NC-SA 4.0*
  - 10.2: The Gas Laws - *CC BY-NC-SA 4.0*
  - 10.3: The Protective Atmosphere - *CC BY-NC-SA 4.0*
  - 10.4: Atmospheric Chemistry and Photochemical Reactions - *CC BY-NC-SA 4.0*
  - 10.5: Energy and Mass Transfer in the Atmosphere - *CC BY-NC-SA 4.0*
  - 10.6: The Enormous Importance of Climate - *CC BY-NC-SA 4.0*
  - 10.7: Atmospheric Particle Pollutants - *CC BY-NC-SA 4.0*
  - 10.8: Pollutant Gaseous Oxides - *CC BY-NC-SA 4.0*
  - 10.9: Acid Rain - *CC BY-NC-SA 4.0*
  - 10.10: Miscellaneous Gases in the Atmosphere - *CC BY-NC-SA 4.0*
  - 10.11: Photochemical Smog - *CC BY-NC-SA 4.0*
  - 10.12: Natural Capital of the Atmosphere - *CC BY-NC-SA 4.0*
  - Questions and Problems - *Undeclared*
  - Supplementary References - *Undeclared*
- 11: The Geosphere and a Green Earth - *CC BY-NC-SA 4.0*
  - 11.1: Probing Deep into the Geosphere - A Well Too Far? - *CC BY-NC-SA 4.0*
  - 11.2: The Nature of the Geosphere - *CC BY-NC-SA 4.0*
  - 11.3: The Geosphere as a Source of Natural Capital - *CC BY-NC-SA 4.0*
  - 11.4: Environmental Hazards of the Geosphere - *CC BY-NC-SA 4.0*
  - 11.5: Water on and in the Geosphere - *CC BY-NC-SA 4.0*
  - 11.6: Anthrospheric Influences on the Geosphere - *CC BY-NC-SA 4.0*
  - 11.7: The Geosphere as a Waste Repository - *CC BY-NC-SA 4.0*
  - 11.8: Have You Thanked a Clod Today? - *CC BY-NC-SA 4.0*
  - 11.9: Plant Nutrients and Fertilizers in Soil - *CC BY-NC-SA 4.0*
  - 11.10: Soil and Plants Related To Wastes and Pollutants - *CC BY-NC-SA 4.0*
  - 11.11: Soil Loss - Desertification and Deforestation - *CC BY-NC-SA 4.0*
  - Literature Cited and Supplementary References - *Undeclared*
  - Questions and Problems - *Undeclared*
- 12: The Biosphere and the Role of Green Chemistry in Feeding a Hungry World - *CC BY-NC-SA 4.0*
  - 12.1: Pigweed’s Revenge - *CC BY-NC-SA 4.0*
  - 12.2: The Biosphere - *CC BY-NC-SA 4.0*
  - 12.3: Cells - Basic Units of Life - *CC BY-NC-SA 4.0*
  - 12.4: Metabolism and Control in Organisms - *CC BY-NC-SA 4.0*
  - 12.5: Reproduction and Inherited Traits - *CC BY-NC-SA 4.0*
  - 12.6: Stability and Equilibrium of the Biosphere - *CC BY-NC-SA 4.0*
  - 12.7: DNA and the Human Genome - *CC BY-NC-SA 4.0*
  - 12.8: Genetic Engineering - *CC BY-NC-SA 4.0*
  - 12.9: Biological Interaction with Environmental Chemicals - *CC BY-NC-SA 4.0*
  - 12.10: Biodegradation - *CC BY-NC-SA 4.0*
  - 12.11: Production of Food and Fiber by the Biosphere - Agriculture - *CC BY-NC-SA 4.0*
  - 12.12: Agricultural Applications of Genetically Modified Organisms - *CC BY-NC-SA 4.0*
  - 12.13: The Anthrosphere in Support of the Biosphere - *CC BY-NC-SA 4.0*
  - 12.14: Livestock and their Wastes - *CC BY-NC-SA 4.0*
  - Questions and Problems - *Undeclared*
  - Supplementary References - *Undeclared*
- 13: The Anthrosphere, Industrial Ecology, and Green Chemistry - *CC BY-NC-SA 4.0*
  - 13.1: Industrial Ecology and Industrial Ecosystems - *CC BY-NC-SA 4.0*
  - 13.2: Metabolic Processes in Industrial Ecosystems - *CC BY-NC-SA 4.0*
  - 13.3: Life Cycles in Industrial Ecosystems - *CC BY-NC-SA 4.0*
  - 13.4: Kinds of Products - *CC BY-NC-SA 4.0*
  - 13.5: Attributes Required by an Industrial Ecosystem - *CC BY-NC-SA 4.0*
  - 13.6: The Kalundborg Industrial Ecosystem - *CC BY-NC-SA 4.0*
  - 13.7: Environmental Impacts of Industrial Ecosystems - *CC BY-NC-SA 4.0*
  - 13.8: Green Chemistry and Industrial Ecology - *CC BY-NC-SA 4.0*
  - 13.9: Predicting and Reducing Hazards - *CC BY-NC-SA 4.0*
  - 13.10: The E-Factor in Green Chemistry - *CC BY-NC-SA 4.0*

    - 13.11: Catalysts and Catalysis - *CC BY-NC-SA 4.0*
    - 13.12: Biocatalysis with Enzymes - *CC BY-NC-SA 4.0*
    - 13.13: Energizing Chemical Reactions and Process Intensification - *CC BY-NC-SA 4.0*
    - 13.14: Solvents and Alternate Reaction Media - *CC BY-NC-SA 4.0*
    - 13.15: Feedstocks and Reagents - *CC BY-NC-SA 4.0*
    - Literature Cited and Supplementary References - *Undeclared*
    - Questions and Problems - *Undeclared*
  - 14: Feeding the Anthrosphere- Utilizing Renewable and Biological Materials - *CC BY-NC-SA 4.0*
    - 14.1: Feeding the Anthrosphere - *CC BY-NC-SA 4.0*
    - 14.2: Utilization of Feedstocks - *CC BY-NC-SA 4.0*
    - 14.3: Biological Feedstocks - *CC BY-NC-SA 4.0*
    - 14.4: Biological Sources of Chemicals - *CC BY-NC-SA 4.0*
    - 14.5: Biorefineries and Biomass Utilization - *CC BY-NC-SA 4.0*
    - 14.6: Monosaccharide Feedstocks - Glucose, Fructose, and Xylose - *CC BY-NC-SA 4.0*
    - 14.7: Cellulose - *CC BY-NC-SA 4.0*
    - 14.8: Feedstocks from Cellulose Wastes - *CC BY-NC-SA 4.0*
    - 14.9: Lignin - *CC BY-NC-SA 4.0*
    - 14.10: Direct Biosynthesis of Polymers - *CC BY-NC-SA 4.0*
    - 14.11: Bioconversion Processes for Synthetic Chemicals - *Undeclared*
    - 14.12: Bamboo - Ancient Material for the Future - *CC BY-NC-SA 4.0*
    - Literature Cited - *Undeclared*
    - Questions and Problems - *Undeclared*
  - 15: Sustainable Energy- The Essential Basis of Green Systems - *CC BY-NC-SA 4.0*
    - 15.1: Sustainability and Energy - *CC BY-NC-SA 4.0*
    - 15.2: What is Energy? - *CC BY-NC-SA 4.0*
    - 15.3: Radiant Energy from the Sun - *CC BY-NC-SA 4.0*
    - 15.4: Sources of Energy Used in the Anthrosphere - *CC BY-NC-SA 4.0*
    - 15.5: Conversions Between Forms of Energy - *CC BY-NC-SA 4.0*
    - 15.6: Green Technology for Energy Conversion - *CC BY-NC-SA 4.0*
    - 15.7: Energy Conservation - *CC BY-NC-SA 4.0*
    - 15.8: Depletable Fossil Fuels - *CC BY-NC-SA 4.0*
    - 15.9: Carbon Sequestration for Fossil Fuel Utilization - *CC BY-NC-SA 4.0*
    - 15.10: Nuclear Energy - *CC BY-NC-SA 4.0*
    - 15.11: Renewable Energy Sources - Solar Energy - *CC BY-NC-SA 4.0*
    - 15.12: Energy from Wind and Water - *CC BY-NC-SA 4.0*
    - 15.13: Biomass Energy - *CC BY-NC-SA 4.0*
    - 15.14: Geothermal Energy - *CC BY-NC-SA 4.0*
    - 15.15: Hydrogen for Energy Storage and Utilization - *CC BY-NC-SA 4.0*
    - Literature Cited and Supplementary References - *Undeclared*
    - Questions and Problems - *Undeclared*
  - 16: Terrorism, Toxicity, and Vulnerability- Green Chemistry and Technology in Defense of Human Welfare - *CC BY-NC-SA 4.0*
    - 16.1: Vulnerability to Terrorist Attack - *CC BY-NC-SA 4.0*
    - 16.2: Protecting the Anthrosphere - *CC BY-NC-SA 4.0*
    - 16.3: Substances That Explode, Burn, or React Violently - *CC BY-NC-SA 4.0*
    - 16.4: Toxic Substances and Toxicology - *CC BY-NC-SA 4.0*
    - 16.5: Toxic Chemical Attack - *CC BY-NC-SA 4.0*
    - 16.6: Protecting Water, Food, and Air - *CC BY-NC-SA 4.0*
    - 16.7: Detecting Hazards - *CC BY-NC-SA 4.0*
    - 16.8: Green Chemistry to Combat Terrorism - *CC BY-NC-SA 4.0*
    - 16.9: Green Chemistry for Sustainable Prosperity and a Safer World - *CC BY-NC-SA 4.0*
    - 16.10: Green Chemistry to Combat Terrorism - *Undeclared*
    - 16.11: Green Chemistry for Sustainable Prosperity and and a Safer World - *Undeclared*
    - Literature Cited - *Undeclared*
    - Questions and Problems - *Undeclared*
  - 17: The Ten Commandments of Sustainability and Sensible Measure - *CC BY-NC-SA 4.0*
    - 17.1: We Cannot Go on Like This - *CC BY-NC-SA 4.0*
    - 17.2: The First Commandment - *CC BY-NC-SA 4.0*
    - 17.3: The Second Commandment - *CC BY-NC-SA 4.0*
    - 17.4: The Third Commandment - *CC BY-NC-SA 4.0*
    - 17.5: The Fourth Commandment - *CC BY-NC-SA 4.0*
    - 17.6: The Fifth Commandment - *CC BY-NC-SA 4.0*
    - 17.7: The Sixth Commandment - *CC BY-NC-SA 4.0*
    - 17.8: The Seventh Commandment - *CC BY-NC-SA 4.0*
    - 17.9: The Eighth Commandment - *CC BY-NC-SA 4.0*
    - 17.10: The Ninth Commandment - *Undeclared*
    - 17.11: The Tenth Commandment - *Undeclared*
    - 17.12: Some Sensible Measures for Sustainability - *Undeclared*
    - Literature Cited - *Undeclared*

        - Questions and Problems - *Undeclared*
        - Supplementary References - *Undeclared*
    - Back Matter - *CC BY-NC-SA 4.0*
        - Index - *CC BY-NC-SA 4.0*
        - Glossary - *CC BY-NC-SA 4.0*
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