

THE ENVIRONMENT CHEMISTRY & SUSTAINABLE DEVELOPMENT

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Abstract :

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 environmental chemistry must take into account five interacting and overlapping compartments or spheres of the environment, which affect each other and which undergo continual interchanges of matter and energy. Traditionally, environmental science has considered water, air, earth, and life — that is, the hydrosphere, the atmosphere, the geosphere, and the biosphere. When considered at all, human activities were generally viewed as undesirable perturbations on these other spheres, causing pollution and generally adverse effects. Such a view is too narrow, and we must include a fifth sphere, the anthrosphere, consisting of the things humans make and do. By regarding the anthrosphere as an integral part of the environment, humans can modify their anthrospheric activities to do minimal harm to the environment, or to even improve it.

shows the five spheres of the environment, including the anthrosphere, and some of the exchanges of material between them. Each of these spheres is described briefly below. 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.

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 1.2 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.

Showing the five environmental spheres may provide an idea of the complexity of environmental chemistry as a discipline. Enormous quantities of materials and energies 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. Chap. 1,

Chemistry, Green Chemistry, and Environmental Chemistry Nitric oxide and hydrocarbons emitted to the atmosphere Air pollutants transported to the atmosphere Solar energy is used to transform primary air pollutants to ozone and noxious organic materials in photochemical smog Adverse effects, such as reduced visibility from particles formed by smog. Fate, such as deposition onto plants Illustration of the definition of environmental chemistry with a common environmental contaminant.

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.

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 anthropogenic influences. Aspects of aquatic chemistry are considered in various parts of this book and are addressed specifically in Chapter 7, “Green Water.”

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 concentration of DDT and other 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 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. 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.

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 N₂ with about 1/4 as much oxygen, O₂, by volume. We only become aware of this gas when something is wrong with it, such as contamination by irritating air pollutants. A

person stepping into an atmosphere of pure N₂ would not notice anything wrong immediately, but would die within a few minutes, not because N₂ 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.

The 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 H₂O molecules, but which also contains dissolved O₂ and N₂ from air, dissolved calcium ions (Ca²⁺), chlorine added for disinfection, and other materials.

A heterogeneous mixture is one that contains discernable 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. 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

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. General Electric has agreed to spend tens of millions of dollars to remove PCBs from Hudson River deposits that were discarded to the river as wastes from the company's manufacture of electrical equipment. DuPont is paying up to \$600 million as settlement for environmental damage caused by the production of Teflon and Gore-Tex. The cleanup of pollutants including asbestos, dioxins, pesticide manufacture residues, perchlorate and mercury are costing various concerns hundreds of millions of dollars. From a purely economic standpoint, therefore, a green chemistry approach that avoids these costs is very attractive, in addition to its large environmental benefits. 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.

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 cost of doing business. Companies must now do full cost accounting, taking into full account the costs of emissions, waste disposal, cleanup, and protection of personnel and the environment, none of the proceeds of which go into the final product.

States of Matter :

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.

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 bounding 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 8.

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 retain their shapes regardless of the container in which they are placed

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.

Conclusion :

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 1.6 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 pose health hazards 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 Chapter 12.

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. 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 time devoted in the media to the salacious antics of some fool-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.

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