7

Characterizing Air Pollution

Discussions of environmental fate and transport must always consider both physical processes associated with chemical reactions and other chemical processes. Thus, air pollution physics must be considered mutually with air pollution chemistry. Any complete discussion of the physical process of solubility, for example, must include a discussion of chemical phenomenon *polarity*. Further, any discussion of polarity must include a discussion of electronegativity. Likewise, discussions of sorption and air–water exchanges must consider both chemical and physical processes. Such is the nature of environmental science; all concepts are interrelated.

I. RELATIONSHIP BETWEEN PHYSICS AND CHEMISTRY

The interconnectedness between physical and chemical processes is evident in Table 6.1, which lists some of the most important processes involved in the fate of environmental contaminants. This chapter highlights basic physicochemical processes that affect air pollution.

It is important to bear in mind that the air pollution processes are a function of both the chemical characteristics of the compartment (e.g. air) and those of the contaminant. The inherent properties of the air pollutant are influenced and changed by the extrinsic properties of the air and other media in which the pollutant resides in the environment. Thus, to characterize air pollution, the physical and chemical properties of the pollutant and the air must be considered together.

II. BASIC CHEMICAL CONCEPTS

Environmental chemistry is the discipline that concerns itself with how chemicals are formed, how they are introduced into the environment, how they change after being introduced, where they end up in organisms and other receptors, and the effects they have (usually the damage they do) once they get there. To cover these concepts, environmental chemistry must address the processes in effect in every environmental compartment. This is evident by the diverse subdisciplines within environmental chemistry, including atmospheric chemistry. There are even fields such as environmental physical chemistry (such as environmental photochemistry), environmental analytical chemistry (including environmental separation sciences and chromatography), and environmental chemical engineering (including fields addressing environmental thermodynamics).

The element is a material substance that has decomposed chemically to its simplest form. These are what appear on the periodic table of elements (Fig. 7.1). Elements may be further broken down only by nuclear reactions, where they are released as subatomic particles. Such particles are important sources of pollution and often are environmental contaminants. An atom is

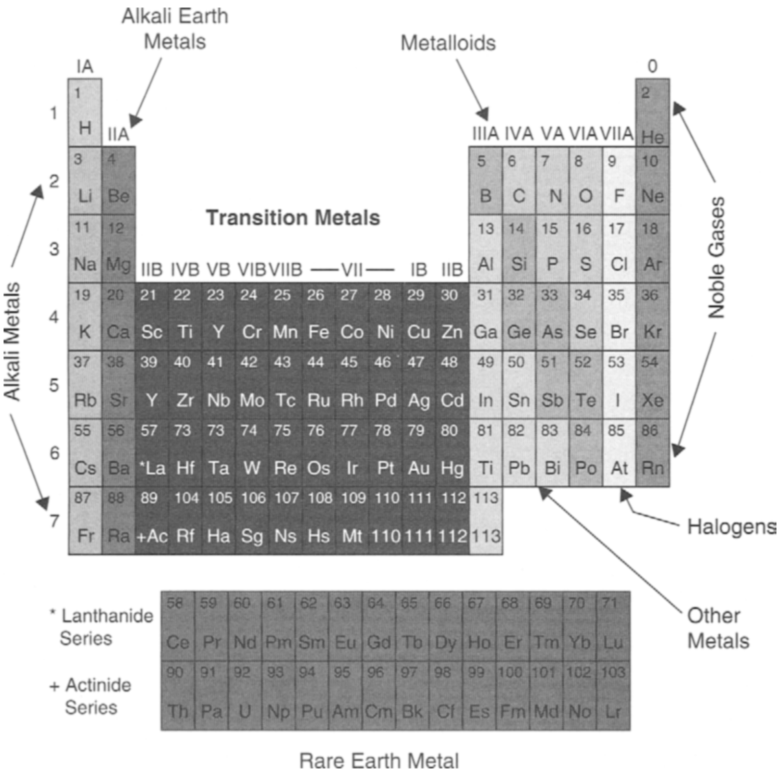

Fig. 7.1. Periodic table of elements.

the smallest part of an element that can enter into a chemical reaction. The molecule, which may also be an atom, is the smallest subdivision of an element that is able to exist as a natural state of matter. The nucleus of an atom, consisting of protons and neutrons (hydrogen has only one proton in its nucleus), account for virtually all of the atomic mass, or the atomic mass unit (amu). The term nucleon is inclusive of protons and neutrons (i.e. the particles comprising the atom's nucleus). An amu is defined as one-twelfth of the mass of carbon (C^{12}), or 1.66×10^{-27} kg. The atomic weight of an element listed in most texts and handbooks is the relative atomic weight, which is the total number of nucleons in the atom. So, for example, oxygen (O) has an atomic mass of 16. The atomic number (Z) is the number of protons in the nucleus. The chemical nomenclature for atomic weight A and number of element E is in the form:

$$_{z}E^{A} \tag{7.1}$$

However, since an element has only one atomic number, Z is usually not shown. For example, the most stable form of carbon is seldom shown as $_{12}C^{12}$, and is usually indicated as C^{12}.

Elements may have different atomic weights if they have different numbers of neutrons (the number of electrons and protons of stable atoms must be the same). The elements' forms with differing atomic weights are known as *isotopes*. All atoms of a given element have the same atomic number, but atoms of a given element may contain different numbers of neutrons in the nucleus. An element may have numerous isotopes. Stable isotopes do not undergo natural radioactive decay, whereas radioactive isotopes involve spontaneous radioactive decay, as their nuclei disintegrate. This decay leads to the formation of new isotopes or new elements. The stable product of an element's radioactive decay is known as a radiogenic isotope. For example, lead (Pb; $Z = 82$) has four naturally occurring isotopes of different masses (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb). Only the isotope ^{204}Pb is stable. The isotopes ^{206}Pb and ^{207}Pb are daughter (or progeny) products from the radioactive decay of uranium (U), while ^{208}Pb is a product from thorium (Th) decay. Owing to the radioactive decay, the heavier isotopes of lead will increase in abundance compared to ^{204}Pb.

The kinds of chemical reactions for all isotopes of the same element are the same. However, the rates of reactions may vary. This can be an important factor, for example, in dating material. Such processes have been used to ascertain the sources of pollution (see Discussion Box: Carbon Dating).

Radiogenic isotopes are useful in determining the relative age of materials. The length of time necessary for the original number of atoms of a radioactive element in a rock to be reduced by half (*radioactive half-life*) can range from a few seconds to billions of years. Scientists use these "radioactive clocks" by the following procedure[1] by:

1. Extracting and purifying the radioactive parent and daughter from the relevant rock or mineral.

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[1] US Geological Survey, Radiogenic Isotopes and the Eastern Mineral Resources Program of the US Geological Survey, 2003.

2. Measuring variations in the masses of the parent and daughter isotopes.
3. Combining the abundances with the known rates of decay to calculate an age.

Radiogenic isotopes are being increasingly used as *tracers*, the movement of substances through the environment. Radiogenic isotope tracer applications using Pb, strontium (Sr), and neodymium (Nd), among others make use of the fact that these are heavy isotopes, in contrast to lighter isotopes such as hydrogen (H), oxygen (O), and sulfur (S). Heavy isotopes are relatively unaffected by changes in temperature and pressure during transport and accumulation, variations in the rates of chemical reactions, and the coexistence of different chemical species available in the environment. Chemical reactions and processes involving Pb, for example, will not discriminate among the naturally occurring isotopes of this element on the basis of atomic mass differences (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb).

Long-term monitoring data are frequently not available for environmental systems, so indirect methods, like radiogenic isotope calculations must be used. For example, in sediments, chronological scales can be determined by the distribution of radioactive isotopes in the sediment, based on the isotopes' half-lives.[2] The age of the sediment containing a radioactive isotope with a known half-life can be calculated by knowing the original concentration of the isotope and measuring the percentage of the remaining radioactive substance. For this process to work the chemistry of the isotope must be understood, the half-life known, and the initial amount of the isotope per unit substrate accurately estimated. The only change in concentration of the isotope must be entirely attributable to radioactive decay, with a reliable means for measuring the concentrations. The effective range covers approximately eight half-lives. The four isotopes meeting these criteria (^{137}Cs, ^{7}Be, ^{14}C, and ^{210}Pb) are being used to measure the movement (e.g. deposition and lateral transport) for the past 150 years. The following summarizes the uses and potential uses of these four radioisotopes in dating recent sediment. This process also lends itself to differentiating sources of air pollutants (e.g. that caused by recent human activities from that of geological or biological origins, as discussed in the box below).

The process is analogous to an hourglass (see Fig. 7.2), where the number of grains of sand in the top reservoir represents the parent isotope and the sand in the bottom reservoir represents the daughter isotopes. A measurement of the ratio of the number of sand grains in the two reservoirs will give the length of time that the sand has been flowing, which represents the process of radioactive decay. For deposited material like an aerosol deposited from the troposphere onto the soil or taken up by flora, the counting begins when the aerosol is deposited so that the carbon or other element is taken up into the plant (t_0), and the exchange between the water and particle ceases. As the particles and plant life are subsequently buried, the parent isotope decays to the daughter products.

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[2] US Geological Survey, Short-Lived Isotopic Chronometers: A Means of Measuring Decadal Sedimentary Dynamics, FS-073-98, 2003.

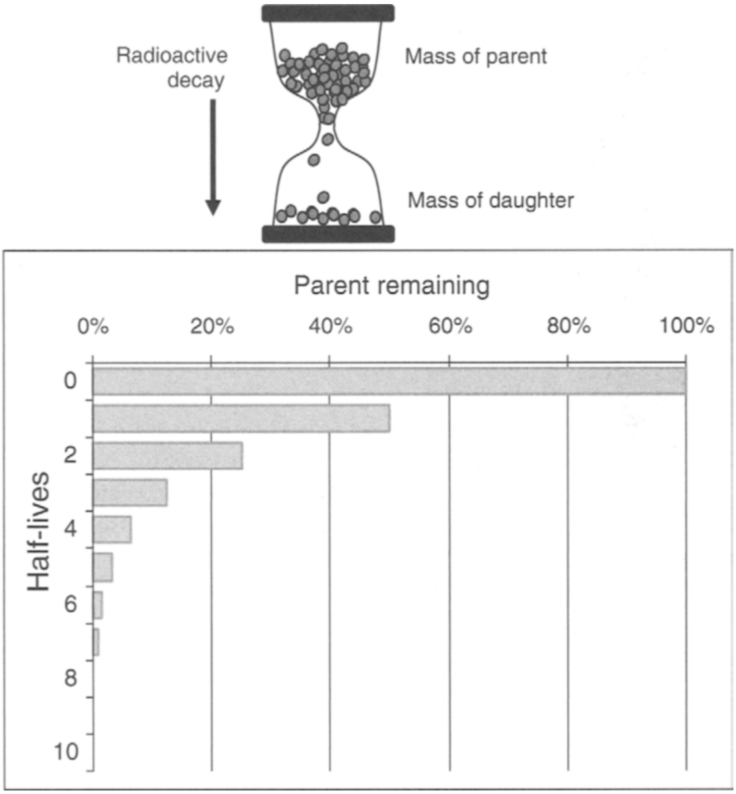

Fig. 7.2. Radio-dating is a function of the radioactive decay of specific isotopes in a substance. The hourglass analogy holds, where the number of grains of sand in the top reservoir represents the parent isotope and the sand in the bottom reservoir represents the daughter isotopes. A measurement of the ratio of the number of sand grains in the two reservoirs will give the length of time that the sand has been flowing (radioactive decay). *Source*: US Geological Survey, *Short-Lived Isotopic Chronometers: A Means of Measuring Decadal Sedimentary Dynamics*, FS-073-98, 2003.

SOURCE APPORTIONMENT, RECEPTOR MODELS, AND CARBON DATING

When the results of air pollution measurements are interpreted, one of the first questions asked by scientists, engineers, and policy makers is where did it come from? Sorting out the various sources of pollution is known as *source apportionment*. A number of tools are used to try to locate the sources of pollutants. A widely used approach is the "source-receptor model" or as it is more commonly known, the *receptor model*.

Receptor models are often distinguished from the atmospheric and hydrologic dispersion models. For example, dispersion models usually start from the source and estimate where the plume and its contaminants is heading (see Fig. 7.3). Conversely, receptor models are based on measurements taken in the ambient environment and from these observations, make use of algorithms and functions to determine pollution sources. One common approach is the mathematical "back trajectory" model. Often, chemical co-occurrences are applied. So, it may be that a certain fuel is frequently contaminated with a conservative and, hopefully, unique element. Some fuel oils, for example, contain trace amounts of the element vanadium. Since there are few other sources of vanadium in most ambient atmospheric environments, its presence is a strong indication that the burning of fuel oil is a most likely source of the plume. The model, if constructed properly, can even quantify the contribution. So, if measurements show that sulfur dioxide (SO_2) concentrations are found to be $10\,\mu g\,m^{-3}$ in an urban area, and vanadium is also found at sufficient levels to indicate home heating systems are contributing a certain amount of the SO_2 to the atmosphere, the model will correlate with the amount of SO_2 coming from home heating systems. If other combustion sources, e.g. cars and

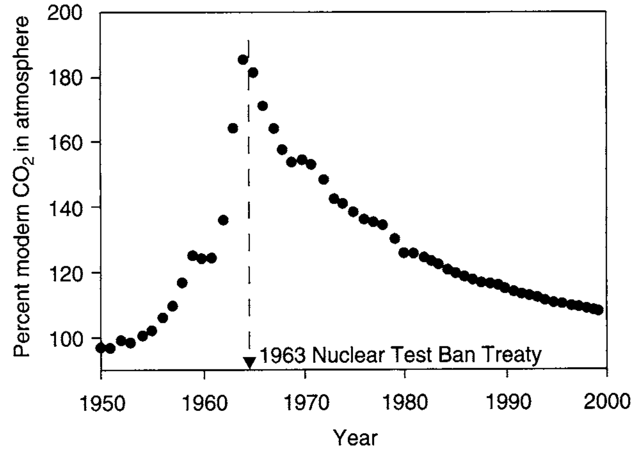

Fig. 7.3. Biospheric 14C enhancement of atmospheric modern carbon as a result of radiocarbon additions from nuclear testing and nuclear power generation. The plot indicates the time record of ^{14}C in the biosphere. The ^{14}C content of northern hemisphere biomass carbon was doubled in 1963, but since the cessation of atmospheric nuclear testing, the excess ^{14}C is now nearing natural, cosmic ray background levels. Fraction of modern carbon relative standard uncertainties are typically <0.5%. *Source*: National Institute of Standards and Technology, A critical evaluation of interlaboratory data on total, elemental, and isotopic carbon in the carbonaceous particle reference material, NIST SRM 1649a. **107** (3) (2002); and Lewis, C., Klouda, G., and Ellenson, W., *Cars or Trees: Which Contribute More to Particulate Matter Air Pollution?* US Environmental Protection Agency, Science Forum, Washington, DC, 2003.

power plants, also have unique trace elements associated with their SO_2 emissions, further SO_2 source apportionment can occur, so that the total may look something like Table 7.1.

Receptor models need tracers that are sufficiently sensitive and specific to identify sources. We also mentioned that they be "conservative." This, perhaps, needs some explanation. A conservative tracer is a chemical that strongly resists chemical reactions but has transport properties similar to those of other, more reactive chemicals (i.e. the contaminant of concern). A good tracer is one that moves exactly with the fluid (i.e. the air), so if a chemical is reactive, its mass diminishes and does not allow direct interpretation of the advective movement of the plume in an air mass. A conservative tracer also makes for a sufficiently stable compound to sample form the atmosphere and to analyze in the laboratory.

One very promising development for such tracers is the comparison of carbon isotopes. Since combustion involves the oxidation of organic matter, which always contains carbon, it stands to reason that if there were a way to distinguish "old carbon" from "new carbon" we may have a reliable means of differentiating fossil fuels from *biogenic* hydrocarbon sources (e.g. volatile organic carbons released from coniferous trees, including pinene). As the name implies, fossil fuels are made up of carbon deposited long ago and until now, the carbon has been sequestered. During that time the ratio of the isotopes of carbon has changed. So, the ratios can tell us whether the carbon we are measuring had been first sequestered a few years ago or many thousands of years ago.

TABLE 7.1

Hypothetical Source Apportionment of Measured Sulfur Dioxide Concentrations

Source	Distance from measurement (km)	SO_2 concentration contributed to ambient measurement ($\mu g\ m^{-3}$)	Percent contribution to measured SO_2
Coal-fired electric generating station	25	3.0	30
Coal-fired electric generating station	5	2.0	20
Mobile sources (cars, trucks, trains, and planes)	0–10	1.5	15
Oil refinery	30	1.5	15
Home heating (fuel oil)	0–1	1.0	10
Unknown	Not applicable	1.0	10
Total		10.0	100

Naturally occurring radioactive carbon (^{14}C) is present at very low concentrations in all biotic (living) matter. The ^{14}C concentrations result from plants' photosynthesis of atmospheric carbon dioxide (CO_2), which contains all of the natural isotopes of carbon. However, no ^{14}C is found in fossil fuels since all of the carbon has had sufficient time to undergo radioactive decay. Studies have begun to take advantage of this dichotomy in ratios. For example, they have begun to address an elusive contributor to particulate matter (PM), i.e. *biogenic* hydrocarbons. In the summer months, biogenic aerosols are formed from gas-to-particle atmospheric conversions of volatile organic compounds (VOCs) that are emitted by vegetation.[3] New methods for estimating the contribution of biogenic sources of VOCs and PM are needed because current estimates of the importance of biogenic aerosols as contributors to total summertime PM have very large ranges (from negligible to dominant). There are large uncertainties in both the conversion mechanisms, and the amount and characteristics of biogenic VOC emissions.

The good news seems to be that direct experimental estimates can be gained by measuring the quantity of ^{14}C in a PM sample. The method depends on the nearly constant fraction of ^{14}C relative to ordinary carbon (^{12}C) in all living and recently living material, and its absence in fossil fuels. The fine fraction of PM ($PM_{2.5}$) summertime samples are available from numerous locations in the United States, from which ^{14}C measurements, can be conducted. Some recent studies have shown that the carbonaceous biogenic fraction may be contributing as much as one-half of the particles formed from VOCs.

The method for measuring and calculating the isotope ratios is straightforward. The percent of modern carbon (pMC) equals the percentage of ^{14}C in a sample of unknown origin relative to that in a sample of living material, and this pMC is about equal to the percentage of carbon in a sample that originated from non-fossil (i.e. biogenic) sources. So, for sample[4] X:

$$\mathrm{pMC}_x = \frac{\left({}^{14}\mathrm{C}/{}^{13}\mathrm{C}\right)\mathrm{X}}{0.95 \cdot \left({}^{14}\mathrm{C}/{}^{13}\mathrm{C}\right)_{\mathrm{SRM4990B}}} \times 100 \qquad (7.2)$$

Where, the numerator is the ratio measured in the $PM_{2.5}$ sample, and the denominator is the ratio measured using the method specified by the

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[3] Lewis, C., Klouda, G., and Ellenson, W., *Cars or Trees: Which Contribute More to Particulate Matter Air Pollution?* US Environmental Protection Agency, Science Forum, Washington, DC, 2003.

[4] This is the carbon component of a fine particulate sample ($PM_{2.5}$), such as those measured at ambient air monitoring stations. The ratios are calculated according to the National Bureau of Standards, Oxalic Acid Standard Reference Method SRM 4990B.

National Institute of Standards and Testing (NIST) for modern carbon.[5] Further:

$$pMC_{\text{Fossilfuel}} = 0 \tag{7.3}$$

Thus, for a sample X, the biogenic fraction is:

$$\%\text{BiogenicC}_x = \frac{pMC_x}{pMC_{\text{Biogenic}}} \times 100 \tag{7.4}$$

The 0.95 correction is needed to address the increasing in radiocarbon due to nuclear weapons testing in the 1950s and 1960s (see Fig. 7.2) and to calibrate the measurements with the standard used for radiocarbon dating (i.e. wood from 1890).[6] Although the levels have dropped since the 1963 test ban treaty, they are still elevated above the pre-1950s background level.

III. EXPRESSIONS OF CHEMICAL CHARACTERISTICS

The gravimetric fraction of an element in a compound is the fraction by mass of the element in that compound. This is found by a gravimetric (or ultimate) analysis of the compound. The empirical formula of a compound provides the relative number of atoms in the compound. The empirical formula is found by dividing the gravimetric fractions (percent elemental composition) by atomic weights of each element in the compound, and dividing all of the gravimetric fraction-to-atomic weight ratios by the smallest ratio.

EMPIRICAL FORMULA DEVELOPMENT EXAMPLE

An air sampling stainless steel canister was evacuated by the local fire department and brought to the environmental laboratory for analysis. The person who brought in the sample said that the sample was taken near a site where a rusty 55-gallon drum was found by some children in creek near their school. The children and neighbors reported an unpleasant smell near the site where the drum was found.

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[5] National Bureau of Standards, Oxalic Acid Standard Reference Method SRM 4990B.

[6] The defined reference standard for ^{14}C is 0.95 times the ^{14}C specific activity of the original NBS Oxalic Acid Standard Reference Material (SRM 4990B), adjusted to a ^{13}C delta value of −19.09‰. This is "modern" carbon. It approximates wood grown in 1890 that was relatively free of CO_2 from fossil sources. Due to the anthropogenic release of radiocarbon from nuclear weapons testing and nuclear power generation, oxalic acid from plant material grown after World War II is used currently to standardize ^{14}C measurements contains more ^{14}C than 1890 wood.

The gravimetric analysis of the gas in the canister indicated the following elemental compositions:

Carbon: 40.0%
Hydrogen: 6.7%
Carbon: 53.3%

Solution

First, divide the elemental percentage compositions by the respective atomic weights:

$$C : \frac{40.0}{12} = 3.3$$

$$H : \frac{6.7}{1} = 6.7$$

$$O : \frac{53.3}{16} = 3.3$$

Next, divide every ratio by the smallest ratio (3.3):

$$C : \frac{3.3}{3.3} = 1$$

$$H : \frac{6.7}{3.3} = 2$$

$$O : \frac{3.3}{3.3} = 1$$

So, the empirical formula is CH_2O or HCHO. This is formaldehyde, a toxic substance.

Preliminary Interpretation

The challenge of formaldehyde, however, is that it comes from many sources, including emissions from factories and automobiles, and even natural sources. However, since the drum seems to be a likely source, the liquid contents should be analyzed (and a search for additional drums should begin immediately—the illegal dumping often is not limited to a single unit).

The first likelihood is that the liquid is formalin, a mixture that contains formaldehyde. The high vapor pressure of the formaldehyde may be causing it to leave the solution and move into the air.

Since children are in the area and there may be a relatively large amount of the substance, steps must be taken to prevent exposures and to remove the formaldehyde.

A. The Periodic Table

The periodic table (Fig. 7.1) follows the periodic law, which states that the properties of elements depend on the atomic structure and vary systematically according to atomic number. The elements in the table are arranged according to increasing atomic numbers from left to right.

An element shares many physicochemical properties with its vertical neighbors, but differs markedly from its horizontal neighbors. For example, oxygen (O) will chemically bind and react similarly to sulfur (S) and selenium (Se), but behaves very differently from nitrogen (N) and fluorine (F). Elements in the horizontal rows, known as periods, grow increasingly different with the distance moved to the left or right. So, O differs physically and chemically more from boron (B) than O does from F, and O is a very different from lithium (e.g. O is a nonmetal and Li is a light metal).

The groups (vertical columns) are designated by numerals (often Roman numerals). For example, O is a group VIA element and gold (Au) is in group IB. The A and B designations are elemental families. Elements within families share many common characteristics. Within families, elements with increasing atomic weights become more metallic in their properties.

Metals (elements to the left of the periodic table) form positive ions (*cations*), are reducing agents, have low electron affinities, and have positive valences (oxidation numbers). Nonmetals (on the right side of the table) form negative ions (*anions*), are oxidizing agents, have high electron affinities, and have negative valences. Metalloids have properties of both metals and nonmetals. However, two environmentally important metalloids, arsenic (As) and antimony (Sb) are often treated as heavy metals in terms of fate, transport, and toxicity.

Some common period table chemical categories are:

- *Metals*: Every element except the nonmetals
- *Heavy metals*: Metals near the center of the table
- *Light metals*: Groups I and II
- *Alkaline earth metals*: Group IIA
- *Alkali metals*: Group IA
- *Transition metals*: All Group VIII and B families
- *Actinons*: Elements 90–102
- *Rare earths*: Lanthanons (Lanthanides), Elements 58–71
- *Metalloids*: Elements separating metals and nonmetals, Elements 5, 14, 32, 33, 51, 52, and 84
- *Nonmetals*: Elements 2, 5–10, 14–18, 33–36, 52–54, 85, and 86
- *Halogens*: Group VIIA
- *Noble gases*: Inert elements, Group 0

It is important to keep in mind that every element in the table has environmental relevance. In fact, at some concentration, every element except those generated artificially by fission in nuclear reactors are found in soils. Thus, it would be absurd to think of how to "eliminate" them. This is a common misconception, especially with regard to heavy metal and metalloid contamination.

For example, mercury (Hg) and lead (Pb) are known to be important contaminants that cause neurotoxic and other human health effects and environmental pollution. However, the global mass balance of these metals does not change, only their locations and forms (i.e. *speciation*). So, protecting health and ecological resources is a matter of reducing and eliminating exposures and changing the form of the compounds of these elements so that they are less mobile and less toxic. The first place to start such a strategy is to consider the oxidation states, or valence, of elements.

IV. ELECTROMAGNETIC RADIATION, ELECTRON DENSITY, ORBITALS, AND VALENCE

Quantum mechanics tells us that the energy of a photon of light can cause an electron to change its energy state, so that the electron is disturbed from its original state. *Electromagnetic radiation* (EMR) is related to atomic structure. Much that is known about atomic structure, especially an atom's arrangement of electrons around its nucleus, is from what scientists have learned about the relationship between matter and different types of EMR. One principle is that EMR has properties of both a *particle* and a *wave*. Particles have a definite mass and occupy space (i.e. they conform to the classic description of matter). Waves have no mass but hold energy with them as they travel through space. Waves have four principle characteristics, i.e. speed (v), frequency (ν), wavelength (λ), and amplitude. These are demonstrated in Fig. 7.4.

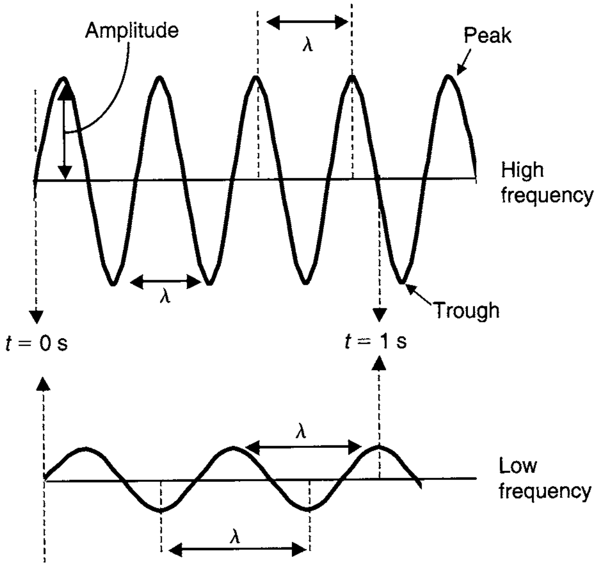

Fig. 7.4. EMR. The amplitude of the wave in the top chart is higher than that in lower chart. The bottom wave is 2.5 cycles per seconds (2.5 Hz). The top wave is 3.5 Hz, so the bottom wave has a 1 Hz lower frequency than the top wave.

Measuring ν in cycles per second (hertz, Hz) and λ in meters, the product gives the velocity of the wave moving through space:

$$v = \nu \lambda \tag{7.5}$$

For example, if a certain light's λ is 10^{-7} m and its ν is 10^{15} Hz, then the velocity of that light is $10^{8}\,\mathrm{m\,s^{-1}}$.

ELECTROMAGNETIC RADIATION

Most of the time, when someone mentions the term "environmental contaminant," it calls to mind some chemical compound. However, contaminants may also come in the form of biological or physical agents. Biological contaminants may be pathogenic bacteria or viruses that adversely affect health, or introduced species (e.g. the zebra mussel or kudzu) that harm ecosystems. Physical agents are often the least likely to come to mind. A common physical contaminant is energy. Life depends on energy, but like most resources, when it comes in the wrong form and quantity, it may be harmful. EMR is comprised of wave functions that are propagated by simultaneous periodic variations in electrical and magnetic field intensities (see Fig. 7.3). Natural and many anthropogenic sources produce EMR energy in the form of waves, which are oscillating energy fields that can interact with an organism's cells. The waves are described according to their wavelength and frequency, and the energy that they produce.

Wave frequency is the number of oscillations that passes a fixed point per unit of time, measured in cycles per second (cps). 1 cps = 1 hertz (Hz). Thus, the shorter the wavelength, the higher the frequency. For example, the middle of the amplitude modulated (AM) radio broadcast band has a frequency of one million hertz (i.e. 1 megahertz = 1 MHz) and a wavelength of about 300 m. Microwave ovens use a frequency of about 2.5 billion hertz (i.e. 2.5 gigahertz = 2.5 GHz) and a wavelength of 12 cm. So, the microwave, with its shorter wavelength has a much higher frequency.

An EMR wave is made of tiny packets of energy called photons. The energy in each photon is directly proportional to the frequency of the wave. So the higher the frequency, the more energy there will be in each photon. Biological tissue and cellular material is affected in part by the intensity of the field and partly by quantity of energy in each photon.

At low frequencies EMR waves are known as electromagnetic fields and at high frequencies EMR waves are referred to as electromagnetic radiations. Also, the frequency and energy determines whether an EMR will be ionizing or non-ionizing radiation. Ionizing radiation consists of high frequency electromagnetic waves (e.g. X-rays and gamma rays), having sufficient photon energy to produce ionization (producing positive and negative electrically charged atoms or parts of molecules) by breaking bonds of molecules. The general term non-ionizing radiation is the portion of the electromagnetic spectrum where photon energies are not strong enough to break atomic bonds. This segment of the spectrum includes ultraviolet (UV) radiation, visible light, infrared radiation, radio waves, and microwaves, along with static electrical and magnetic fields. Even at high intensities, non-ionizing radiation cannot ionize atoms in biological systems, but such radiation has been associated with other effects, such as cellular heating, changes in chemical reactions and rates, and the induction of electrical currents within and between cells.

Of course, not every EMR effect causes harm to an organism; such as when a mammal may respond to EMR by increasing blood flow in the skin in response to slightly greater heating from the sun. Life as we know it depends on various EMR wavelengths and frequencies, including the conversion of visible and UV wavelengths to infrared by the earth's surface which warms the planet. Photosynthesis depends on incoming light. EMR also induces positive health effects, such as the sun's role in helping the body produce vitamin D. Unfortunately, certain direct or indirect responses to EMR may lead to adverse effects, including skin cancer.

The data supporting UV as a contaminant are stronger than those associated with more subtle fears that sources, like high-energy power transmission lines and cell phones may be producing health effects. The World Health Organization (WHO) is addressing the health concerns raised about exposure to radio frequency (RF) and microwave fields, intermediate frequencies (IF), extremely low frequency (ELF) fields, and static electric and magnetic fields. IF and RF fields produce heating and the induction of electrical currents, so it is highly plausible that this is occurring to some extent in cells exposed to IF and RF fields. Fields at frequencies above about 1 MHz primarily cause heating by transporting ions and water molecules through a medium. Even very low energy levels generate a small amount of heat, but this heat is carried away by the body's normal thermoregulatory processes. However, some studies indicate that exposure to fields too weak to cause heating may still produce adverse health consequences, including cancer and neurological disorders (i.e. memory loss).

Since, electrical currents already exist in the body as a normal part of the biochemical reactions and metabolic process, the fear is that should electromagnetic fields induce sufficiently high currents, the additive effects may overload the system and engender adverse biological effects.

ELF electric fields exist when a charge is generated, but hardly any of the electric field penetrates into the human body. At very high field strengths they can feel like one's skin is "crawling" or their hair is raised. Some studies, however, have associated low level ELF electric fields with elevated incidence of childhood cancer or other diseases, while other studies have not been able to establish a relationship. The WHO is recommending that more focused research be conducted to improve health risk assessments. ELF magnetic fields also exist whenever an electric current is flowing. However, unlike the ELF electric fields, magnetic fields readily penetrate an organism's tissue with virtually no attenuation. Again the epidemiology is mixed, with some studies associating ELF fields with cancer, especially in children, and others finding no such association. WHO continues to conduct studies in this area.

The primary action in biological systems by these static electrical and magnetic fields is by inducing electrical and magnetic reliable data to come to any conclusions about chronic effects associated with long-term exposure to static magnetic fields at levels found in the working environment.

The challenge of EMR is similar to that of chemical contamination. The exposure and risks associated with this hazard is highly uncertain. The key decision is whether sufficient scientific evidence exists to encourage limits on certain types of activities (either as an individual or as a public agency) where adverse effects may be occurring. Just walk in a mall, on a campus, or into a restaurant. Chances are you will see a number of people using cell phones. Drive through a neighborhood. Chances are you will see some overhead power lines. The challenge is deciding what level of evidence linking EMR to adverse effects would be sufficient to require actions to protect public health.

Quantum mechanics is the basis for numerous chemical analyses (e.g. mass spectrometry) of air pollutants. An atom's electrons occupy orbitals where the electrons contain various amounts of energy. Electrons vary in the spatial orientations and average distances from the nucleus, so that electrons occupying inner orbitals are closer to the nucleus (see Fig. 7.5). The electron's velocity or position changes. If we can measure the electron's position we will not know its velocity, and if we measure the electron's velocity, we will not be able to know its position. We are uncertain about the electron's simultaneous position and velocity. This is the basis for the Heisenberg Uncertainty Principle, which tells us that the more we know about an electron's position, the less we can know about its velocity. Further, to keep an electron from escaping from an atom, the electron must maintain a minimum velocity, which corresponds back to the uncertainty of the electron's position in the

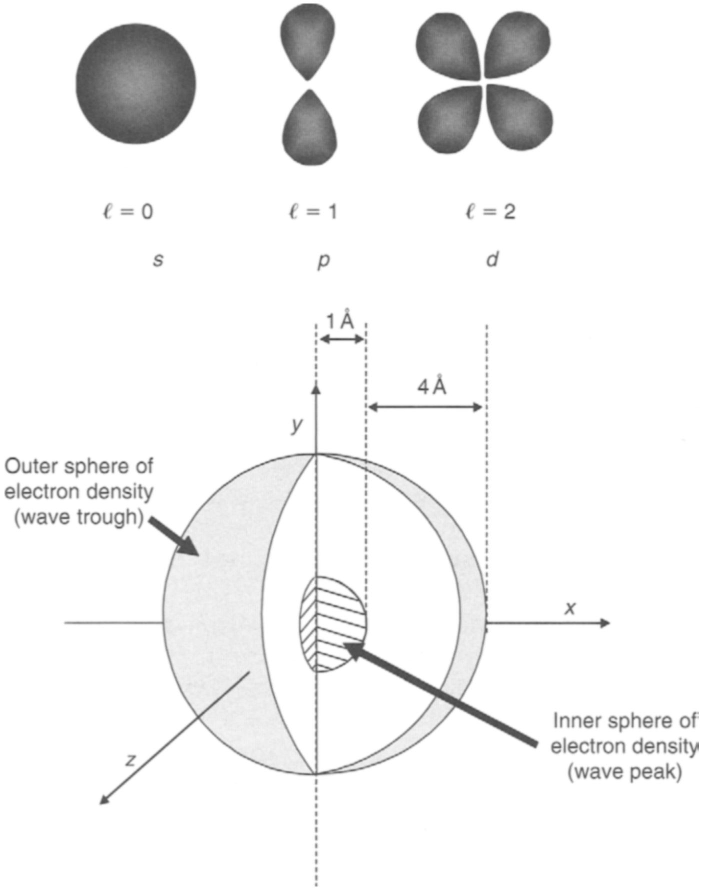

Fig. 7.5. Two-dimensional orbital shapes, showing three angular quantum numbers (ℓ) and subshells *s*, *p*, and *d* (top). The three-dimensional 2*s* orbital (bottom) is shown as a cutaway view into the atom, the peak (inner sphere) and trough (outer concentric sphere) of the electron wave. The orbital is two concentric spheres of electron densities. *Source*: Loudon, G., *Organic Chemistry*, 3rd ed. Benjamin/Cummings Publishing Company, Inc., Redwood City, CA, 1995.

atom. Since, the uncertainty of the position is actually the whole atom, i.e. the electron can be anywhere in the atom, chemists refer to an electron as a "cloud of electron density" within the atom rather than describing an electron as a finite particle. So, the electron orbitals are envisioned as regions in space where the electrons are statistically most likely to be located. We do not know where an electron is, but we know where it might be; that is, somewhere in the electron cloud.

The Schrödinger model applies three coordinates to locate electrons, known as quantum numbers. The coordinates are principal (n), angular (ℓ), and magnetic (m_l) quantum numbers. These characterize the shape, size, and orientation of the electron cloud orbitals of the atom. The principal quantum number n gives the size of the orbital. A relative size of $n = 2$ is larger than a cloud with the size $n = 1$. Energy is needed to excite an electron to make it move from a position closer to the nucleus (e.g. $n = 1$) to a position further from the nucleus ($n = 2, 3$, or higher). So, n is an indirect expression of an orbital's energy level.

The angular quantum number ℓ maps the shape of the cloud. A spherical orbital has an $\ell = 0$. Polar shaped orbitals have $\ell = 1$. Cloverleaf orbitals have $\ell = 2$. See Fig. 7.4 for renderings of these shapes. The magnetic quantum number $m_<$ describes the orientation of the orbital in space. Orbitals with the same value of n form a shell. Within a shell, orbitals are divided into subshells labeled by their ℓ value. The commonly used two-character description of shells (e.g. 2*p* or 3*d*) exemplifies the shell and subshell. For example, 2*p* indicates the shell ($n = 2$) and the subshell (*p*). Subshells are indicted by:

s: $\ell = 0$
p: $\ell = 1$
d: $\ell = 2$
f: $\ell = 3$
g: $\ell = 4$
h: $\ell = 5$

The number of subshells in any shell will equal the n for the shell. So, for example, the $n = 2$ shell contains two subshells (i.e. 2*s* and 2*p*) and $n = 5$ shell contains five subshells (i.e. 5*s*, 5*p*, 5*d*, 5*f*, and 5*g* orbitals).

The electrons occupying the outermost shell are known as valence electrons. Valence is the number of bonds that an element can form, which is related to number of electrons in the outermost shell. The arrangement of the electrons in the outermost (i.e. valence) determines the ultimate chemical behavior of the atom. The outer electrons become involved in transfer to and sharing with shells in other atoms, i.e. forming new compounds and ions. Note that the number of valence electrons in an "A" group in the periodic table (except helium, whose shell is filled with 2) is equal to the group number. So, sodium (Na), a Group 1A element, has one valence electron. Carbon (C) is a Group 4A compound, so it has four valence electrons. Chlorine (Cl), fluorine (F), and the other halogens of Group 7A have seven valence electrons. The noble gases, except He, in Group 8A, have eight valence electrons.

The noble gases are actually the only elements that exist as individual atoms, because the noble gases have no valence electrons. Conversely, carbon has four electrons in its outermost shell, so it has just as many electrons to gain or to lose (i.e. 4 is just as close to 8, for a newly filled shell, as it to 0, for the loss of a shell), so there are many ways for it to reach chemical stability. This is one of the reasons that so many subtly, but profoundly different compounds, i.e. organic compounds, are in existence. Most atoms combine by chemical bonding to other atoms, creating molecules.

Thus, the outermost electrons tell the story of how readily an element will engage in a chemical reaction and the type of reaction that will occur. The oxidation number is the electrical charge assigned to an atom. The sum of the oxidation numbers is equal to the net charge. Table 7.2 shows the oxidation numbers of certain atoms that form contaminants and nutrients in the environment. Table 7.3 gives the oxidation numbers for environmentally important radicals, i.e. groups of atoms that combine and behave as a single chemical unit. An atom will gain or lose valence electrons to form a stable ion that have the same number of electrons as the noble gas nearest the atom's atomic number. For example, Na with a single valence electron and a total of 11 electrons, will tend to lose an electron to form Na^+, the sodium

TABLE 7.2

Oxidation Numbers for Atoms Important to Air Pollution

Atom	Chemical Symbol	Oxidation Number(s)
Aluminum	Al	+3
Antimony	Sb	−3, +3, +5
Arsenic	As	−3, 0, +3, +5
Barium	Ba	+2
Boron	B	+3
Calcium	Ca	+2
Carbon	C	+2, +3, +4, −4
Chlorine	Cl	−1
Chromium	Cr	+2, +3, +6
Cobalt	Co	+2, +3
Copper	Cu	+1, +2
Fluorine	F	−1
Gold	Au	+1, +3
Hydrogen	H	+1
Iron	Fe	+2, +3
Lead	Pb	0, +2, +4
Lithium	Li	+1
Magnesium	Mg	+2
Manganese	Mn	+2, +3, +4, +6, +7
Mercury	Hg	0, +1, +2
Nickel	Ni	+2, +3
Nitrogen	N	−3, +2, +3, +4, +5
Oxygen	O	−2
Phosphorus	P	−3, +3, +5
Plutonium	Pu	+3, +4, +5, +6
Potassium	K	+1
Radium	Ra	+2
Radon	Rn	0 (noble gas)
Selenium	Se	−2, +4, +6
Silver	Ag	+1
Sodium	Na	+1
Sulfur	S	−2, +4, +6
Tin	Sn	+2, +4
Uranium	U	+3, +4, +5, +6
Zinc	Zn	+2

TABLE 7.3

Oxidation Numbers for Radicals Important to Air Pollution

Radical	Chemical symbol	Oxidation number(s)
Acetate	$C_2H_3O_2$	−1
Acrylate	$CHCO_2$	−1
Ammonium	NH_4	+1
Bicarbonate	HCO_3	−1
Borate	BO_3	−3
Carbonate	CO_3	−2
Chlorate	ClO_3	−1
Chlorite	ClO_2	−1
Chromate	CrO_4	−2
Cyanide	CN	−1
Dichromate	Cr_2O_7	−2
Hydroperoxide	HO_2	−1
Hydroxide	OH	−1
Hypochlorite	ClO	−1
Nitrate	NO_3	−1
Nitrate	NO_2	−1
Perchlorate	ClO_4	−1
Permanganate	MnO_4	−1
Phosphate	PO_4	−3
Sulfate	SO_4	−2
Sulfite	SO_3	−2
Thiocyanate	SCN	−1
Thiosulfate	S_2O_3	−2

cation. This ion has the same number of electrons (eight) as the nearest noble gas, neon (Ne). Fluorine, with seven valence electrons and nine total electrons, tends to gain (accept) an electron to form a 10-electron fluorine anion, F^- that, like the sodium ion, has the same number of electrons as Ne (eight).

Noble gases have an octet (i.e. group of eight) of electrons in their valence shells, meaning that the tendency of an atom to gain or to lose its valence electrons to form ions in the noble gas arrangement is called the "octet rule."[7] Chemical species of atoms are particularly stable when their outermost shells contain eight electrons.

Elements combine to form compounds. Two-element compounds are known as binary compounds. Three-element compounds are ternary or tertiary compounds. The representation of the relative numbers of each element is a chemical formula. Compounds are formed according to the law of definite proportions. That is, a pure compound must always be composed of the same elements that are always combined in a definite proportion by mass. Also, compounds form consistently with the law of multiple proportions, which states that when two elements combine to make more than one compound, the

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[7] Obviously, for the atoms near He, it is the "duet rule."

combining mass of each element must always exist as small integer ratios to one another. The sum of all oxidation numbers must equal zero in a stable, neutral compound. The simplest example is water. Oxygen's −2 valence is balanced by the two hydrogen's +1 valences.

COMPOUND FORMATION EXAMPLE

Is $PbC_2H_3O_2$ a valid compound?

Answer

Consulting Tables 7.3 and 7.4, we find that lead (Pb) has two common oxidation numbers (+2 and +4), and that acetate ($C_2H_3O_2$) has an oxidation number of −1, so the molecular formula given is *not* valid.

Lead acetate is $Pb(C_2H_3O_2)_2$. Two atoms of acetate are needed to balance the +2 valence of Pb. The molecule is often called lead (II) acetate to show that in this instance it is the "divalent" form of lead that has reacted with the acetate radical. Incidentally, lead (II) compounds are suspected human carcinogens, based on experiments conducted on laboratory animals. Lead acetate is also very acutely toxic and may be fatal if swallowed, and is harmful if inhaled or absorbed through the skin. Like other lead compounds, long-term exposure may harm the central nervous system, blood, and gastrointestinal tract.

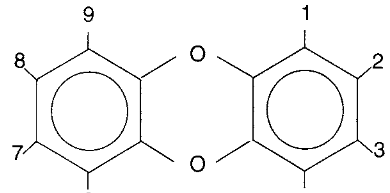
A. Physicochemical Processes in the Formation of Air Toxics

Atoms and molecules combine in many ways, according to the reactions described in Chapter 6. Let us consider some of the important processes under which toxic compounds are formed.

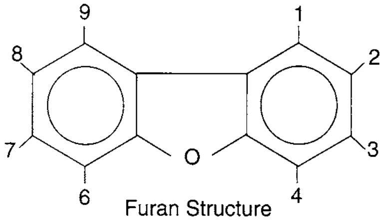
1. *Combustions Reactions*

Dioxins and furans are important air pollutants. Dioxin formation is illustrative of the complex set of combustion reactions that can generate toxic air pollutants. Chlorinated dioxins have 75 different forms and there are 135 different chlorinated furans, simply by the number and arrangement of chlorine atoms on the molecules. The compounds can be separated into groups that have the same number of chlorine atoms attached to the furan or dioxin ring. Each form varies in its chemical, physical, and toxicological characteristics (see Fig. 7.6).

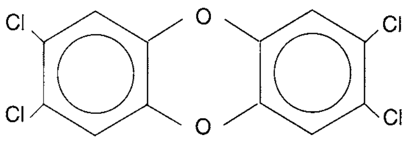
Dioxins are highly toxic compounds that are created unintentionally during combustion processes. The most toxic form is the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) isomer. Other isomers with the 2,3,7,8 configuration are also



Dioxin Structure



Furan Structure



2,3,7,8-Tetrachlorodibenzo-para-dioxin

Fig. 7.6. Molecular structures of dioxins and furans. Bottom structure is of the most toxic dioxin congener, tetrachlorodibenzo-*p*-dioxin (TCDD), formed by the substitution of chlorine for hydrogen atoms at positions 2, 3, 7, and 8 on the molecule.

considered to have higher toxicity than the dioxins and furans with different chlorine atom arrangements.

What is currently known about the conditions needed to form these compounds has been derived from studying full-scale municipal solid waste incinerators, and the experimental combustion of fuels and feeds in the laboratory. Most of the chemical and physical mechanisms identified by these studies can relate to combustion systems in which organic substances combusted in the presence of chlorine (Cl). Incinerators of chlorinated wastes are the most common environmental sources of dioxins, accounting for about 95% of the volume.

The emission of dioxins and furans from combustion processes may follow three general physicochemical pathways. The first pathway occurs when the feed material going to the incinerator contains dioxins and/or furans and a fraction of these compounds survives thermal breakdown mechanisms, and pass through to be emitted from vents or stacks. This is not considered to account for a large volume of dioxin released to the environment, but it may account for the production of dioxin-like, coplanar polychlorinated biphenyls (PCBs).

The second process is the formation of dioxins and furans from the thermal breakdown and molecular rearrangement of precursor compounds, such as the chlorinated benzenes, chlorinated phenols (such as pentachlorophenol, PCP), and PCBs, which are chlorinated aromatic compounds with structural resemblances to the chlorinated dioxin and furan molecules. Dioxins appear to form after the precursor has condensed and adsorbed onto the surface of particles, such as fly ash. This is a heterogeneous process, where the active sorption sites on the particles allow for the chemical reactions, which are catalyzed by the presence of inorganic chloride compounds and ions sorbed to the particle surface. The process occurs within the temperature range, 250–450°C, so most of the dioxin formation under the precursor mechanism occurs away from the high-temperature zone in the incinerator, where the gases and smoke derived from combustion of the organic materials have cooled during conduction through flue ducts, heat exchanger and boiler tubes, air pollution control equipment or the vents and the stack.

The third means of synthesizing dioxins is *de novo* within the so-called "cool zone" of the incinerator, wherein dioxins are formed from moieties different from those of the molecular structure of dioxins, furans, or precursor compounds. Generally, these can include a wide range of both halogenated compounds like polyvinyl chloride (PVC), and non-halogenated organic compounds like petroleum products, non-chlorinated plastics (polystyrene), cellulose, lignin, coke, coal, and inorganic compounds like particulate carbon, and hydrogen chloride gas. No matter which *de novo* compounds are involved, however, the process needs a chlorine donor (a molecule that "donates" a chlorine atom to the precursor molecule). This leads to the formation and chlorination of a chemical intermediate that is a precursor. The reaction steps after this precursor is formed can be identical to the precursor mechanism discussed in the previous paragraph.

De novo formation of dioxins and furans may involve even more fundamental substances than those moieties mentioned above. For example, dioxins may be generated[8] by heating of carbon particles absorbed with mixtures of magnesium–aluminum silicate complexes when the catalyst copper chloride ($CuCl_2$) is present (see Table 7.4 and Fig. 7.7). The *de novo* formation of chlorinated dioxins and furans from the oxidation of carbonaceous particles seems to occur at around 300°C. Other chlorinated benzenes, chlorinated biphenyls, and chlorinated naphthalene compounds are also generated by this type of mechanism.

Other processes generate dioxin pollution. A source that has been greatly reduced in the last decade is the paper production process, which formerly used chlorine bleaching. This process has been dramatically changed, so that most paper mills no longer use the chlorine bleaching process. Dioxin is also produced in the making of PVC plastics, which may follow chemical and physical mechanisms similar to the second and third processes discussed above.

Since dioxin and dioxin-like compounds are lipophilic and persistent, they accumulate in soils, sediments, and organic matter and can persist in solid

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[8] Stieglitz, L., Zwick, G., Beck, J., Bautz, H., and Roth, W., *Chemosphere* **19**, 283 (1989).

TABLE 7.4

***De Novo* Formation of Chlorinated Dioxins and Furans after Heating Mg–Al Silicate, 4% Charcoal, 7% Cl, 1% $CuCl_2 \cdot H_2O$ at 300°C**

	Concentrations (ng g^{-1})				
	Reaction time (h)				
Compound	0.25	0.5	1	2	4
Tetrachlorodioxin	2	4	14	30	100
Pentachlorodioxin	110	120	250	490	820
Hexachlorodioxin	730	780	1600	2200	3800
Heptachlorodioxin	1700	1840	3500	4100	6300
Octachlorodioxin	800	1000	2000	2250	6000
Total chlorinated dioxins	*3342*	*3744*	*7364*	*9070*	*17 020*
Tetrachlorofuran	240	280	670	1170	1960
Pentachlorofuran	1360	1670	3720	5550	8300
Hexachlorofuran	2500	3350	6240	8900	14 000
Heptachlorofuran	3000	3600	5500	6700	9800
Octachlorofuran	1260	1450	1840	1840	4330
Total chlorinated furans	*8360*	*10 350*	*17 970*	*24 160*	*38 390*

Source: Stieglitz, L., Zwick, G., Beck, J., Bautz, H., and Roth, W. *Chemosphere* **19**, 283 (1989).

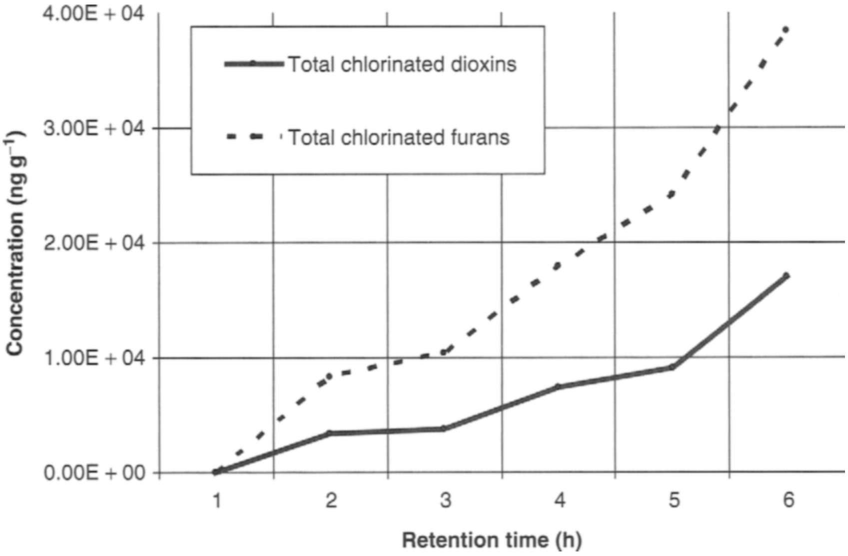

Fig. 7.7. *De novo* formation of chlorinated dioxins and furans after heating Mg–Al silicate, 4% charcoal, 7% Cl, 1% $CuCl_2$ H_2O at 300°C. *Source*: Stieglitz, L., Zwick, G., Beck, J., Bautz, H., and Roth,W. *Chemosphere* **19**, 283 (1989).

and hazardous waste disposal sites.[9] These compounds are semivolatile, so they may migrate away from these sites and transported in the atmosphere either as aerosols (solid and liquid phase) or as gases (the portion of the compound that volatilizes). Therefore, the engineer must take great care in removal, and remediation efforts not to unwittingly cause releases from soils and sediments via volatilization or via perturbations, such as landfill and dredging operations.

Dioxin demonstrates the complexity of air pollution's physicochemical processes. However, at the most basic level only a few types of chemical reactions dominate in the environment. These include ionization, acid–base, precipitation, and oxidation–reduction (redox).

2. *Ionization*

When a salt is dissolved in water, it dissociates into ionic forms. Notwithstanding their variability in doing so, under the right conditions all complexes can become dissolved in water. Ions that are dissolved in a solution can react with one another, and can form solid complexes and compounds. Actually, a salt compound does not exist in water. For example, when the salts calcium sulfate and sodium chloride are added to water, it is commonly held that $CaSO_4$ and NaCl are in the water. However, what is really happening is that the metals and nonmetals are associated with one another as:

$$CaSO_4(s) \Leftrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq) \tag{7.6}$$

and

$$NaCl(s) \Leftrightarrow Na^{+}(aq) + Cl^{-}(aq) \tag{7.7}$$

Thus, all four of the dissociated ions are free and no longer associated with each other. That is, the Na, Ca, Cl, and SO_4 ions are "unassociated" in the water. The Na and the Cl are no longer linked to each other as they were before the compound was added to the water.

Even though atoms are neutral, in the process of losing or gaining electrons, they become electrically charged, i.e. they become *ions*. An atom that loses one or more electrons is positively charged, known as a *cation*. For example, the sodium atom loses one electron and becomes the monovalent potassium cation:

$$K - e^{-} \rightarrow K^{+} \tag{7.8}$$

When the mercury atom loses two electrons, it becomes the divalent mercury cation:

$$Hg - 2e^{-} \rightarrow Hg^{2+} \tag{7.9}$$

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[9] For discussion of the transport of dioxins, see Koester, C. J., and Hites, R. A., Wet and dry deposition of chlorinated dioxins and furans, *Environ. Sci. Technol.* **26**, 1375–1382 (1992); and Hites, R. A., Atmospheric transport and deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans, EPA/600/3-91/002. Research Triangle Park, NC, 1991.

When the chromium atom loses three electrons it becomes the trivalent chromium cation:

$$Cr - 3e^- \rightarrow Cr^{3+}$$

Conversely, an atom that gains electrons becomes a negatively charged ion, known as an *anion*. For example, when chlorine gains an electron it becomes the chlorine anion:

$$Cl + e^- \rightarrow Cl^- \tag{7.10}$$

When sulfur gains two electrons, it becomes the divalent sulfide anion:

$$S + 2e^- \rightarrow S^{2-} \tag{7.11}$$

Note that the Greek prefix (mono-, di-, tri-, ...) denoting the valence is the number of electrons that the ion differs from neutrality.

Reactions between ions, known as ionic reactions, frequently occur as ions of water-soluble salts can react in aqueous solution to form salts that are nearly insoluble in water. This causes them to separate into insoluble precipitates:

$$\begin{aligned}&(\text{Ions in Solution 1}) + (\text{Ions in Solution 2}) \rightarrow \\ &\text{Precipitate} + \text{Unreacted ions}\end{aligned} \tag{7.12}$$

3. *Solubility and Electrolytes*

The aqueous solubility of contaminants ranges from completely soluble in water to virtually insoluble. Solubility equilibrium is the phenomenon that keeps molecules dissolved in a solvent. Solubility and precipitation are in a way, two sides of the same coin. There is truth in the old chemists' pun, "If you're not part of the solution, you are part of the precipitate!" Solubilities typically are quantitatively expressed in mass of solute per volume of solvent (e.g. $mg\,L^{-1}$), and sometimes expressed by the adjectives "soluble," "slightly soluble," or "insoluble."

In the solid phase, a salt is actually a collection of ions in a lattice, where the ions are surrounded by one another. However, when the salt is dissolved in water, the ions become surrounded by the water, rather than by the other ions. Each ion now has its own coordinating water envelope or "hydration sphere," i.e. a collection of water molecules surrounding it. An ion-association reaction is an ion–ion interaction between ions in an electrolyte (i.e. ion-containing) solution.[10] So, when the salt lattice enters the

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[10] The Swedish chemist, Svante Arrhenius, is credited with establishing the relationship between electrical and chemical properties of molecules. He observed that particular chemical compounds (later to be known as electrolytes) conduct electricity when they are dissolved in water, while other chemicals do not. He also saw that certain chemicals are involved in seemingly instantaneous reactions, while others took much longer to react. Finally, he observed that particular chemical compounds showed extremely strange colligative properties while others were consistent with Raoult's Law, which states that the solvent's vapor pressure in an ideal solution is equal to the product of the mole fraction of the solvent and the vapor pressure of the pure solvent. The four colligative properties of solutions are the elevation of boiling point, the depression of freezing point, the decreasing of vapor pressure, and osmotic pressure.

water, the ions assemble into couplets of separate oppositely charged ions, i.e. cations and anions, the so-called "ion pairs." The pairs are held together by electrostatic attraction. Ion association is the reverse of dissociation where the ions separate from a compound into free ions. Ions (or molecules) surrounded by water exist in the aqueous phase. So, ionic compounds that are soluble in water break apart (i.e. dissociate) into their ionic components, i.e. anions and cations (see Fig. 7.8).

Solutions may contain nonelectrolytes, strong electrolytes, and/or weak electrolytes. Nonelectrolytes do not ionize. They are nonionic molecular compounds that are neither acids nor bases. Sugars, alcohols, and most other organic compounds are nonelectrolytic. Some inorganic compounds are also nonelectrolytes.

Weak electrolytes only partially dissociate in water. Most weak electrolytes dissociate less than 10%, i.e. greater than 90% of these substances remain undissociated. Organic acids, such as acetic acid, are generally weak electrolytes.

An example of dissociation is strontium carbonate dissolved in water:

$$SrCO_3(s) \rightarrow Sr^{2+}\ (aq) + CO_3^{2-}\ (aq) \tag{7.13}$$

Conversely, the reverse reaction forms a solid; that is, it returns from the solution to again form the lattice of ions surrounding ions. This is a precipitation reaction. In our Sr example, the carbonate species is precipitated:

$$Sr^{2+}\ (aq) + CO_3^{2-}\ (aq) \rightarrow SrCO_3\ (s) \tag{7.14}$$

The *ionic product* (Q) is a measure of the ions present in the solvent. The *solubility product constant* (K_{sp}) is the ionic product when the system is in equilibrium. So, solubility is often expressed as the specific K_{sp}, the equilibrium constant for dissolution of the substance in water. Since K_{sp} is another type of chemical equilibrium, it is a state of balance of opposing reversible chemical reactions which proceed at constant and equal rates, resulting in no net change in the system (hence the symbol, ↔). Like sorption, Henry's law and other equilibrium constants, solubility follows Le Chatelier's Principle, which states that in a balanced equilibrium, if one or more factors change,

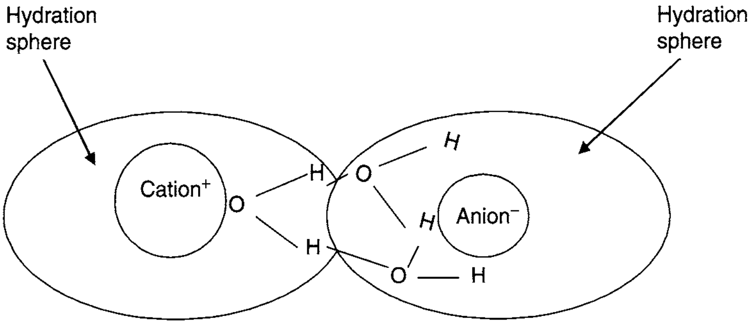

Fig. 7.8. Ion pairs. *Source*: Evangelou, V., *Environmental Soil and Water Chemistry: Principles and Applications*. John Wiley & Sons, New York, NY, 1998.

TABLE 7.5

Solubility Product Constant versus Solubility for Four Types of Salts

Salt	Example	Solubility product, K_{sp}	Solubility, S
AB	$CaCO_3$	$[Ca_{2+}][CO_3^2] = 4.7 \times 10^{-9}$	$(K_{sp})^{1/2} = 6.85 \times 10^{-5}M$
AB_2	$Zn(OH)_2$	$[Zn^{2+}][OH^-]^2 = 4.5 \times 10^{-17}$	$(K_{sp}/4)^{1/3} = 2.24 \times 10^{-6}M$
AB_3	$Cr(OH)_3$	$[Zn^{3+}][OH^-]^3 = 6.7 \times 10^{-31}$	$(K_{sp}/27)^{1/4} = 1.25 \times 10^{-8}M$
A_3B_2	$Ca_3(PO_4)_2$	$[Ca^{2+}]^3[PO_4^3]^2 = 1.3 \times 10^{-32}$	$(K_{sp}/108)^{1/5} = 1.64 \times 10^{-7}M$

Source: US Army Corps of Engineers, *Engineering and Design: Precipitation/Coagulation/Flocculation*, Chapter 2, EM 1110-1-4012, 2001.

the system will readjust to reach equilibrium. K_{sp} values and the resulting solubility calculations for some important reactions are shown in Table 7.5. K_{sp} constants for many reactions can be found in engineering handbooks.

Since $SrCO_3$ is a highly insoluble salt (aqueous solubility = 6×10^{-3} mg L^{-1}), its equilibrium constant for the reaction is quite small:

$$K_{sp} = [Sr^{+2}][CO_3^{2-}] = 1.6 \times 10^{-9} \tag{7.15}$$

The small K_{sp} value of the constant reflects the low concentration of dissolved ions. So, as the number of dissolved ions approaches zero, the compound is being increasingly insoluble in water. This does not mean that that an insoluble product cannot be dissolved, but that chemical treatment is needed. In this case, strontium carbonate requires the addition of an acid to *solubilize* the Sr^{+2} ion.

To precipitate a compound, the product of the concentration of the dissolved ions in the equilibrium expression must exceed the value of the K_{sp}. The concentration of each of these ions does not need to be the same. For example, if $[Sr^{+2}]$ is 1×10^{-5} molar, the carbonate ion concentration must exceed 0.0016 molar for precipitation to occur because $(1 \times 10^{-5}) \times (1.6 \times 10^{-4}) = 1.6 \times 10^{-9}$ (i.e. the K_{sp} for strontium carbonate).

DISSOCIATION AND PRECIPITATION REACTION EXAMPLE

An environmental analytical chemist adds 100 mL of 0.050 M NaCl to 200 mL of 0.020 M $Pb(NO_3)_2$. Will the lead chloride that is formed precipitate from the 300 mL sample?

Solution

Calculate the *ion product* (Q) and compare it to the K_{sp} for the reaction:

$$PbCl_2(s) \rightarrow Pb^{2+}(aq) + 2Cl^-(aq)$$

When the two solutions are mixed, the unassociated ions are formed as:

$$[Pb^{2+}] = 0.2\,L \times 2.0 \times 10^{-2}M/0.3\,L = 1.3 \times 10^{-2}M$$

and

$$[Cl^-] = 0.1\,L \times 5.0 \times 10^{-2}M/0.3\,L = 1.7 \times 10^{-2}M$$

The value for the ion product is calculated as:

$$Q = [Pb^{2+}][Cl^-]^2 = [1.3 \times 10^{-2}][1.7 \times 10^{-2}]^2 = 3.8 \times 10^{-7}$$

The K_{sp} for this reaction is 1.6×10^{-5}.

$Q < K_{sp}$, so no precipitate will be formed. If the ion product were greater than the K_{sp} a precipitate would have been formed.

Environmental conditions can affect solubility. One such instance is the *common ion effect*. Compared to a solution in pure water, an ion's solubility is decreased in an aqueous solution that contains a common ion (i.e. one of the ions that make up the compound). This allows a precipitate to form if the K_{sp} is exceeded. For example, soluble sodium carbonate (Na_2CO_3) in solution with strontium ions can cause the precipitation of strontium carbonate, since the carbonate ions from the sodium salt are contributing to their overall concentration in solution and reversing the solubility equilibrium of the "insoluble" compound, strontium carbonate:

$$Na_2CO_3\,(s) \rightarrow 2\,Na^+(aq) + CO_3^{2-}\,(aq) \tag{7.16}$$

$$SrCO_3\,(s) \rightarrow Sr^+(aq)^{2+}\,CO_3^{2-}\,(aq) \tag{7.17}$$

Also, a complexing agent or *ligand* may react with the cation of a precipitate, enhancing the solubility of the compound. In addition, several metal ions are weakly acidic and readily hydrolyze in solution. For example, hydrolyzing ferric ion (Fe^{3+}) forms a hydroxide and hydrogen ion:

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+ \tag{7.18}$$

When such metal ions hydrolyze, they produce a less soluble complex. The solubility of the salt is inversely related to the pH of the solution, with solubility increasing as the pH decreases. The minimum solubility is found under acidic conditions when the concentrations of the hydrolyzed species approach zero.

IONIZATION EXAMPLE

What exactly is the pH scale? Why do pH values range from 0 to 14?

Answer

Water ionizes. It does not exist only as molecular water (H_2O), but also includes hydrogen (H^+) and hydroxide (OH^-) ions:

$$H_2O \leftrightarrow H^+ + OH^- \tag{7.19}$$

The negative logarithm of the molar concentration of hydrogen ions, i.e. $[H^+]$ in a solution (usually water in the environmental sciences), is referred to as pH. This convention is used because the actual number of ions is extremely small. Thus pH is defined as:

$$\mathrm{pH} = -\log_{10}[H^+] = \log_{10}([H^+]^{-1}) \tag{7.20}$$

The brackets refer to the molar concentrations of chemicals, and in this case it is the ionic concentration in moles of hydrogen ions per liter. The reciprocal relationship of molar concentrations and pH means that the more hydrogen ions you have in solution the lower your pH value will be.

Likewise, the negative logarithm of the molar concentration of hydroxide ions, i.e. $[OH^-]$ in a solution is pOH:

$$\mathrm{pOH} = -\log_{10}[OH^-] = \log_{10}([OH^-]^{-1}) \tag{7.21}$$

The relationship between pH and pOH is constant. At 25°C, this constant is:

$$K = [H^+]\,[OH^-] = 10^{-14} \tag{7.22}$$

When expressed as a negative log, one can see that the pH and pOH scales are reciprocal to one another and that they both range from 0 to 14. Thus, a pH 7 must be neutral (just as many hydrogen ions as hydroxide ions).

Upon further investigation, the log relationship means that for each factor pH unit change there is a factor of 10 change in the molar concentration of hydrogen ions. Thus, a pH 2 solution has 100 000 times more hydrogen ions than neutral water (pH 7), or $[H^+] = 10^{12}$ versus $[H^+] = 10^7$, respectively.

B. Environmental Acid and Base Chemistry

For many air pollution situations, an acid is considered to be any substance that causes hydrogen ions to be produced when dissolved in water. Conversely, a base is any substance that produces hydroxide ions when dissolved in water. Acids are proton donors and bases are proton acceptors (this is known as the Brönsted–Lowry model). Acids are electron-pair acceptors and bases are electron-pair donors (following the Lewis model). Actually, the H^+ is a bare proton, having lost its electron, so it is highly reactive. In reality, the acid produces a hydronium ion:

$$[H^+\,(H_2O)] = H_3O^+ \tag{7.23}$$

When acids react with bases, a double-replacement reaction takes place, resulting in neutralization. The products are water and a salt. One mole of acid neutralizes precisely one mole of base. Being electrolytes, a strong acid dissociates and ionizes 100% into H_3O^+ and anions. These anions are the acid's specific conjugate base. A strong base also dissociates and ionizes completely. The ionization results in hydroxide ions and cations, known as the base's conjugate acid. Weak acids and weak bases dissociate less than 100% into the respective ions.

There are four strong acids, that are important in air pollution. These are hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), and perchloric acid ($HClO_4$). Many weak acids are also important, such as carbonic acid, acetic acid, and phosphoric acid.

Strong bases include sodium hydroxide (NaOH) and potassium hydroxide (KOH). Weak bases include ammonia (NH_3), which dissolves in water to become ammonium hydroxide (NH_4OH) and organic amines (i.e. compounds with the radical: −NH).

Nonmetal oxides, such as carbonate (CO_2) and sulfate (SO_2), are generally acidic, e.g. forming carbonic acid and sulfuric acid, respectively in water, while metal oxides like those of calcium (e.g. CaO) and magnesium (e.g. MgO), are generally basic. These two metal oxides, for example, form calcium hydroxide (CaOH) and magnesium hydroxide (MgOH) in water, respectively.

The principal environmental metric for acidity and basicity in assessing and controlling air pollution is pH. As mentioned, the "p" in pH represents the negative log and the "H" represents the hydrogen ion or hydronium ion molar concentration:

$$\mathrm{pH} = -\log[\mathrm{H}^+] \text{ and } [\mathrm{H}^+] = 10^{-\mathrm{pH}} \tag{7.24}$$

The autoionization of water into its hydrogen ion and hydroxide ions is an equilibrium constant, i.e. the water dissociation equilibrium constant (K_w). At 25 °C, the molar concentration of the product of these ions is 1.0×10^{-14}. That is:

$$K_w = [\mathrm{H}^+][\mathrm{OH}^-] = 1.0 \times 10^{-14} \tag{7.25}$$

Thus, pH ranges from 0 to 14, with 7 being neutral. Values below 7 are acidic and values above 7 are basic.

STRONG ACID/BASE EXAMPLE 1

An air pollution analytical laboratory is using an aqueous solution of sulfuric acid, which is 0.05 M. What is the hydrogen ion and chlorine ion molar concentration of the solution?

Answer

Since this is a strong acid, it should ionize and dissociate completely. Thus:

$[\mathrm{H}^+] = 0.05$ and $[\mathrm{Cl}^-] = 0.05$, so none of the associated acid remains.

Strong Acid/Base Example 2

What is the pH of the solution above? What is the $[OH^-]$ of the solution above?

Answer

Since $[H^+] = 0.05$, and $pH = -\log[H^+] = -\log 0.05\,M = 1.3$

Also, recall that:

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

$$\text{So, } [OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-4}}{0.05} = 2.0 \times 10^{-13}$$

Thus, even with a very high relative concentration of hydrogen ions in the acidic solution, there is still a small amount of hydroxide ion concentration.

Characterizing an acid or base as strong or weak has nothing to do with the concentration (i.e. molarity) of the solution, and everything to do with the extent to which the acid or base dissociates when it enters water. In other words, whether at a concentration of 6.0 M or at 0.00001 M, sulfuric acid will completely ionize in the water, but acetic acid will not completely ionize at any concentration. To demonstrate this, Table 7.6 shows the pH for a number of acids and bases, all with the same molar concentration. The strongest acids are at the top and the strongest bases are at the bottom. The weak acids and bases are in the middle of the table.

Most acid–base reactions in the atmosphere involve weak substances. In fact the amount of ionization in most environmental reactions, especially those in the ambient environment (as opposed to those in chemical engineering and laboratory reactors), are quite weak, usually well below 10% dissociation.[11]

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[11] Note that by this definition, water itself is a weak acid in that it ionizes (autoionizes into 10^{-14} molar concentration of ions) into hydroxide and hydronium ions. Hydronium is the hydrogen ion bound to a water molecule. The importance of water's ionization in virtually all biological processes should not be underestimated. At 25°C, there are 55.35 mol water per liter. So, since half of the ions are hydronium ions, this means:

$$\frac{1.0 \times 10^{-7}\,M\,H_3O^+}{55.35\,M\,H_2O} = 1.8 \times 10^{-9} \text{ hydronium ions per water molecule!}$$

Even this small ratio provides enough H^+ given the amount of water available in the hydrological cycle and the highly reactive nature of each hydrogen ion.

TABLE 7.6

The Experimentally Derived pH Values for 0.1 M Solutions of Acids and Bases at 25°C

Compound	pH
HCl	1.1
H_2SO_4	1.2
H_3PO_4	1.5
CH_3COOH	2.9
H_2CO_3 (in saturated solution)	3.8
HCN	5.1
NaCl	6.4
H_2O (distilled)	7.0
$NaCH_3CO_2$	8.4
$NaSO_3$	9.8
NaCN	11.0
NH_3 (aqueous)	11.1
$NaPO_4$	12.0
NaOH	13.0

Source: Spencer, J., Bodner, G., and Rickard, L., *Chemistry: Structure and Dynamics*, 2nd ed. John Wiley & Sons, New York, NY, 2003.

So, for every 1000 molecules of a weak acid, only a few, say 50, molecules of the acid will dissociate into hydronium ions in the water. So, taking acetic acid as an example, the acid–base equilibrium reaction is:

$$CH_3COOH\ (aq) + H_2O\ (l) \Leftrightarrow H_3O^+\ (aq) + CH_3COO^-\ (aq) \quad (7.26)$$

The acetate ion (CH_3COO^-) is the reaction's conjugate base and the hydronium ion is the active acid chemical species. Because the reaction is in equilibrium all for species exist together, so we can establish another equilibrium constant for acid reactions, i.e. the acid constant (K_a):

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \quad (7.27)$$

At 25°C, the K_a for acetic acid is 1.8×10^{-5} (see Table 7.7). If the percent dissociation in an acid reaction is known, the product of this percentage and the initial acid concentration will give the molar concentration of hydrogen ions, $[H^+]$. For example, if a 0.1 M solution of cyanic acid (HOCN) is 2.8% ionized, the $[H^+]$ can be found. We know that HOCN is a weak acid because the percent ionization is less than 100. In fact, it is well below 10%. This means that the hydrogen ion molar concentration is

$$[H^+] = 2.8\% \times 0.1\,M = 0.0028 \text{ or } 2.8 \times 10^{-3}$$

Published K_a constants show that the HOCN constant at 25°C is 3.5×10^{-3}, so environmental conditions, likely temperature, are slightly affecting the pH of the solution. Remember that all equilibrium constants are temperature dependent.

Weak bases follow the exact same protocol as weak acids, with a base equilibrium constant, K_b. Some important acid and base equilibrium constants are provided in Tables 7.7 and 7.8.

TABLE 7.7

Equilibrium Constants for Selected Environmentally Important Weak Monoprotic (Single H Atom) Acids and Bases at 25°C

Monoprotic acid	Dissociation reaction	K_a
Hydrofluoric acid	$HF + H_2O \Leftrightarrow H_3O^+ + F^-$	7.2×10^{-4}
Nitrous acid	$HNO_2 + H_2O \Leftrightarrow NO_2^- + H_3O^+$	4.0×10^{-4}
Lactic acid	$CH_3CH\,(OH)\,CO_2H + H_2O \Leftrightarrow CH_3CH\,(OH)\,CO_2^- + H_3O^+$	1.38×10^{-4}
Benzoic acid	$C_6H_5CO_2H + H_2O \Leftrightarrow C_6H_5CO_2^- + H_3O^+$	6.4×10^{-5}
Acetic acid	$HC_2H_3O_2 + H_2O \Leftrightarrow C_2H_3O_2^- + H_3O^+$	1.8×10^{-5}
Propionic acid	$CH_3CH_2CO_2H + H_2O \Leftrightarrow CH_3CH_2CO_2^- + H_3O^+$	1.3×10^{-5}
Hypochlorous acid	$HOCl + H_2O \Leftrightarrow OCl^- + H_3O^+$	3.5×10^{-8}
Hypobromous acid	$HOBr + H_2O \Leftrightarrow OBr^- + H_3O^+$	2×10^{-9}
Hydrocyanic acid	$HCN + H_2O \Leftrightarrow CN^- + H_3O^+$	6.2×10^{-10}
Phenol	$HOC_6H_5 + H_2O \Leftrightarrow OC_6H_5^- + H_3O^+$	1.6×10^{-10}
Base	Dissociation reaction	K_b
Dimethylamine	$(CH_3)_2NH + H_2O \Leftrightarrow (CH_3)_2NH_2^+ + OH^-$	5.9×10^{-5}
Methylamine	$CH_3NH_2 + H_2O \Leftrightarrow CH_3\,NH_3^+ + OH^-$	7.2×10^{-4}
Ammonia	$NH_3 + H_2O \Leftrightarrow NH_3^+ + OH^-$	1.8×10^{-5}
Hydrazine	$H_2NNH_2 + H_2O \Leftrightarrow H_2NNH_3^+ + OH^-$	1.2×10^{-6}
Analine	$C_6H_5NH_2 + H_2O \Leftrightarrow C_6H_5NH_3^+ + OH^-$	4.0×10^{-10}
Urea	$H_2NCONH_2 + H_2O \Leftrightarrow H_2NCONH_3^+ + OH^-$	1.5×10^{-14}

Source: Casparian, A., Chemistry, in *How to Prepare for the Fundamentals of Engineering (FE/EIT) Exam* (Olia, M., ed.). Barron's Educational Series, Inc., Hauppauge, NY, 2000.

TABLE 7.8

Equilibrium Constants for Selected Environmentally Important Polyprotic (Two or More H Atom) Acids at 25°C

Acid	Dissociation reactions	K_{a1}	K_{a2}	K_{a3}
Sulfuric acid	$H_2SO_4 + H_2O \Leftrightarrow HSO_4^- + H_3O^+$	1.0×10^{3}		
	$HSO_4^- + H_2O \Leftrightarrow SO_4^{2-} + H_3O^+$		1.2×10^{-2}	
Hydrogen sulfide	$H_2S + H_2O \Leftrightarrow HS^- + H_3O^+$	1.0×10^{-7}		
	$HS^- + H_2O \Leftrightarrow S^{2-} + H_3O^+$		1.3×10^{-13}	
Phosphoric acid	$H_3PO_4 + H_2O \Leftrightarrow HPO_4^- + H_3O^+$	7.1×10^{-3}		
	$HPO_4^- + H_2O \Leftrightarrow HPO_4^{2-} + H_3O^+$		6.3×10^{-8}	
	$HPO_4^{2-} + H_2O \Leftrightarrow PO_4^{3-} + H_3O^+$			4.2×10^{-13}
Carbonic acid	$H_2CO_3 + H_2O \Leftrightarrow HCO_3^- + H_3O^+$	4.5×10^{-7}		
	$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+$		4.7×10^{-11}	

Source: Casparian, A., Chemistry, in *How to Prepare for the Fundamentals of Engineering (FE/EIT) Exam* (Olia, M. ed.). Barron's Educational Series, Inc., Hauppauge, NY, 2000.

Because the atmosphere contains relatively large amounts of carbon dioxide (on average about 350 ppm), the CO_2 becomes dissolved in surface water and in soil water (because CO_2 is a common soil gas). Thus, one of the most important environmental acid–base reactions[12] is the dissociation of CO_2:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3^* \tag{7.28}$$

The asterisk (*) denotes that this compound is actually the sum of two compounds, i.e. the dissolved CO_2 and the reaction product, carbonic acid H_2CO_3.

Since the carbonic acid that is formed is a diprotic acid (i.e. it has two hydrogen atoms), an additional equilibrium step reaction occurs in water. The first reactions forms bicarbonate and hydrogen ions:

$$H_2CO_3^* \Leftrightarrow HCO_3^- + H^+$$

Followed by a reaction that forms carbonate and hydrogen:

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+ \tag{7.29}$$

Each of the two-step reactions has its own acid equilibrium constant (K_{a1} and K_{a2}, respectively), as shown in Table 7.9. For a triprotic acid, there would be three unique constants. Note that the constants decrease substantially with each step. In other words, most of the hydrogen ion production occurs in the first step.

Numerous reactions can be predicted from the relative strength of acids and bases, since their strength results from how well the protons via the hydronium ion is transferred from the acid and the electron is transferred via the hydroxide ion from the base. If an acid is weak, its conjugate base must be strong, and if an acid is strong, its conjugate base must be weak. Likewise, if a base is weak, its conjugate acid must be strong, and if the base is strong, its conjugate acid must be weak. Our tables show actual K_a and K_b constants, however, many sources value for pK_a and pK_b values. Since the "p" denotes negative logarithm, the larger the pK_a, the weaker the acid, and the larger the pK_b, the weaker the base.

An example of how the K_a is an indicator of relative strength of reactants and products is that of hydrocyanic acid:

$$\underset{\substack{\uparrow \\ \text{Stronger acid} \\ (K_a = 6.2 \times 10^{-10})}}{HCN} + \overset{\substack{\text{Stronger base} \\ \searrow}}{OH^-} \Leftrightarrow \overset{\substack{\text{Weaker base} \\ \swarrow}}{CN^-} + \underset{\substack{\uparrow \\ \text{Weaker acid} \\ (K_a = 1.8 \times 10^{-16})}}{H_2O} \tag{7.30}$$

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[12] For an excellent discussion of carbon dioxide equilibrium in water see Hemond, H. F., and Fechner-Levy, E. J., *Chemical Fate and Transport in the Environment*. Academic Press, San Diego, CA, 2000.

The ratio of the K_a constant values of the two acids is a direct way to quantify the equilibrium. In the hydrocyanic acid instance above, the ratio is $\frac{6.2 \times 10^{-10}}{1.8 \times 10^{-16}} \cong 4 \times 10^6$.

This large quotient indicates that the equilibrium is quite far to the right. So, if HCN is dissolved in a hydroxide solution (e.g. NaOH), the resulting reaction will produce much greater amounts of the cyanide ion (CN^-) than the amount of both the hydroxide ion (OH^-) and molecular HCN. Conversely, for an aqueous solution of sodium cyanide (NaCN), the water will only react with a tiny amount of CN^-.

Among the properties of water, one of the most important environmentally is that it can behave as either an acid or a base, i.e. water is an amphoteric compound. That is one of the reasons that water is sometimes shown as HOH. When water acts as a base its $pK_b = -1.7$. When water acts as an acid its $pK_a = 15.7$.

Many air pollution reactions occur in water (e.g. in droplets, on aerosols, and even in the water within organisms), so the relationship between conjugate acid–base equilibrium and pH is important. The Henderson–Hasselbach equation states this relationship:

$$pK_a = pH + \log\frac{[HA]}{[A^-]} \tag{7.31}$$

Thus, Henderson–Hasselbach tells us that when the pH of an aqueous solution equals the pK_a of an acidic component, the concentrations of the conjugate acids and bases must be equal (since the log of $1 = 0$). If pH is 2 or more units lower than pK_a, the acid concentration will be greater than 99%. Conversely, when pH is greater than pK_a by 2 or more units, the conjugate base concentration will account for more than 99% of the solution.[13]

This means that mixtures of acidic and non-acidic compounds can be separated with a pH adjustment, which has strong implications for the design and operation of air pollution control equipment. The application of this principle is also important to the transformation of environmental contaminants in the form of weak organic acids or bases, because these compounds in their non-ionized form are much more lipophilic, meaning they will be absorbed more easily through the skin than when they exist in ionized forms. As a general rule, the smaller the pK_a for an acid and the larger the pK_b for a base, the more extensive will be the dissociation in aqueous environments at normal pH values, and the greater compound's electrolytic nature.

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[13] US Environmental Protection Agency, *Dermal Exposure Assessment: Principles and Applications*, Interim Report, EPA/600/8-91/011B, Washington, DC, 1992.

ACID RAIN EXAMPLE

Acid-base reactions are demonstrated by the acid rain problem. Dissolved CO_2 causes most rainfall to be slightly acidic:

$$CO_2(aq) + H_2O(l) \Leftrightarrow H^+(aq) + HCO_3^-(aq)\ K_a = 4.3 \times 10^{-7} \tag{7.32}$$

Acidic precipitation, popularly known as "acid rain" contains the strong acids H_2SO_4 and HNO_3, mainly from the combustion of fossil fuels that contain sulfur (the air contains molecular nitrogen that is oxidized during internal combustion in engines, i.e. "mobile sources" and in any high temperature furnaces, like those in power plants). The sulfuric acid is stepped process. Recall that the contaminant released from stacks is predominantly sulfur dioxide when the elemental sulfur oxidized:

$$S + O_2 \rightarrow SO_2\ (g) \tag{7.33}$$

The sulfur dioxide in turn is oxidized to sulfur trioxide:

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow SO_3(g) \tag{7.34}$$

The sulfur trioxide then reacts with atmospheric water (vapor, clouds, on particles) to form sulfuric acid:

$$SO_3\ (g) + H_2O \rightarrow H_2SO_4\ (aq) \tag{7.35}$$

The net result is to increase the acidity of the rain, which is a threat to aquatic life, and metallic and carbonate materials (including artwork, statues, and buildings). Near pollution sources, rainwater pH can be found to be less than 3 (i.e. 10 000 times more acidic than neutral).

What are the molar concentrations of $[H^+]$ and $[OH^-]$ of rainwater at pH 3.7 at 25°C? When SO_2 dissolves in water, sulfurous acid (H_2SO_3, $K_{a1} = 1.7 \times 10^{-2}$, $K_{a2} = 6.4 \times 10^{-8}$) is formed. What is the reaction when sulfurous acid donates a proton to a water molecule? What is the Brönsted–Lowry acid and base in this reaction?

Surface waters have a natural buffering capacity, especially in regions where there is limestone which gives rise to dissolved calcium (e.g. central Kansas is less at risk of acid rain's effects than are the Finger Lakes of New York). What is the reaction of a minute amount of acid rain containing sulfuric acid reaching a lake containing carbonate (CO_3^{2-}) ions?

Solution

Since, $pH = -\log[H^+]$, then $[H^+] = 10^{-pH} = 10^{-3.7}\ 2.0 \times 10^{-4}M$ in aqueous solution at 25°C.

The sulfurous acid proton donation reaction is:

$$H_2SO_3\ (aq) + H_2O\ (l) \Leftrightarrow HSO_3^-\ (aq) + H_3O^+\ (aq) \tag{7.36}$$

H_3O^+ is the stronger acid (i.e. $K_{a1} < 1$) and HSO_3^- is the stronger base.

Regarding the buffered water system, CO_3^{2-} is the conjugate base of the weak acid HCO_3^-, so the former can react with the strong acid H_3O^+ in the sulfuric acid solution:

$$CO_3^{2-}\,(aq) + H_3O^+\,(aq) \Leftrightarrow HCO_3^-\,(aq) + H_2O\,(l) \tag{7.37}$$

The $K = 1/K_{a2}$ of H_2CO_3 (making for a large K)
Similarly HSO_4^- also reacts with CO_3^{2-}:

$$CO_3^{2-}\,(aq) + HSO_4^-\,(aq) \Leftrightarrow SO_4^{2-}\,(aq) + HCO_3^-\,(aq) \tag{7.38}$$

The $K = (K_{a2}$ of $H_2SO_4)/(K_{a2}$ of $H_2CO_3)$ (*thus, large* K)
So, a HCO_3^-/CO_3^{2-} buffer is produced.

An excess of acid rain will consume all the CO_3^{2-} and HCO_3^-, converting all to H_2CO_3 (and completely eliminating the buffer).

These are important and representative reactions of the challenging global problem of acid rain.

1. *Hydrolysis*

All of the acid–base reactions involve chemical species reacting with water. It is worth noting that even some so-called neutral compounds have acidic or basic properties. For example, metal[14] acetates $(MeC_2H_3O_2)_x)$ can dissolve in water and actually react with the water to form weak acids and hydrogen ions. The resulting solutions are generally slightly basic ($pH > 7$), since the acetate ion is conjugate base of the weak acid. This process is known as hydrolysis (i.e. lysis or breaking apart water molecules).

Likewise, some compounds produce weak bases when dissolved in water. For example, when ammonium chloride (NH_4Cl) is dissolved in water, the solution becomes more acidic. The NH_4^+ cation serves as the conjugate base of ammonium hydroxide (NH_4OH), or molecular ammonia (NH_3) is the conjugate base of the NH_4^+ cation. Oxide gases (e.g. carbon dioxide and sulfur dioxide) can hydrolyzed to form hydronium ions and anions:

$$CO_2\,(g) + H_2O\,(l) \Leftrightarrow H_3O^+\,(aq) + HCO_3^-(aq) \tag{7.39}$$

And,

$$SO_2\,(g) + H_2O\,(l) \Leftrightarrow H_3O^+\,(aq) + HSO_3^-(aq) \tag{7.40}$$

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[14] The abbreviation "Me" is commonly used for "metals" when a number of metals exhibit identical or similar properties and behavior (e.g. Hg, Cd, Pb, and Mn may behave similarly on an aerosol's surface, catalyzing certain reactions, or they may also exhibit similar physiological processes, such as interferences with neurons and calcium gates in the brain and central nervous system). Rather than listing every metal, the chemical formulae will display Me.

These reactions also take place in organic compounds, where the organic molecule, RX, reacts with water to form a covalent bond with OH and cleaves the covalent bond of the leaving group (X) in RX, which displaces X with the hydroxide ion and an ion formed from the leaving group:

$$RX + H_2O \rightarrow ROH + H^+ + X^- \qquad (7.41)$$

Amides, epoxides, carbonates, esters, organic halides, nitriles, urea compounds, and esters of organophosphate compounds are functional groups that are susceptible to hydrolysis. The process involves an electron-rich nucleus seeker (i.e. a nucleophile) attacking an electron-poor electron seeker (i.e. an electrophile) to displace the leaving group (such as a halogen). This is why hydrolysis is one of the methods of dechlorination, a detoxification process for hazardous chlorinated hydrocarbons.

Environmental engineers use hydrolysis to eliminate or to reduce the toxicity of hazardous contaminants by abiotic transformation and biotransformation, especially bacterial. For example, the highly toxic methyl isocynate, infamous as the contaminant that led to loss of life and health effects in the Bhopal, India incident, can be transformed hydrolytically.

Two factors are particularly enhancing to hydrolysis. Microbial mediation, including enzymatic activity can catalyze hydrolytic reactions. This occurs both in the ambient environment, such as the hydrolysis of inorganic and organic compounds by soil bacteria, as well as in engineered systems, such as acclimating those same bacteria to the treatment of chlorinated organic compounds in solid and liquid wastes.

The second factor is pH. Hydrolysis can be affected by specific acid and base catalysis. In acid catalysis, this H^+ ion catalyzes the reaction; and in base catalysis the OH^- ion serves as the catalyst. The effect of temperature on hydrolysis can be profound. Each 10°C incremental temperature increase results in a hydrolysis rate constant change by a factor of 2.5.[15]

Metal (Me) hydrolysis is a special case. Cations in water act like Lewis acids in that they are prone to accept electrons, while water behaves like a Lewis base because it makes its oxygen's two unshared electrons available to the cations. When strong water–metal (acid–base) interactions take place, H^+ dissociates and hydronium ions form in a prototypical reaction:

$$Me^{n+} + H_2O \Leftrightarrow MeOH^{(n+1)} + H^+ \qquad (7.42)$$

Although reactions such as these have obvious applications to contaminant transformations in surface water, soil water, and groundwater, they occur in any medium where water is present. Water is present in the atmosphere, so hydrolysis occurs in clouds and fog, as well as in the water fraction hygroscopic nuclei. Water is also present in all living things, so hydrolysis is a common process in metabolism (particularly in the first phase, as discussed later)

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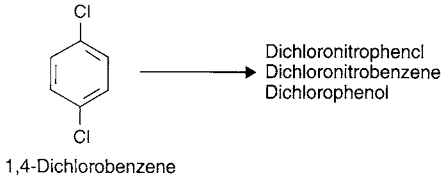
[15] Knox, R., Sabatini, D., and Canter, L., *Subsurface Transport and Fate Processes*. Lewis Publishers, Boca Raton, FL, 1993.

and other organic processes. Thus, hydrolysis is important in numerous environmental and toxicological processes.

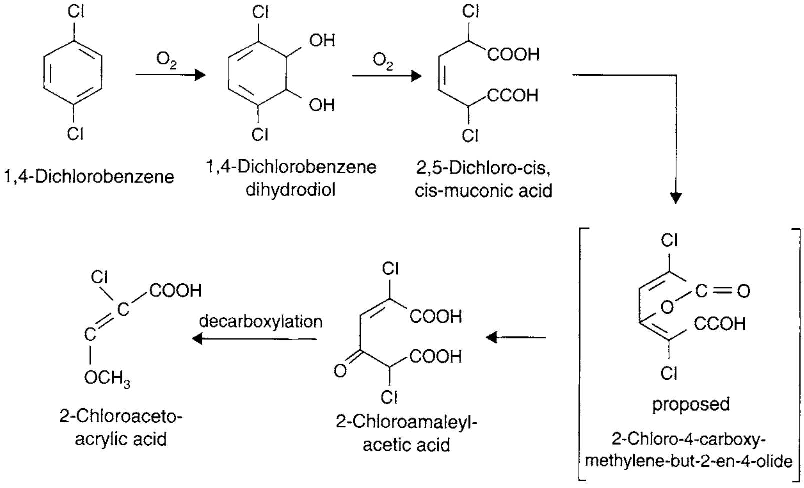
2. *Photolysis*

The sun's EMR at UV and visible wavelengths can induce chemical reactions directly and indirectly. Direct photolysis is the process where sunlight adds activation energy needed to transform a compound. Indirect photolysis is the process by which an intermediate compound is energized, which in turn transfers energy to another compound.

Contaminants are photochemically degraded in both atmospheric and aquatic environments. Photolysis can combine or interchange with other processes, such as in the degradation pathways for chlorinated organic contaminants. For example, the degradation pathway for 1,4-dichlorobenzene in air is reaction with photochemically generated OH^- radicals and oxides of nitrogen. However, in soil and water, the degradation is mainly microbial biodegradation, leading to very different end products (see Fig. 7.9).



Photolytic degradation in air



Biodegradation in soil and water

Fig. 7.9. Different 1,4-dichlorobenzene reactions according to environmental media. *Source*: Agency for Toxic Substances and Disease Registry, 1998, Toxicological Profile for 1,4-Dichlorobenzene, http://www.atsdr.cdc.gov/toxprofiles/tp10.html.

3. *Precipitation Reactions*

Dissolved ions may react with one another to form a solid phase compound under environmental conditions of temperature and pressure. Salts are compounds that form when metals react with nonmetals, such as sodium chloride (NaCl). They may also form from cation and anion combinations, such as ammonium nitrate (NH_4NO_3). Precipitation is both a physical and chemical process, wherein soluble metals and inorganic compounds change into insoluble metallic and inorganic salts. In other words, the dissolved forms become solids. Such reactions in which soluble chemical species become insoluble products are known as "precipitation reactions."

Chemical precipitation occurs within a defined pH and temperature range unique for each metallic salt. Usually in such reactions, an alkaline reagent is added to the solution, thereby raising the solution pH. The higher pH often decreases the solubility of the metallic constituent, bringing about the precipitation (see Fig. 7.10). For example, adding caustic soda (NaOH) decreases the amount of soluble nickel, producing the much less water-soluble species nickel hydroxide precipitate (recall that "s" denotes a solid precipitate):

$$Ni^{2+} + NaOH \Leftrightarrow Na^{+} + Ni\,(OH)_2\,(s) \qquad (7.43)$$

V. ORGANIC CHEMISTRY

Carbon is an amazing element. It can bond to itself and to other elements in a myriad of ways. In fact, it can form single, double, and triple bonds with itself. This makes for millions of possible organic compounds. An organic compound is a compound that includes at least one carbon-to-carbon or carbon-to-hydrogen covalent bond.

The majority of air pollutants are organic.[16] Organic compounds can be further classified into two basic groups: aliphatics and aromatics. Hydrocarbons are the most fundamental type of organic compound. Unsubstituted hydrocarbons contain only the elements carbon and hydrogen. Aliphatic compounds are classified into a few chemical families. Each carbon normally forms four covalent bonds. Alkanes are hydrocarbons that form chains with each link comprised of the carbon. A single link is CH_4, methane. The carbon

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[16] This is true in terms of the actual number of chemical compounds. By far, most contaminants are organic. However, in terms of total mass of reactants and products in the biosphere, inorganic compounds represent a greater mass. For example, most hazardous waste sites are contaminated with organic contaminants, but large-scale waste represented by mining, extraction, transportation, and agricultural activities have larger volumes and masses of metals and inorganic substances.

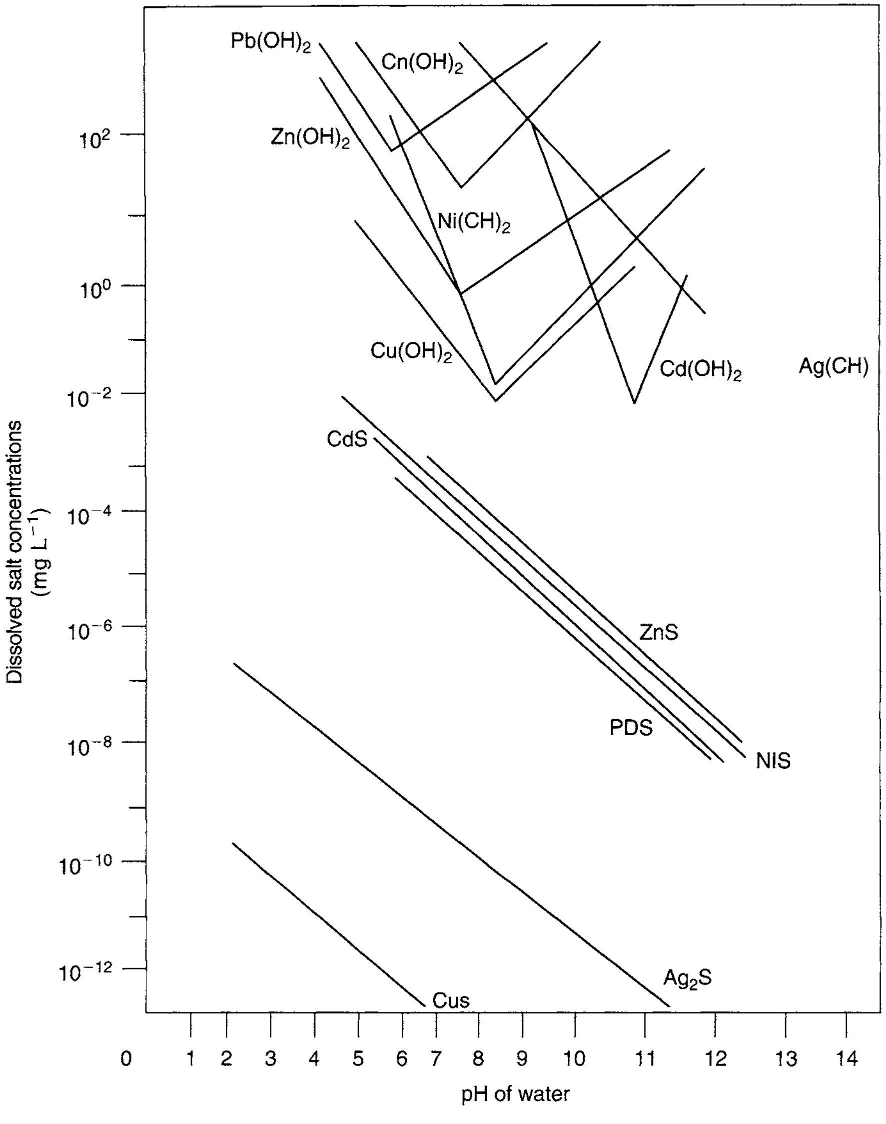
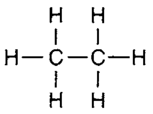
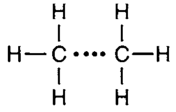


Fig. 7.10. Effect of pH on the solubility of metal hydroxides and sulfides. *Source*: US Environmental Protection Agency, *Summary Report: Control and Treatment Technology for the Metal Finishing Industry; Sulfide Precipitation*, Report No. EPA 625/8-80-003, Washington, DC, 1980.

chain length increases with the addition of carbon atoms. For example, ethane's structure is:


$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$$

And the protypical alkane structure is:



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & \cdots & C & -H \\ & | & & | & \\ & H & & H & \end{array}$$

The alkanes contain a single bond between each carbon atoms, and include the simplest organic compound, methane (CH_4), and its derivative "chains" such as ethane (C_2H_6) and butane (C_4H_{10}). Alkenes contain at least one double bond between carbon atoms. For example, 1,3-butadiene's structure is CH_2—CH—CH—CH_2. The numbers "1" and "3" indicate the position of the double bonds. The alkynes contain triple bonds between carbon atoms, the simplest being ethyne, $CH \equiv CH$, which is commonly known as acetylene (the gas used by welders).

The aromatics are all based on the six-carbon configuration of benzene (C_6H_6). The carbon–carbon bond in this configuration shares more than one electron, so that benzene's structure allows for resonance among the double and single bonds, i.e. the actual benzene bonds flip locations. Benzene is the average of two equally contributing resonance structures.

The term "aromatic" comes from the observation that many compounds derived from benzene are highly fragrant, such as vanilla, wintergreen oil, and sassafras. Aromatic compounds, thus, contain one or more benzene rings. The rings are planar, that is, they remain in the same geometric plane as a unit. However, in compounds with more than one ring, such as the highly toxic PCBs, each ring is planar, but the rings that are bound together may or may not be planar. This is actually a very important property for toxic compounds. It has been shown that some planar aromatic compounds are more toxic than their non-planar counterparts, possibly because living cells may be more likely to allow planar compounds to bind to them and to produce nucleopeptides that lead to biochemical reactions associated with cellular dysfunctions, such as cancer or endocrine disruption.

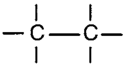
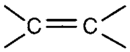
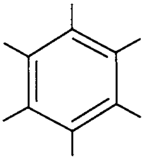
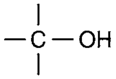
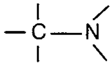
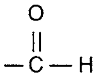
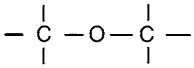
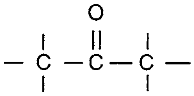
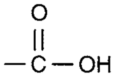
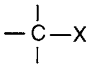
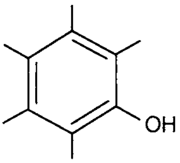
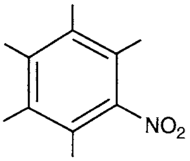
Both the aliphatic and aromatic compounds can undergo substitutions of the hydrogen atoms. These substitutions render new properties to the compounds, including changes in solubility, vapor pressure, and toxicity. For example, halogenation (substitution of a hydrogen atom with a halogen) often makes an organic compound much more toxic. Thus, trichloroethane is a highly carcinogenic liquid that has been found in drinking water supplies, whereas non-substituted ethane is a gas with relatively low toxicity. This is also why one of the means for treating chlorinated hydrocarbons and aromatic compounds involves dehalogenation techniques.

The important functional groups that are part of many organic compounds are shown in Table 7.9.

Structures of organic compounds can induce very different physical and chemical characteristics, as well as change the bioaccumulation and toxicity of these compounds. For example the differences between the estradiol

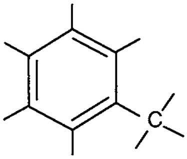
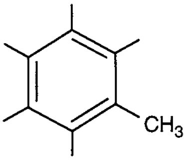
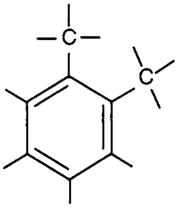
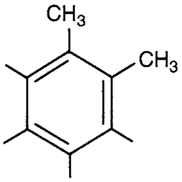
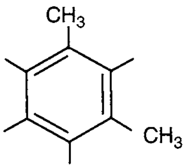
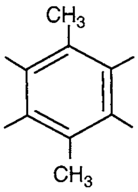
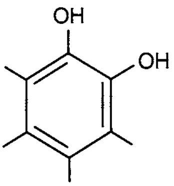
TABLE 7.9

Structures of Organic Compounds

Chemical class	Functional group
Alkanes	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
Alkenes	
Alkynes	$-C\equiv C-$
Aromatics	
Alcohols	 $-\overset{\vert}{\underset{\vert}{C}}-OH$
Amines	
Aldehydes	 $-\overset{O}{\overset{\Vert}{C}}-H$
Ether	 $-\overset{\vert}{\underset{\vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-$
Ketones	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{O}{\overset{\Vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
Carboxylic acids	 $-\overset{O}{\overset{\Vert}{C}}-OH$
Alkyl halides[a]	 $-\overset{\vert}{\underset{\vert}{C}}-X$
Phenols (aromatic alcohols)	
Substituted aromatics (substituted benzene derivatives):	
Nitrobenzene	

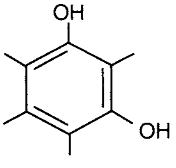
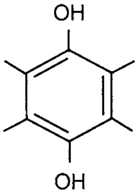
(continued)

TABLE 7.9 (*Continued*)

Chemical class	Functional group
Monosubstituted alkylbenzenes	
Toluene (simplest monosubstituted alky benzene)	
Polysubstituted alkylbenzenes:	
1,2-alkyl benzene (also known as ortho or *o*-...)	
1,2-xylene or *ortho*-xylene (*o*-xylene)	
1,3-xylene or *meta*-xylene (*m*-xylene)	
1,4-xylene or *para*-xylene (*p*-xylene)	
Hydroxyphenols do not follow general nomenclature rules for substituted benzenes:	
Catechol (1,2-hydroxiphenol)	

(*continued*)

TABLE 7.9 (*Continued*)

Chemical class	Functional group
Resorcinol (1,3-hydroxiphenol)	
Hydroquinone (1,4-hydroxiphenol)	

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[a] The letter "X" commonly denotes a halogen, e.g. fluorine, chlorine, or bromine, in organic chemistry. However, in this text, since it is an amalgam of many scientific and engineering disciplines, where "x" often means an unknown variable and horizontal distance on coordinate grids, this rule is sometimes violated. Note that when consulting manuals on the physicochemical properties of organic compounds, such as those for pesticides and synthetic chemistry, the "X" usually denotes a halogen.

and a testosterone molecule may seem small but they cause significant differences in the growth and reproduction of animals. The very subtle differences between an estrogen and an androgen, female and male hormones respectively, can be seen in these structures. But look at the dramatic differences in sexual and developmental changes that these compounds induce in organisms!

Incremental to a simple compound, such as substituting chlorine atoms for three hydrogen atoms on the ethane molecule, can make for large differences (see Table 7.10). Replacing two or three hydrogen atoms with chlorine atoms makes for differences in toxicities between the non-halogenated form and the chlorinated form. The same is true for the simplest aromatic, benzene. Substituting a methyl group for one of the hydrogen atoms forms toluene.

The lessons here are many. There are uncertainties in using surrogate compounds to represent whole groups of chemicals (since a slight change can change the molecule significantly). However, this points to the importance of "green chemistry" and computational chemistry, as tools to prevent dangerous chemical reaching the marketplace and the environment before they are manufactured. Subtle differences in molecular structure can render molecules safer, while maintaining the characteristics that make them useful in the first place, including their market value.

TABLE 7.10

Incremental Differences in Molecular Structure Leading to Changes in Physicochemical Properties and Hazards

Compound	Physical state at 25°C	$-\log P^0$ solubility in H_2O at 25°C ($molL^{-1}$)	$-\log$ vapor pressure at 25°C (atm)	Worker exposure limits (parts per million)	Regulating agency
Methane, CH_4	Gas	2.8	-2.4	25	Canadian Safety Association
Tetrachloromethane (carbon tetrachloride), CCl_4	Liquid	2.2	0.8	2 short-term exposure limit (STEL) = 60 min	National Institute of Occupation Health Sciences (NIOSH)
Ethane, C_2H_6	Gas	2.7	-1.6	None (simple asphyxiant)	Occupational Safety and Health Administration (OSHA)
Trichloroethane, $C_2H\,Cl_3$	Liquid	2.0	1.0	450 STEL (15 min)	OSHA
Benzene, C_6H_6	Liquid	1.6	0.9	5 STEL	OSHA
Phenol, C_6H_6O	Liquid	0.2	3.6	10 ppm	OSHA
Toluene C_7H_8	Liquid	2.3	1.4	150 STEL	UK Occupational & Environmental Safety Services

ORGANIC STRUCTURE EXAMPLE 1

If the aqueous solubility as expressed as $-\log S$ (in mol L^{-1}) of 1-butanol, 1-hexanol, 1-octanol, and 1-nonanol are 0.1, 0.9, 2.4, and 3.1, respectively, what does this tells you about the length of carbon chains and the solubility of alcohols? (Remember that this expression of solubility is a negative log!)

Answer and Discussion

Recall that solubility is expressed as a negative logarithm, so lengthening the carbon chain *decreases polarity and, therefore, aqueous solubility* since "like dissolves like" and water is very polar. Thus, as shown in the Fig. 7.11, butanol is orders of magnitude more hydrophilic than is nonanol.

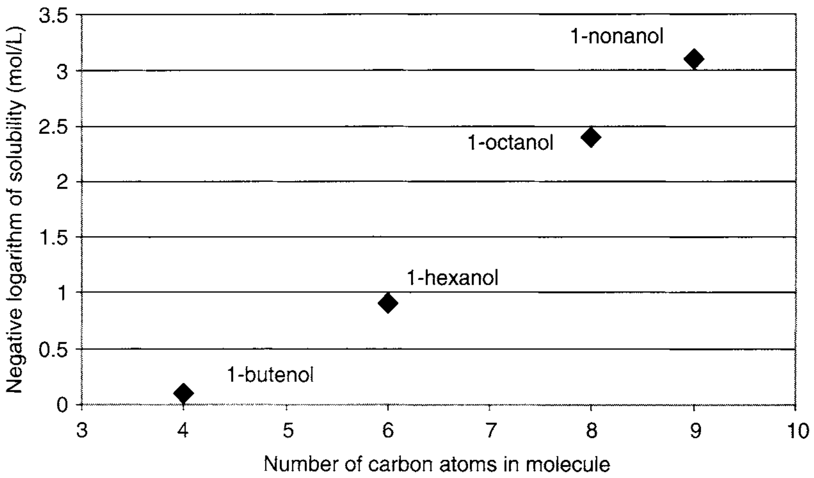

Fig. 7.11. Aqueous solubility of four alcohols.

ORGANIC STRUCTURE EXAMPLE 2

Consider the polarity of the four alcohols in #2 above. If *n*-butane, *n*-hexane, *n*-octane, and *n*-nonane's aqueous solubilities as expressed as $-\log P^0$ are, respectively: 3.0, 3.8, 5.2, and 5.9 $\text{mol}\,L^{-1}$, what effect does the substitution of a hydroxyl functional group for the hydrogen atom have on an alkane's polarity? Can this effect also be observed in aromatics? (*Hint*: Compare S for benzene, toluene to phenol in the table in #1 above; and recall that phenol is a hydroxylated benzene.)

Answer

There is a direct relationship (see Fig. 7.12) between the increase in polarity and hydrophilicity when alkanes are hydroxylated into alcohols. This is why alcohols are miscible in water. This can be an important fact, especially in anaerobic treatment processes where microbes reduce organic compounds and in the process generate alcohols (and ultimately methane and water). Hydroxylation of an aromatic, as indicated by comparing the solubilities of benzene and phenol, also increases polarity and hydrophilicity.

It should be noted that solubility may be modified in environmental systems by using compounds known as "surfactants" (see Fig. 7.13). Surfactants can be very effective in solubilizing adsorbed hydrophobic compounds in soils. The increased solubility and dispersion of hydrocarbons and aromatic compounds with very low aqueous solubility

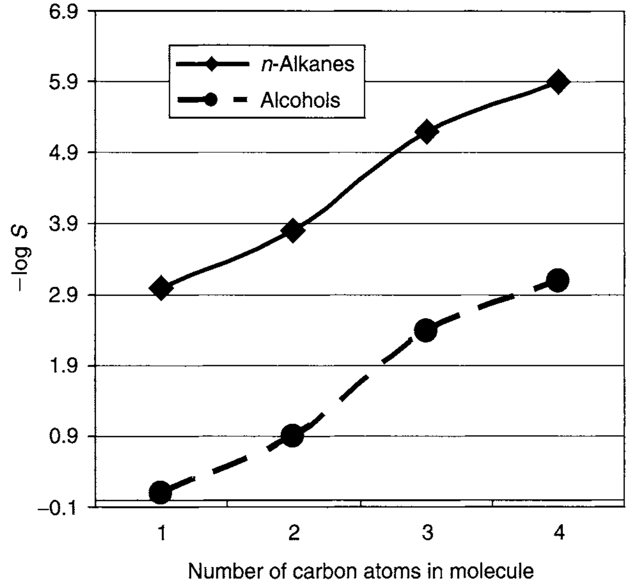

Fig. 7.12. Aqueous solubility of selected aliphatic compounds.

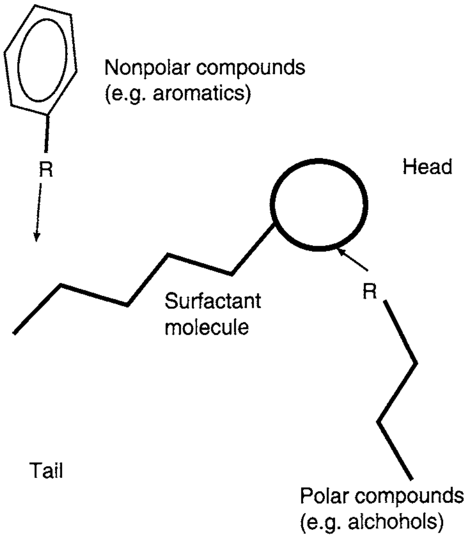

Fig. 7.13. Structure of a surfactant prototype. The head of the molecule is relatively polar and the tail is relatively nonpolar, so in the aqueous phase the more hydrophilic compounds will react with the surfactant molecule at the head position, while the more lipophilic compounds will react at the tail position. The result is that a greater amount of the organic compounds will be in solution when surfactants are present. *Source*: Vallero, D., *Engineering the Risks of Hazardous Wastes*. Butterworth-Heinemann, Boston, MA, 2003.

enhances desorption and bioavailability. Unfortunately, a widely used group of surfactants, i.e. alkylphenolethoxylates (APEs) have been banned in Europe because their breakdown products can be very toxic to aquatic organisms. The APEs have been particularly of concern because of their hormonal effects, particularly their estrogenicity. So, one must keep in mind not only the physical and chemical advantages of such compounds, but also any ancillary risks that they may introduce. This is a classic case of competition among values (i.e. easier and more effective cleanup versus additive health risks from the cleanup chemical).

1. *Isomers*

Isomers are compounds with identical chemical formulae, but different structures. They are very important in air pollution chemistry, because even slightly different structures can evoke dramatic differences in chemical and physical properties. So, isomers may exhibit different chemodynamic behavior and different toxicities. For example, the three isomers of pentane (C_5H_{12}) are shown in Fig. 7.14. The difference in structure accounts for significant physical differences. For example, the boiling points for *n*-pentane, isopentane, and neopentane at 1 atm are 36.1°C, 27.8°C, and 9.5°C, respectively. Thus, neopentane's lower boiling point means that this isomer has a lower vapor pressure, which makes it is more likely to enter the atmosphere than the other two isomers under the same environmental conditions.

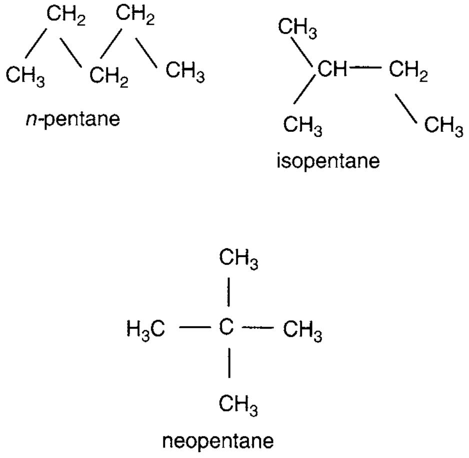

Fig. 7.14. Isomers of pentane. Although the chemical composition is identical, the different molecular arrangements result in molecules that exhibit very dissimilar physical, chemical, and biological properties. *Source*: Vallero, D., *Environmental Contaminants: Assessment and Control.* Academic Press, Burlington, MA, 2004.

Optical isomers or chiral forms of the same compound are those that are mirror images to each other. These difference may make one, e.g. the left-handed form, virtually nontoxic and easily biodegradable, yet the right-handed form may be toxic and persistent.

VI. INTRODUCTION TO ATMOSPHERIC CHEMISTRY

Atmospheric chemistry encompasses all of the chemical transformations occurring in the various atmospheric layers from the troposphere to beyond the stratosphere. Air pollution chemistry represents the subset of these atmospheric chemical processes which have a direct impact on human beings, vegetation, and surface water bodies. Classification of atmospheric chemical processes as either human made (anthropogenic) or natural is useful but not precise. For example, the trace gases nitric oxide (NO) and sulfur dioxide (SO_2) have both anthropogenic and natural sources, and their atmospheric behavior is independent of their source. A vivid example was the 1980 Mt. St. Helen's volcanic eruption in Washington, a gigantic point source for SO_2 and PM in the atmosphere. This natural source was of such magnitude as to become first a regional air pollution problem and subsequently a global atmospheric chemical problem.

A. Types of Atmospheric Chemical Transformations

The chemical transformations occurring in the atmosphere are best characterized as oxidation processes. Reactions involving compounds of carbon (C), nitrogen (N), and sulfur (S) are of most interest. The chemical processes in the troposphere involve oxidation of hydrocarbons, NO, and SO_2 to form oxygenated products such as aldehydes, nitrogen dioxide (NO_2), and sulfuric acid (H_2SO_4). These oxygenated species become the secondary products formed in the atmosphere from the primary emissions of anthropogenic or natural sources (Fig. 7.15).

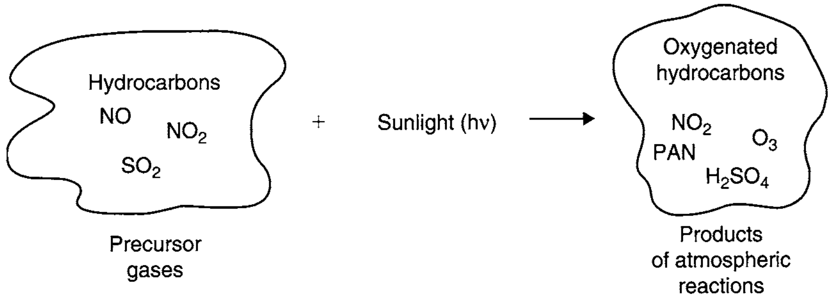

Fig. 7.15. Precursor-product relationship of atmospheric chemical reactions.

Solar radiation influences the chemical processes in the atmosphere by interacting with molecules that act as photoacceptors. Free radicals are formed by the photodissociation of certain types of molecules. Free radicals are neutral fragments of stable molecules and are very reactive. Examples are O, atomic oxygen; H, atomic hydrogen; OH, the hydroxyl radical; and HO_2, the hydroperoxy radical. In areas with photochemical smog, the principal photoacceptors are aldehydes, NO_2, nitrous acid (HNO_2), and ozone. The photodissociation process is energy dependent, and only photons with sufficient energy are capable of causing photodissociation. The wavelength dependence of solar radiation is discussed in Chapter 5.

The reactivity of chemical compounds will differ because of their structure and molecular weight. Hydrocarbon compounds have been ranked according to their rate of reaction with various types of oxidizing species such as OH, NO_3, and O_3.[17] The role of hydrocarbons, along with oxides of nitrogen, in the formation of ozone is very complex. Ozone formation is a function of the mixture of hydrocarbons present and the concentration of NO_x, $[NO_x]$ ($= [NO] + [NO_2]$). The concept of an incremental reactivity scale permits accessing the increment of ozone formation per incremental change in a single hydrocarbon component.[18] Incremental reactivity is determined by calculating the ozone formation potential in a baseline scenario using a simple mixture of hydrocarbons representing an urban atmosphere. Then for each hydrocarbon species of interest, the ozone formation is recalculated with incremental hydrocarbons added to the mixture. From this approach, the $\Delta[O_3]/\Delta[HC]$ values represent the impact of a specific hydrocarbon on urban photochemical smog formation.

The vapor pressure of a compound is important in determining the upper limit of its concentration in the atmosphere. High vapor pressures will permit higher concentrations than low vapor pressures. Examples of organic compounds are methane and benzo[*a*]pyrene. Methane, with a relatively high vapor pressure, is always present as a gas in the atmosphere; in contrast, benzo[*a*]pyrene, with a relatively low vapor pressure, is adsorbed on PM and is therefore not present as a gas. Vapor pressure also affects the rate of evaporation of organic compounds into the atmosphere and the conversion of atmospheric gases to PM, e.g. SO_2 to the aerosol H_2SO_4.[19]

Atmospheric chemical reactions are classified as either photochemical or thermal. Photochemical reactions are the interactions of photons with species which result in the formation of products. These products may undergo

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[17] Pitts Jr., J. N., Winer, A. M., Darnall, K. R., Lloyd, A. C., and Doyle, G. J., in *Proceedings of the International Conference on Photochemical Oxidant Pollution and Its Control*, Vol. II (Dimitriades, B., ed.), EPA-600/3-77-OOlb, pp. 687–707. US Environmental Protection Agency, Research Triangle Park, NC, 1977.

[18] Carter, W. P. L., *Development of Ozone Reactivity Scales for Volatile Organic Compounds*, EPA 600/3-91-050. US Environmental Protection Agency, August 1991.

[19] National Research Council, *Ozone and Other Photochemical Oxidants*. National Academy of Sciences, Washington, DC, 1977.

further chemical reaction. These subsequent chemical reactions are called *thermal* or *dark* reactions.

Finally, atmospheric chemical transformations are classified in terms of whether they occur as a gas (homogeneous), on a surface, or in a liquid droplet (heterogeneous). An example of the last is the oxidation of dissolved sulfur dioxide in a liquid droplet. Thus, chemical transformations can occur in the gas phase, forming secondary products such as NO_2 and O_3; in the liquid phase, such as SO_2 oxidation in liquid droplets or water films; and as gas-to-particle conversion, in which the oxidized product condenses to form an aerosol.

B. Role of Solar Radiation in Atmospheric Chemistry

The time required for atmospheric chemical processes to occur is dependent on chemical kinetics. Many of the air quality problems of major metropolitan areas can develop in just a few days. Most gas-phase chemical reactions in the atmosphere involve the collision of two or three molecules, with subsequent rearrangement of their chemical bonds to form molecules by combination of their atoms. Consider the simple case of a bimolecular reaction of the following type:

$$\mathrm{B} + \mathrm{C} \rightarrow \text{products} \tag{7.44}$$

$$\text{Rate of reaction} = k[\mathrm{B}][\mathrm{C}] \tag{7.45}$$

where $k = A \exp[-E_a/RT]$ and k, the rate constant, is dependent on the frequency factor (A), the temperature (T), the activation energy of the reaction (E_a) and the ideal gas constant (R). The frequency factor, A, is of the same order of magnitude for most gas reactions. For $T = 298\,\mathrm{K}$ the rate of reaction is strongly dependent on the activation energy E_a as shown in Table 7.11.[20] When E_a is $>30\,\mathrm{kJ/mol}$ the rates become very small, limiting the overall rate of reaction. Table 7.12 contains the activation energies for bimolecular collisions of different

TABLE 7.11

Values of exp ($-E_a/RT$) as a Function of the Activation Energy for $T = 298$ K[a]

E_a	$\exp(-E_a/RT)$
1.0	0.67
3.0	0.30
10.0	0.0177
30.0	5.51×10^{-6}
100.0	2.95×10^{-18}
300.0	2.56×10^{-53}

[a] In SI units, $R = 8.31434\,\mathrm{kJ^{-1}mol^{-1}}$.

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[20] Campbell, I. M., *Energy and the Atmosphere*. Wiley, New York, 1977.

TABLE 7.12

Activation Energies for Atmospheric Reactions

Reaction	E_a (kJ mol^{-1})
$N_2 + O_2 \rightarrow N_2O + O$	538
$CO + O_2 \rightarrow CO_2 + O$	251
$SO_2 + NO_2 \rightarrow SO_3 + NO$	106
$O + H_2S \rightarrow OH + HS$	6.3
$O + NO_2 \rightarrow NO + O_2$	<1
$HO_2 + NO \rightarrow NO_2 + OH$	<1

Source: Campbell, I. M., *Energy and the Atmosphere*, pp. 212–213. Wiley, New York, 1977.

TABLE 7.13

Hydrocarbon Compounds Identified in Ambient Air Samples from St. Petersburg, Florida

Acetaldehyde
Acetylene
1,3-Butadiene
n-Butane
trans-2-Butene
Cyclopentane
n-Decane
2,3-Dimethylpentane
Ethane
Ethylbenzene
Ethylene
m-Ethyltoluene
o-Ethyltoluene
p-Ethyltoluene
n-Heptane
Isobutane
Isobutylene
Isopentane
Isopropyl benzene
Limonene
Methane
2-Methyl-1-butene
Methylcyclohexane
3-Methylhexane
2-Methylpentane
Nonane
n-Pentane
1-Pentene
cis-2-Pentene
trans-2-Pentene
alpha-Pinene
beta-Pinene
Propane
Propene
n-Propylbenzene
Toluene
2,2,4 Trimethylpentane
m-Xylene
o-Xylene
p-Xylene
1,2,4-rimethylbenzene
1,3,5-rimethylbenzene

Source: Lonneman, W. A., Seila, R. L., and Bufalini, J. J. *Environ. Sci. Technol.* **12**, 459–463 (1978).

molecular species. For the first three reactions between molecular species, E_a is >100 kJ, but for the last three reactions $E_a < 10$ kJ. The last three reactions involve the participation of free radical or atomic species. The activation energies of reactions involving atomic or free radicals are very small, permitting chemical transformations on a short timescale.

C. Gas-Phase Chemical Reaction Pathways

The complexity of the atmospheric chemical reactions occurring in major metropolitan areas can be staggering. Urban atmospheres are characterized as complex mixtures of hydrocarbons and oxides of sulfur and nitrogen. Table 7.13 show the hydrocarbons identified in the urban air of St. Petersburg, Florida.[21] The interactions among this large number of compounds can be understood by studying simpler systems. Figure 7.16 shows

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[21] Lonneman, W. A., Seila, R. L., and Bufalini, J. J. *Environ. Sci. Technol.* **12**, 459–463 (1978).

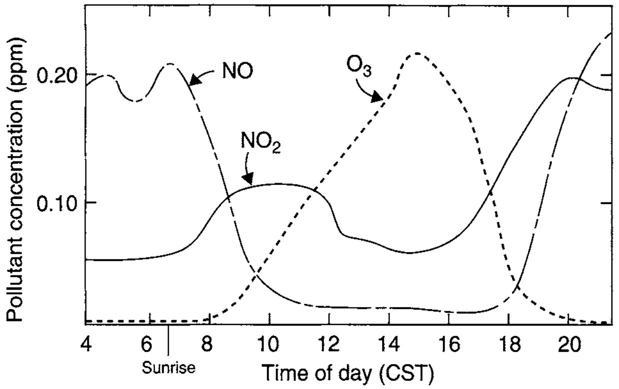

Fig. 7.16. NO–NO_2–O_3 ambient concentration profiles from average of four Regional Air Monitoring Stations (RAPS) in downtown St. Louis, Missouri (USA) on October 1, 1976. *Source*: RAPS, Data obtained from the 1976 data file for the Regional Air Pollution Study Program. US Environmental Protection Agency, Research Triangle Park, NC, 1976.

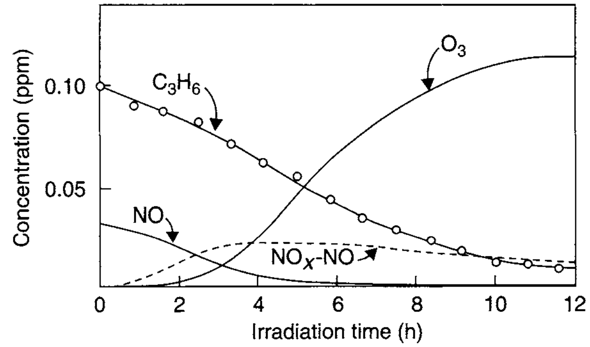

Fig. 7.17. Concentration versus time profiles of propene, NO, NO_x-NO, and O_3 from smog chamber irradiation; $k_1 = 0.16\ \text{min}^{-1}$. *Source*: Akimoto, H., Sakamaki, F., Hoshino, M., Inoue, G., and Oduda, M., *Environ. Sci. Technol.* **13**, 53–58 (1979).

the diurnal patterns of NO, NO_2, and O_3 for St. Louis, Missouri.[22] These diurnal patterns are interrelated. The concentration profiles of Fig. 7.16 are the result of a combination of atmospheric chemical and meteorological processes. To uncouple this combination of factors, laboratory (smog chamber) studies such as those of the propene-NO_x system (Fig. 7.17) have been undertaken.[23] These profiles show chemical transformations separated from meteorological processes.

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[22] Data obtained from the 1976 data file of the Regional Air Pollution Study Program. US Environmental Protection Agency, Research Triangle Park, NC, 1976.

[23] Akimoto, H., Sakamaki, F., Hoshino, M., Inoue, G., and Oduda, M. *Environ. Sci. Technol.* **13**, 53–58 (1979).

Similar chemical steps occur in the ambient air and in laboratory smog chamber simulations. Initially, hydrocarbons and nitric oxide are oxidized to form nitrogen dioxide, ozone, and other oxidation products such as peroxyacyl nitrate (PAN) and aldehydes. The complete process is very complicated, with many reaction steps.

The principal components of atmospheric chemical processes are hydrocarbons, oxides of nitrogen, oxides of sulfur, oxygenated hydrocarbons, ozone, and free radical intermediates. Solar radiation plays a crucial role in the generation of free radicals, whereas water vapor and temperature can influence particular chemical pathways. Table 7.14 lists a few of the components of each of these classes. Although more extensive tabulations may be found in *Atmospheric Chemical Compounds*,[24] those listed in Table 7.14 are sufficient for an understanding of smog chemistry. The major undesirable

TABLE 7.14

Classes and Examples of Atmospheric Compounds

- Hydrocarbons
  - Alkenes
    - Ethene C_2H_4
    - Propene C_3H_6
    - *trans*-2-Butene
  - Alkanes
    - Methane CH_4
    - Ethane C_2H_6
  - Alkynes
    - Acetylene C_2H_2
  - Aromatics
    - Toluene C_6H_6
    - *m*-Xylene C_6H_{10}
- Oxides of nitrogen
  - Nitric oxide NO
  - Nitrogen dioxide NO_2
  - Nitrous acid HNO_2
  - Nitric acid HNO_3
  - Nitrogen trioxide NO_3
  - Dinitrogen pentoxide N_2O_5
  - Ammonium nitrate NH_4NO_3
- Free radicals
  - Atomic oxygen O
  - Atomic hydrogen H
  - Hydroxyl OH
  - Hydroperoxyl HO_2
  - Acyl RCO
  - Peroxyacyl $RCOO_2$
- Oxygenated hydrocarbons
  - Aldehydes
    - Formaldehyde HCHO
    - Acetylaldehyde CH_3CHO
    - Other aldehydes RCHO
  - Acids
    - Formic acid HCOOH
    - Acetic acid CH_3COOH
  - Alcohols
    - Methanol CH_3OH
- Oxides of sulfur
  - Sulfur dioxide SO_2
  - Sulfur trioxide SO_3
  - Sulfuric acid H_2SO_4
  - Ammonium bisulfate $(NH_4)HSO_4$
  - Ammonium sulfate $(NH_4)_2SO_4$
- Oxidants
  - PAN $CH_3COO_2NO_2$
  - Ozone O_3

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[24] Graedel, T. E., Hawkins, D. T., and Claxton, L. D., *Atmospheric Chemical Compounds: Sources, Occurrence, and Bioassay*. Academic Press, Orlando, FL, 1986.

components of photochemical smog are NO_2, O_3, SO_2, H_2SO_4, PAN, and aldehydes. Air quality standards have been established in several countries for SO_2, NO_2, and O_3; H_2SO_4 contributes to acidic deposition and reduction in visibility; and PAN and aldehydes can cause eye irritation and plant damage if their concentrations are sufficiently high.

1. *Photoabsorption of Solar Radiation*

Solar radiation initiates the formation of free radicals. According to the elementary quantum theory of atoms and molecules, the internal energy of molecules is composed of electronic energy states. Molecules interact with solar radiation by absorbing photons. This absorption process causes the molecule to undergo a transition from the ground electronic state to an excited state. The change in energy between the two states corresponds to a quantum or photon of solar radiation. The frequencies v of absorption are expressed by Planck's law:

$$E = hv = hc/\lambda \tag{7.46}$$

where h is Planck's constant, c is the speed of light, and v and λ are the frequency and wavelength of the light of the photon, respectively. The spectrum of solar radiation in the lower troposphere starts at ~295 nm and increases. Photons of shorter wavelength and higher energy are absorbed in the upper atmosphere and therefore do not reach the lower troposphere.

Molecules and atoms interact with photons of solar radiation under certain conditions to absorb photons of light of various wavelengths. Figure 14.4 shows the absorption spectrum of NO_2 as a function of the wavelength of light from 240 to 500 nm. This molecule absorbs solar radiation from 295 nm through the visible region. The absorption of photons at these different wavelengths causes the NO_2 molecule to enter an excited state. For longer wavelengths, transitions only in the rotational–vibrational states occur, whereas for shorter wavelengths changes in electronic states may occur. The process of photoabsorption for NO_2 is expressed as

$$NO_2 + hv \rightarrow NO_2^* \tag{7.47}$$

where hv represents the photon of solar radiation of energy and NO_2^* is the NO_2 molecule in the excited state. The excited NO_2 molecule can follow several pathways:

Fluorescence $$NO_2^* \rightarrow NO_2 + hv \tag{7.48}$$

Collisional deactivation where X_2 is

N_2 or O_2 $$NO_2^* + X_2 \rightarrow NO_2 + X_2 \tag{7.49}$$

Direct reaction $$NO_2^* + O_2 \rightarrow NO_3 + O \tag{7.50}$$

Photodissociation $$NO_2^* \rightarrow NO + O \tag{7.51}$$

In the case of NO_2, for each photon absorbed below 400 nm, photodissociation occurs. For other photoabsorbers, HNO_2 and aldehydes, the photodissociation process leads to the formation of free radicals.

2. *Nitric Oxide, Nitrogen Dioxide, and Ozone Cycles*

Three relatively simple reactions can describe the interrelationships among these components.

$$NO_2 + h\nu \rightarrow NO + O \tag{7.52}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{7.53}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{7.54}$$

Equation (7.52) shows the photochemical dissociation of NO_2. Equation (7.53) shows the formation of ozone from the combination of O and molecular O_2 where M is any third-body molecule (principally N_2 and O_2 in the atmosphere). Equation (7.54) shows the oxidation of NO by O_3 to form NO_2 and molecular oxygen. These three reactions represent a cyclic pathway (Fig. 7.18) driven by photons represented by $h\nu$. Throughout the daytime period, the flux of solar radiation changes with the movement of the sun. However, over short-time periods (~10 min) the flux may be considered constant, in which case the rate of Eq. (7.52) may be expressed as

$$\text{Rate} = k_1[NO_2] \tag{7.55}$$

where k_1 is a function of time of day. Expressions for the time rate of change for each of the components may be written. If this cycle reaches a steady state, the change in concentration with time no longer occurs, so that d[conc]/dt is equal to zero.

$$d[NO]/dt = -k_1[NO_2] + k_3[NO][O_3] \tag{7.56}$$

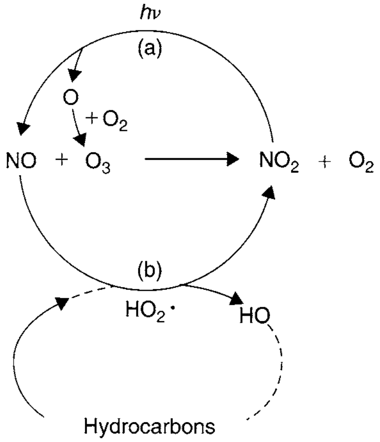

Fig. 7.18. Photochemical cycle of NO, NO_2, O_3, and free radicals.

$$d[O]/dt = k_1[NO_2] - k_2[O][O_2][M] \tag{7.57}$$

$$d[O_3]/dt = k_2[O][O_2][M] - k_3[NO][O_3] \tag{7.58}$$

From Eq. (7.56), it is possible to obtain an expression for the relationship of NO, NO_2, and O_3:

$$d[NO]/dt = O; \quad k_1[NO_2] = k_3[NO][O_3] \tag{7.59}$$

$$[O_3] = k_1[NO_2]/k_3[NO] \tag{7.60}$$

Equation (7.60) is called the *photostationary state expression* for ozone. Upon examination, one sees that the concentration of ozone is dependent on the ratio NO_2/NO for any value of k_1. The maximum value of k_1 is dependent on the latitude, time of year, and time of day. In the United States, the range of k_1 is from 0 to 0.55 min^{-1}. Table 7.15 illustrates the importance of the NO_2/NO ratio with respect to how much ozone is required for the photostationary state to exist. The conclusion to be drawn from this table is that most of the NO must be converted to NO_2 before O_3 will build up in the atmosphere. This is also seen in the diurnal ambient air patterns shown in Fig. 7.15 and the smog chamber simulations shown in Fig. 7.16. It is apparent that without hydrocarbons, the NO is not converted to NO_2 efficiently enough to permit the buildup of O_3 to levels observed in urban areas.

The cycle represented by Eqs. (7.52–7.54) is illustrated by the upper loop (a) in Fig. 7.17. In this figure, the photolysis of NO_2 by a photon forms an NO and an O_3 molecule. If no other chemical reaction is occurring, these two species react to form NO_2, which can start the cycle over again. In order for the O_3 concentration to build up, oxidizers other than O_3 must participate in the oxidation of NO to form NO_2. This will permit the NO_2/NO ratio to build up and steady-state O_3 concentrations as represented by Eq. (7.60) to achieve typical ambient values. The other oxidizers in the atmosphere are free radicals. In the lower loop (b) of Fig. 7.17, a second pathway for NO oxidation is shown, with free radicals participating. These free radicals are derived from the participation of hydrocarbons in atmospheric chemical reactions.

TABLE 7.15

$[O_3]$ Predicted from Photostationary State Approximation as a Function of Initial $[NO_2]$[a]

$[NO_2]$ (ppm)	$[NO_2]_{final}$ (ppm)	$[O_3]_{final}$ (ppm)	$[NO_2]/[NO]$
0.1	0.064	0.036	1.78
0.2	0.145	0.055	2.64
0.3	0.231	0.069	3.35
0.4	0.319	0.081	3.94
0.5	0.408	0.092	4.43

[a] $k_1 = 0.5\ min^{-1}$; $k_3 = 24.2\ ppm^{-1}min^{-1}$.

3. *Role of Hydrocarbons*

The important hydrocarbon classes are alkanes, alkenes, aromatics, and oxygenates. The first three classes are generally released to the atmosphere, whereas the fourth class, the oxygenates, is generally formed in the atmosphere. Propene will be used to illustrate the types of reactions that take place with alkenes. Propene reactions are initiated by a chemical reaction of OH or O_3 with the carbon–carbon double bond. The chemical steps that follow result in the formation of free radicals of several different types which can undergo reaction with O_2, NO, SO_2, and NO_2 to promote the formation of photochemical smog products.

Ozone Reaction with Propene A schematic diagram of the O_3 reaction with propene (Fig. 7.19) is based on the work of Atkinson and Lloyd.[25] The molozonide formed by addition of ozone to the double bond decomposes to form an aldehyde and an energy-rich (‡) biradical. In the case of propene, two sets of products are formed. Along the pathway on the right, approximately 40% of the biradicals $(H\dot{C}HOO\cdot)^{\ddagger}$ form a thermalized biradical $(\dot{C}H_2OO\cdot)$.* (*The dots represent unpaired electrons.) The remainder undergo rearrangement to form

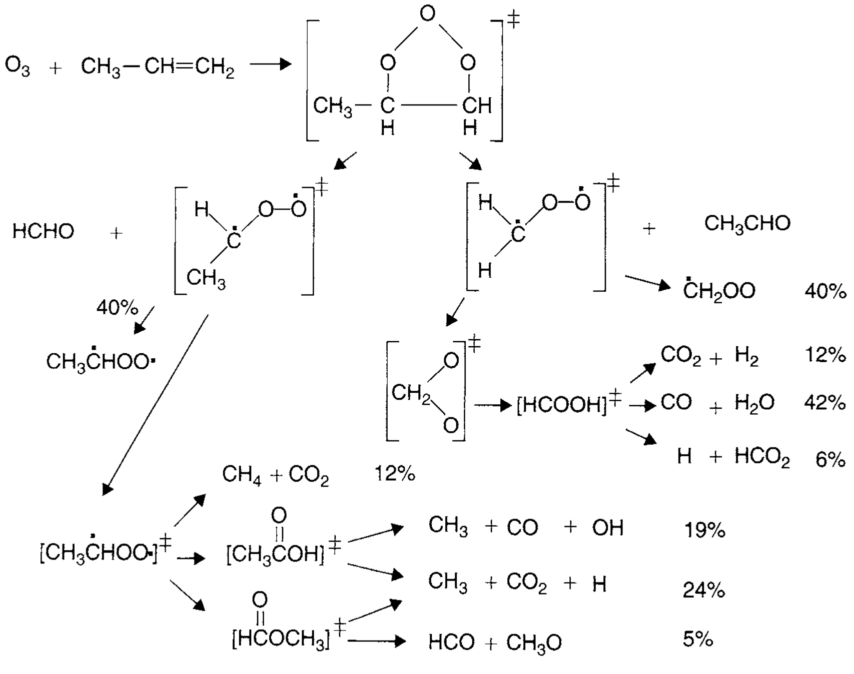

Fig. 7.19. Ozone–propene reaction pathways showing oxidation products.

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[25] Atkinson, R., and Lloyd, A. C. *J. Phys. Chem. Ref. Data* **13**, 315–444 (1984).

energy-rich acetic acid (HCOOH)‡, which subsequently decomposes to form H_2O, CO, CO_2, H_2, H, and HCO_2 radicals with percentages assigned to each pathway. The larger biradical ($CH_3\dot{C}HOO\cdot$)‡ follows a slightly different pathway. Approximately 40% forms a thermalized biradical ($CH_3\dot{C}HOO\cdot$). Of the remaining 60%, a portion decomposes to CH_4 and CO_2 and two additional energy-rich species (CH_3COOH)‡ and ($CHOOCH_3$)‡. These two unstable species decompose as shown to form CH_3, OH, H, HCO, CH_3O, CO, and CO_2.

Alkyl radicals, R, react very rapidly with O_2 to form alkylperoxy radicals. H reacts to form the hydroperoxy radical HO_2. Alkoxy radicals, RO, react with O_2 to form HO_2 and R′CHO, where R′ contains one less carbon. This formation of an aldehyde from an alkoxy radical ultimately leads to the process of hydrocarbon chain shortening or clipping upon subsequent reaction of the aldehyde. This aldehyde can undergo photodecomposition forming R, H, and CO; or, after OH attack, forming CH(O)OO, the peroxyacyl radical.

Hydroxyl Radical Addition to Propene As shown in Fig. 7.20, hydroxyl radicals primarily add to either of the carbon atoms which form the double bond. The remaining carbon atom has an unpaired electron which combines with molecular oxygen, forming an RO_2 radical. There are two types of RO_2 radicals labeled C_3OHO_2 in Fig. 7.20. Each of these RO_2 radicals reacts with NO to form NO_2, and an alkoxy radical reacts with O_2 to form formaldehyde, acetaldehyde, and HO_2.

Aldehyde Photolysis and Reactions Aldehydes undergo two primary reactions: photolysis and reaction with OH radicals. These reactions lead to formation of CO, H, and R radicals.

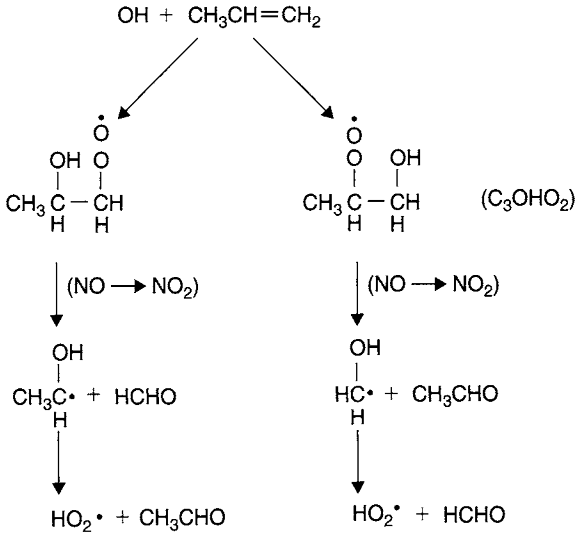

Fig. 7.20. OH–propene reaction pathways showing oxidation products.

Radical Reactions with Nitric Oxide and Nitrogen Dioxide Alkylperoxy (RO_2) and peroxyacyl (RC(O)OO) radicals react with NO to form NO_2. The alkylperoxy radicals (RO_2) react with NO_2 to form pernitric acid-type compounds, which decompose thermally as the temperature increases. The peroxyacyl radical reacts with NO_2 to form PAN-type compounds, which also decompose thermally.

Radical Oxidation of Sulfur Dioxide Sulfur dioxide is oxidized in the atmosphere eventually to form sulfate compounds. The oxidation process includes both homogeneous and heterogeneous pathways. The free radicals produced from the degradation of hydrocarbons can and do react with SO_2 in the gas phase. Both OH and HO_2 oxidize SO_2 to reactive intermediates such as HSO_3 and SO_3.[26] These intermediates combine rapidly with water vapor in the atmosphere to form sulfuric acid aerosol. This type of process is dependent on atmospheric conditions. In urban areas with existing photochemical smog problems, the homogeneous oxidation of SO_2 by free radicals is probably dominant during the daytime.

VII. HETEROGENEOUS REACTIONS

Heterogeneous reactions are defined as those involving the gas–liquid or gas–solid phases. The chemistry of NO_2 and SO_2 has a heterogeneous component in the atmosphere. Heterogeneous reactions involve the dissolving of NO_2 and SO_2 in water droplets, with subsequent chemical reactions occurring to form HNO_3 and H_2SO_4 in the liquid phase. The heterogeneous oxidation of SO_2 in liquid droplets and water films is also a major pathway for conversion to sulfate in wet plumes and during humid or foggy conditions.

VIII. SCAVENGING AND REMOVAL FROM THE ATMOSPHERE

The atmosphere is a dynamic system, with gases and PM entering, undergoing transformation, and leaving. Atmospheric chemical processes of oxidation transform gases into more highly oxidized products, e.g., NO to NO_2 to HNO_3, hydrocarbons to aldehydes, and SO_2 to sulfate particles. The removal of material from the atmosphere involves two processes: wet and dry deposition. The water solubility of gases influences the extent of removal by wet versus dry deposition. Gases such as SO_2 and NO_2 are sufficiently soluble to dissolve in water associated with in-cloud formation of rain droplets. These soluble gases may be removed by wet deposition of liquid droplets in the form of rain or fog. Less soluble gases such as O_3 and hydrocarbon vapors are removed by transport to the surface of the earth, where they diffuse to vegetation, materials, or water bodies (see Chapter 14).

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[26] Calvert, J. G., Su, F., Bottenheim, J. W., and Strausz, O. P. *Atmos. Environ.* **12**, 197–226 (1978).

REFERENCES

1. US Geological Survey, *Radiogenic Isotopes and the Eastern Mineral Resources Program of the US Geological Survey*, 2003.
2. US Geological Survey, *Short-Lived Isotopic Chronometers: A Means of Measuring Decadal Sedimentary Dynamics*, FS-073-98, 2003.
3. Lewis, C., Klouda, G., and Ellenson, W., *Cars or Trees: Which Contribute More to Particulate Matter Air Pollution?* US Environmental Protection Agency, Science Forum, Washington, DC, 2003.
4. National Bureau of Standards, *Oxalic Acid Standard Reference Method*, SRM 4990B.
5. Stieglitz, L., Zwick, G., Beck, J., Bautz, H., and Roth, W., *Chemosphere* **19**, 283 (1989).
6. Koester, C. J., and Hites, R. A., Wet and dry deposition of chlorinated dioxins and furans, *Environ. Sci. Technol.* **26**, 1375–1382 (1992); and Hites, R. A., Atmospheric transport and deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans, EPA/600/3-91/002. Research Triangle Park, NC, 1991.
7. Evangelou, V., *Environmental Soil and Water Chemistry: Principles and Applications*. John Wiley & Sons, New York, 1998.
8. US Army Corps of Engineers, *Engineering and Design: Precipitation/Coagulation/Flocculation*, Chapter 2, EM 1110-1-4012, 2001.
9. Spencer, J., Bodner, G., and Rickard, L., *Chemistry: Structure and Dynamics*, 2nd ed. John Wiley & Sons, New York, 2003.
10. Casparian, A., Chemistry, in *How to Prepare for the Fundamentals of Engineering (FE/EIT) Exam* (Olia, M., ed.). Barron's Educational Series, Inc., Hauppauge, NY, 2000.
11. Hemond, H. F., and Fechner-Levy, E. J., *Chemical Fate and Transport in the Environment*. Academic Press, San Diego, CA, 2000.
12. US Environmental Protection Agency, *Dermal Exposure Assessment: Principles and Applications*. Interim Report, EPA/600/8-91/011B, Washington, DC, 1992.
13. Knox, R., Sabatini, D., and Canter, L., *Subsurface Transport and Fate Processes*. Lewis Publishers, Boca Raton, FL, 1993.
14. US Environmental Protection Agency, *Summary Report: Control and Treatment Technology for the Metal Finishing Industry; Sulfide Precipitation*. Report No. EPA 625/8-80-003, Washington, DC, 1980.
15. Vallero, D., *Engineering the Risks of Hazardous Wastes*. Butterworth-Heinemann, Boston, MA, 2003.
16. Vallero, D., *Environmental Contaminants: Assessment and Control*. Academic Press, Burlington, MA, 2004.
17. Pitts Jr., J. N., Winer, A. M., Darnall, K. R., Lloyd, A. C., and Doyle, G. J., in *Proceedings of the International Conference on Photochemical Oxidant Pollution and Its Control*, Vol. II (Dimitriades, B., ed.), EPA-600/3-77-OOlb, pp. 687–707. US Environmental Protection Agency, Research Triangle Park, NC, 1977.
18. Carter, W. P. L., *Development of Ozone Reactivity Scales for Volatile Organic Compounds*, EPA 600/3-91-050. US Environmental Protection Agency, August 1991.
19. National Research Council, *Ozone and Other Photochemical Oxidants*. National Academy of Sciences, Washington, DC, 1977.
20. Campbell, I. M., *Energy and the Atmosphere*. Wiley, New York, 1977.
21. Lonneman, W. A., Seila, R. L., and Bufalini, J. J. *Environ. Sci. Technol.* **12**, 459–463 (1978).
22. Data obtained from the 1976 data file of the Regional Air Pollution Study Program. US Environmental Protection Agency, Research Triangle Park, NC, 1976.
23. Akimoto, H., Sakamaki, F., Hoshino, M., Inoue, G., and Oduda, M. *Environ. Sci. Technol.* **13**, 53–58 (1979).

24. Graedel, T. E., Hawkins, D. T., and Claxton, L. D., *Atmospheric Chemical Compounds: Sources, Occurrence, and Bioassay*. Academic Press, Orlando, FL, 1986.
25. Atkinson, R., and Lloyd, A. C. *J. Phys. Chem. Ref. Data* **13**, 315–444 (1984).
26. Calvert, J. G., Su, F., Bottenheim, J. W., and Strausz, O. P. *Atmos. Environ.* **12**, 197–226 (1978).

SUGGESTED READING

National Research Council, *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. National Academy Press, Washington, DC, 1991.

Sloane, C. S., and Tesche, T. W., *Atmospheric Chemistry: Models and Predictions for Climate and Air Quality*. Lewis Publishers, Chelsea, MI, 1991.

Warneck, P., *Chemistry of the Natural Atmosphere*. Academic Press, San Diego, CA, 1988.

QUESTIONS

1. What adjustments would have to be made if a non-conservative tracer were used to characterize a plume? Why might such a tracer need to be used instead of a conservative tracer?
2. Review the following table with data from a southeaster US city. What is the contribution of non-fossil-fuel sources to particulate-laden carbon during the summer? Why are concurrent measurements of OC/EC ratios important to characterizing biogenic secondary organic aerosols (SOA), especially as an indicator of biogenic sources (i.e. from other than human activities) being a significant non-fossil-fuel contributor? Identify and describe confounders (e.g. dates) that should be explained (Table 7.16).

TABLE 7.16

Air Mass Origin, $PM_{2.5}$ Total Carbon Concentration, Organic to Elemental Carbon Ratio (OC/EC), and Percent Modern Carbon (pMC), and Biogenic Percentage for Total Carbon (Bio TC)

Start date 1999	Start time (h)	Duration (h)	Air mass origin	TC[a] ($\mu g\,m^{-3}$)	OC/EC[b]	pMC_{TC}[b,c] (%)	Bio TC[b,d] (%)
June 21	1900	11.5	ENE	8.2	12.6 ± 1.9	75 ± 1	69 ± 1
June 22	0700	11.5	S	8.0	15.5 ± 2.7	66 ± 1	61 ± 1
June 28	0700	10.5	SW	2.9	10.3 ± 3.0	66 ± 2	61 ± 2
June 29	0700	11.5	NW	3.2	15.8 ± 5.6	80 ± 2	73 ± 2
June 29	1900	11.5	NW	4.3	5.4 ± 0.8	56 ± 1	51 ± 1
July 1	0700	5.5	S	3.9	10.2 ± 4.0	68 ± 3	62 ± 3
July 1	1250	5.7	S	3.9	29.2 ± 27.3[e]	67 ± 3	61 ± 3
July 1	1900	11.5	SSW	2.8	9.9 ± 2.7	75 ± 2	69 ± 2
July 4	1900	11.5	S	7.6	3.6 ± 0.4	64 ± 1	59 ± 1
						66 ± 1[f]	61 ± 1[f]
July 5	0700	5.5	S	7.7	11.8 ± 2.1	63 ± 1	58 ± 1
July 5	1300	5.5	S	7.9	13.1 ± 3.5	64 ± 1	59 ± 1
July 6	1900	11.5	WNW	4.6	5.7 ± 0.8	65 ± 1	60 ± 1
July 7	0700	11.5	N	5.6	14.0 ± 2.9	66 ± 1	61 ± 1
July 8	1900	11.5	S	5.0	8.4 ± 1.4	70 ± 1	64 ± 1

(*continued*)

TABLE 7.16 (*Continued*)

Start date 1999	Start time (h)	Duration (h)	Air mass origin	TC[a] ($\mu g\,m^{-3}$)	OC/EC[b]	pMC_{TC}[b,c] (%)	Bio TC[b,d] (%)
July 9	0700	11.5	SW	4.8	17.5 ± 4.8	78 ± 1	72 ± 1
July 10	1900	11.5	N	3.8	11.2 ± 2.7	75 ± 1	69 ± 1
July 11	0700	5.5	NE	3.5	7.1 ± 2.3	70 ± 3	64 ± 3
July 11	1300	5.5	NE	4.1	7.1 ± 2.3	78 ± 3	72 ± 3
July 12	1900	11.5	NNE	5.7	15.0 ± 2.2	79 ± 1	72 ± 1
July 13	0700	5.5	N	3.6	7.9 ± 2.8	65 ± 3	60 ± 3
July 13	1300	5.5	NNW	4.1	15.1 ± 7.7	67 ± 2	61 ± 2

Source: Lewis, C. W., Klouda, G. A., and Ellenson, W. D., Radiocarbon measurement of the biogenic contribution to summertime $PM_{2.5}$ ambient aerosol in Nashville, TN. *Atmos. Environ.* **39**(35), 6053–6061.

[a] Estimated uncertainty, ±15%.

[b] Uncertainty calculated by usual error propagation using the standard deviations of the measured value and the blank used to correct the measured value.

[c] Corrected for TC composite ($n = 3$) filter blank: pMC = 43 ± 1, concentration = 1.7 ± 0.2 $\mu g\,TC\,cm^{-2}$.

3. Consider a combustion reaction other than the ones described in this chapter and explain how products of incomplete combustion may form.
4. Consider an acid–base reaction other than those described in this chapter and explain how an air toxic may form in a water droplet.
5. What wavelength band of solar radiation leads to photodissociation for nitrogen dioxide? What determines the lower limit?
6. Equation (7.60) describes the steady-state $[O_3]$ in the presence of solar radiation. If $k_1 = 0.3\ \text{min}^{-1}$ and $k_3 = 30\ \text{ppm}^{-1}\text{min}^{-1}$, which sets of conditions given in the table below are consistent with $[O_3] = 0.1$ ppm?

[NO] (ppm)	$[NO_2]$ (ppm)
0.005	0.050
0.125	0.125
0.047	0.47
0.47	0.047
0.001	0.010

7. What does the answer to question 6 indicate about the functional dependence of ozone concentrations on the absolute magnitude of $[NO_x] = [NO] + [NO_2]$?
8. How are free radicals formed, and why are they so reactive?
9. From Fig. 7.19, how many molecules of NO can be oxidized to NO_2 by the reaction of one OH free radical with one propene molecule?
10. List various classification approaches used to account for hydrocarbon reactivity.
11. Classify the compounds in Table 7.15 into precursors (reactants) and products of atmospheric reaction processes.
12. List two photoacceptors in addition to nitrogen dioxide that provide an initial source of free radicals.
13. Describe the role of hydrocarbons in photochemical oxidant formation.
14. What are the molar concentrations of $[H^+]$ and $[OH^-]$ of rainwater at pH 3.7 at 25°C?