

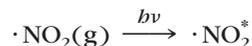
EXERCISE 10.17 Errors Caused by Deviations from Ideal Gas Behavior

In Problem-Solving Example 10.10 (p. 453), the molar mass calculated using the ideal gas law was slightly larger than that calculated using atomic weights. This means that the number of moles, n , must have been too small. Look at the Strategy and Explanation for Problem-Solving Example 10.10 and explain why the number of moles is less than it should be.

10.10 Chemical Reactions in the Atmosphere

Molecules in the atmosphere are continually moving and colliding with one another, as described by the kinetic-molecular theory. The atmosphere is also continually illuminated during daylight hours. As a result, absorption of light energy by atmospheric molecules can cause **photochemical reactions**, reactions that would not occur at normal atmospheric temperatures in the absence of light. Such reactions play an important role in determining the composition of the atmosphere itself and the fate of many chemical species that contribute to air pollution.

Nitrogen dioxide, NO_2 , is one of the most photochemically active species in the atmosphere. The NO_2 molecule is an example of a *free radical* because it contains an unpaired electron (see p. 361), represented by a \cdot next to its formula. When an NO_2 molecule absorbs a photon of light with energy $h\nu$, the molecule is raised to a higher energy level; it becomes an **electronically excited molecule**, designated by an asterisk (*).



The excited molecule, $\cdot\text{NO}_2^*$, may quickly re-emit a photon of light, or the energy may break an N—O bond to form a nitrogen monoxide (NO) molecule and an oxygen atom (O).



Both NO and O are free radicals, because they have one or more unpaired electrons each denoted by a dot.

Photodissociation is another mechanism of formation of radicals, in which a molecule absorbs an ultraviolet photon and produces two free radicals as products. Molecular oxygen can photodissociate to form two oxygen atoms.



Some free radicals, such as an oxygen atom, react with another atom or molecule almost immediately. Others, such as an $\cdot\text{NO}_2$ molecule, are not quite so reactive and are stable enough to exist for a somewhat longer time. Most radicals are highly reactive and short-lived.

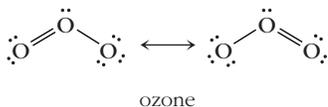
10.11 Ozone and Stratospheric Ozone Depletion

Ozone, O_3 , is an important substance that is currently very much in the news because of its role in the troposphere, where it is a pollutant. It irritates mucous membranes in the nose when it is inhaled. In the stratosphere, however, ozone

Recall that some simple molecules, like NO and NO_2 , have unpaired electrons (see p. 361).

Recall from Chapter 7 that $E = h\nu$.

Remember that the oxygen atom has the electron configuration $[\text{He}] 2s^2 2p_x^2 2p_y^1 2p_z^1$, and it is a free radical with two unpaired electrons.



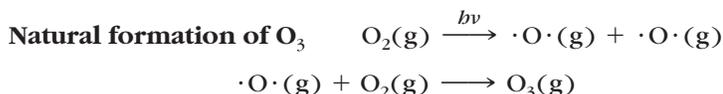
Ozone resonance structures.

is essential for life on earth. A hybrid of two resonance structures, ozone has a bent (angular) geometry (☞ *p.* 358) with a bond angle of 116.8° . Ozone's ΔH_f° of 142.3 kJ/mol shows that it is less stable than O_2 (which is assigned an enthalpy of formation of zero).



Ozone is highly reactive and does not survive long after formation.

In the stratosphere ozone is formed by a natural photodissociation process in which ultraviolet solar radiation with $\lambda < 242 \text{ nm}$ splits an O_2 molecule to produce oxygen atoms. The oxygen atoms then combine with O_2 to form ozone.



The bond energy of O_2 is 495 kJ/mol , so a calculation using $E = hc/\lambda$ shows that the energy in a photon of $\lambda \leq 242 \text{ nm}$ is needed to break the O_2 bond.

The region of maximum ozone concentration, known as the **stratospheric ozone layer**, is at an altitude of 25 to 30 km, where the concentration can reach 10 ppm. The ozone concentration in the stratosphere under natural conditions is maintained at a constant level by a reaction that destroys ozone at the same rate at which it is produced.



Because ozone molecules and oxygen atoms are at very low concentrations, this reaction is relatively slow. However, it consumes ozone fast enough to maintain a balance with the ozone-forming reaction so that under normal circumstances the concentration of ozone in the stratosphere remains constant. Every day, 3×10^8 tons of stratospheric ozone are formed and destroyed by these two competing natural processes.

Protection of earth's surface

The importance of stratospheric ozone is that by undergoing a photodissociation reaction it prevents damaging ultraviolet radiation from reaching the earth's surface. Wavelengths in the range of 200 to 310 nm are absorbed during the decomposition reaction. The oxygen atoms from the photodissociation of O_3 react with O_2 to regenerate O_3 , so this reaction results in no net O_3 loss.

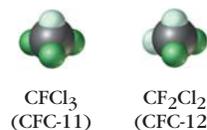


Absorption of ultraviolet radiation in the stratosphere is essential for living things on earth. Stratospheric ozone prevents 95% to 99% of the sun's ultraviolet radiation from reaching the earth's surface. Photons in this 200- to 310-nm range have enough energy to cause skin cancer in humans and damage to living plants. For every 1% decrease in the stratospheric ozone, an additional 2% of this damaging radiation reaches the earth's surface. Stratospheric ozone depletion therefore has the potential to drastically damage our environment.

This answers the question posed in Chapter 1 (☞ *p.* 3): "Why is ozone depletion harmful? I thought too much ozone was bad for your lungs."

Chlorofluorocarbons

Chlorofluorocarbons (CFCs) are small molecules with halogen atoms bonded to central carbons. CFCs play a major role in ozone depletion. Specific examples of CFCs include CFCl_3 (CFC-11) and CF_2Cl_2 (CFC-12). These compounds are nonflammable, relatively inert, volatile yet readily liquefied, and nontoxic—an extremely useful set of properties. CFCs have been used as coolants for refrigeration, in foam plastics manufacture, as aerosol propellants, and as industrial solvents. Unfortunately, the same properties that make them useful are also the reason for their destructive effect on the stratospheric ozone. Once gaseous CFCs are released into





Hal Carb/AFP/Corbis-Bettmann

F. Sherwood Rowland

1927–

Born in Ohio, Sherwood Rowland entered Ohio Wesleyan University at age 12. He received his Ph.D. from the University of Chicago in 1952. He held faculty appointments at several institutions and joined the newly formed University of California at Irvine in 1964 as Chair of the Chemistry Department. In 1974 he and Mario Molina recognized that CFCs could deplete the ozone layer in the atmosphere. Their work was received skeptically at first, but it was confirmed by others in later experiments, notably in 1985 by satellite data showing an "ozone hole" over Antarctica. Rowland, Molina, and Paul Crutzen shared the 1995 Nobel Prize in chemistry "... for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."

Seasons are reversed in the Southern Hemisphere—spring in Antarctica is fall in the Northern Hemisphere.

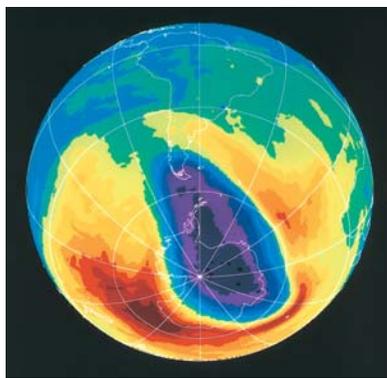
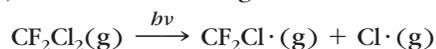


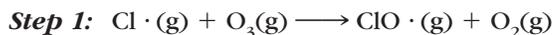
Figure 10.18 The Antarctic ozone hole. The darker colors indicate where ozone is depleted.

the atmosphere, they persist for a very long time in the troposphere because of their chemical nonreactivity. On average, a CF_2Cl_2 molecule survives roughly 100 years in the troposphere. Eventually, CFCs released into the troposphere rise to the stratosphere through atmospheric mixing, where they are decomposed by high-energy solar radiation. The decomposition products of CFCs participate in reactions in the stratosphere that result in a lowering of the concentration of ozone there.

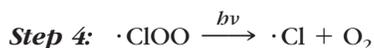
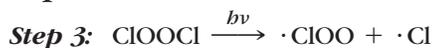
Destruction of the stratospheric ozone layer by CFCs begins when a photon of high enough energy breaks a carbon-chlorine bond in a CFC molecule. This produces a chlorine atom, as shown here using CFC-12 as an example.



The chlorine atom, a free radical, then participates in what is called a *chain reaction mechanism*. It first combines with an ozone molecule, producing a chlorine monoxide ($\text{ClO}\cdot$) radical and an oxygen molecule.



Thus, an ozone molecule has been destroyed. If this were the only reaction that particular CFC molecule caused, there would be little danger to the ozone layer. However, once Step 1 has occurred twice, the two ClO radicals produced can react further.

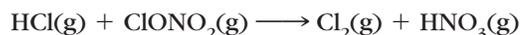


The net reaction obtained by adding two Step 1 reactions to Steps 2, 3, and 4 and canceling species that appear as both reactants and products is the conversion of two ozone molecules to three oxygen molecules.

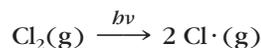


That is, this chain reaction increases the rate at which stratospheric ozone is destroyed, but it does not affect the rate at which ozone is formed. It is called a chain reaction because the reaction steps can repeat over and over. The two chlorine atoms that react when Step 1 occurs twice are regenerated in Steps 3 and 4, so there is no net change in concentration of chlorine atoms. It has been estimated that a single chlorine atom can destroy as many as 100,000 molecules of O_3 before it is inactivated or returned to the troposphere (probably as HCl). This sequence of ozone-destroying reactions upsets the balance in the stratosphere because ozone is being destroyed faster than it is being produced. As a consequence, the concentration of stratospheric ozone decreases.

The most prominent manifestation of stratospheric ozone depletion is the Antarctic **ozone hole**. In 1985 the British Antarctic Survey reported a startlingly large depletion of ozone in September and October, at the end of the Antarctic winter. This ozone hole has reappeared at this time each year (Figure 10.18). Subsequent measurements by several research teams showed that loss of ozone was correlated with high concentrations of ClOCl , supporting the theory that a chain reaction involving chlorine atoms was responsible. However, the huge depletion of ozone in the Antarctic could not be explained solely by the reaction steps given above. In the dark Antarctic winter, a vortex of intensely cold air containing ice crystals, unique to the region, builds up. On the surfaces of these crystals additional reactions produce hydrogen chloride and chlorine nitrate (ClONO_2). They can react with each other to form chlorine molecules.



When sunlight returns in the spring, the Cl_2 molecules are readily photodissociated into chlorine atoms, which can then become involved in the ozone destruction reactions.



The first direct confirmation of the relationship between stratospheric ozone depletion and increased ultraviolet intensity on the earth was reported in the September 10, 1999, issue of *Science* by scientists from the New Zealand National Institute of Water and Atmospheric Research. They found that “. . . over the past 10 years, peak levels of skin-frying and DNA-damaging ultraviolet (UV) rays have been increasing in New Zealand, just as the concentrations of protective stratospheric ozone have decreased.” Figure 10.19 shows a plot of declining stratospheric ozone concentration and increasing UV radiation over a period of 20 years, as reported by the New Zealand scientists.

Dealing with the Problem

Stratospheric ozone depletion is a global problem, and it has led to global cooperation designed to combat the problem. In an effort to reduce the harm done by CFCs and other chemicals to the stratospheric ozone layer, the Montreal Protocol on Substances that Deplete the Ozone Layer (1987) was implemented. The Protocol has been amended four times—London (1990), Copenhagen (1992), Montreal (1997), and Beijing (1999)—and has now been signed by more than 150 countries. This protocol, and its amendments, form the basis of amended Title VI of the Clean Air Act in the United States. CFC production was banned as of 1996 in the developed countries. Other chemicals that deplete the ozone layer were also banned. For example, halons, used as fire-suppression agents, were banned in the developed countries as of 1994, and methyl bromide, used as a pesticide, was banned as of 2001. Developing countries were given extra time to phase out production of CFCs.

The efforts to halt production of ozone-depleting chemicals are beginning to show positive results. The United Nations Environment Programme (UNEP) and the World Meteorological Organization (WMO) periodically issue reports, the latest of

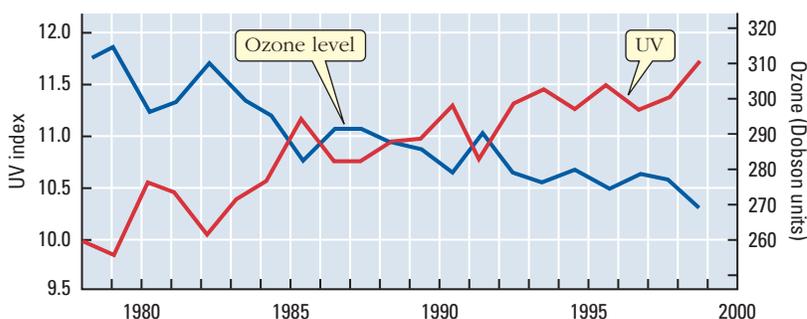


Figure 10.19 The stratospheric ozone level is decreasing, and the UV intensity is increasing. These measurements were made in Lauder, New Zealand. The red line indicates ultraviolet (UV) radiation at noon calculated from measured ozone levels, shown by the blue line. Dobson units: $1 \text{ DU} = 2.69 \times 10^{16} \text{ molecules/cm}^2$. One Dobson unit refers to a layer of ozone that would be 10 micrometers thick under standard temperature and pressure. The UV index is a standardized way to report UV radiation to the public. The higher the UV index, the more intense the UV radiation. (Source: Reprinted with permission from McKenzie, R., Connor, B., and Bodeker, G. “Increased Summertime UV Radiation in New Zealand in Response to Ozone Loss.” *Science*, Vol. 285, September 10, 1999; p. 1709.)



Carlye Calvin. Courtesy of Susan Solomon

Susan Solomon

1956–

A senior scientist at NOAA (National Oceanic and Atmospheric Administration), Susan Solomon was the first to propose a good explanation for the Antarctic ozone hole. Her chemist's intuition told her that the ice crystals that form during the Antarctic winter could provide a surface on which chemical reactions of CFC decomposition products could take place. In 1986, NASA chose Solomon (then 30 years old) to lead a team to Antarctica. Experiments performed during that visit showed that her cloud theory was correct and provided the first solid proof of a connection between CFCs and stratospheric ozone depletion. Currently, Solomon is one of the youngest members of the National Academy of Sciences. She won a National Medal of Science in March 2000, the 2002 Weizmann Women & Science Award, and the 2004 Blue Planet Prize for “. . . achievements . . . that have contributed to the resolution of global environmental problems.” Solomon has said that her winters as a young girl in Chicago prepared her for her visits to Antarctica.

The United Nations Environment Programme Web site reports activities relevant to stratospheric ozone control at www.unep.org/ozone.

The U.S. EPA Web site (www.epa.gov/ozone) and its many links provide current information about stratospheric ozone depletion.

which is *UNEP/WMO Scientific Assessment of Ozone Depletion: 2002*. Levels of ozone-depleting compounds in the troposphere are slowly declining from the peak that occurred in 1992–1994. However, total chlorine abundance in the stratosphere is now at or near a peak. The latest report predicts that Antarctic ozone levels will be increasing by 2010 because of decreasing amounts of halogens in the atmosphere. The report suggests that it will be about 2050 before the total ozone returns to pre-1980 levels.

Manufacturers began seeking alternatives to CFCs almost immediately after it became clear that CFCs would eventually be phased out. One class of possible CFC substitutes includes molecules called HCFCs in which some C—Cl or C—F bonds are replaced with C—H bonds. An example of such a molecule is CH_2Cl_2 . Because they contain C—H bonds, HCFC molecules are more reactive in the troposphere than CFC molecules. Therefore, fewer HCFCs survive long enough to reach the stratosphere, where they could lead to ozone depletion. Even better alternatives are hydrofluorocarbons (HFCs). They contain only carbon, fluorine, and hydrogen, so they have no chlorine atoms to catalyze ozone destruction. In refrigerators, for example, $\text{C}_2\text{H}_2\text{F}_4$ can be substituted for CFC-12. Older car air conditioners used CFC-12, but automakers switched the air-conditioning systems in their new cars to $\text{C}_2\text{H}_2\text{F}_4$ (HFC-134a) by 1995. In the United States, the phaseout of CFCs for auto air conditioners, and the cost associated with switching older cars to new coolants, has led to a substantial amount of smuggling of CFCs into the United States.

10.12 Chemistry and Pollution in the Troposphere

An **air pollutant** is any substance that degrades air quality. Nature pollutes the air on a massive scale with volcanic ash, sulfur oxides, mercury vapor, hydrogen chloride, and hydrogen sulfide from volcanoes and with reactive, odorous organic compounds from coniferous plants such as pine trees. Decaying vegetation, ruminant animals, and even termites add large quantities of methane gas to the atmosphere, and decaying animal carcasses and other protein materials add dinitrogen monoxide (N_2O). But automobiles, electric power plants, smelting and other metallurgic processes, and petroleum refining also add significant quantities of unwanted substances to the atmosphere. Atmospheric pollutants, whatever their origin, can have adverse effects, including burning eyes, coughing, decreased lung capacity, harm to vegetation, and even the destruction of ancient monuments. Millions of tons of soot, dust, smoke particles, and chemicals are discharged directly into the atmosphere every year. Such pollutants, which enter the environment directly from their sources, are called **primary pollutants**.

Primary Pollutants

Particle Pollutants

Pollutant particles range in size from fly ash particles, which are big enough to see, to individual molecules, ions, or atoms. Many pollutants are incorporated into water droplets and form **aerosols**, which are colloids (Section 15.9) consisting of liquid droplets or finely divided solids dispersed in a gas. Fogs and smoke are common examples of aerosols. Larger solid particles in the atmosphere are called **particulates**. The solids in an aerosol or particulate may be metal oxides, soil particles, sea salt, fly ash from electrical generating plants and incinerators, elemental carbon, or even small metal particles. Aerosol particles can range in diameter from about 1 nm to about 10,000 nm (10 μm) and can contain 10^{12} atoms, ions, or small molecules. Particles in

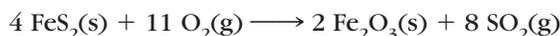
the 2000-nm range are largely responsible for the deterioration of visibility often observed in highly populated urban centers such as Houston and Mexico City.

In 1997 the EPA revised its national ambient air quality standards (NAAQS) for particulate matter and set standards for the first time for particles with diameters less than 2.5 μm . The fine-particle rule set an annual limit on the mass per unit volume of particulates with diameters less than 2.5 μm in the air to 15 $\mu\text{g}/\text{m}^3$. A series of court cases in 1997–2002 ultimately led to the upholding of the U.S. EPA standards by the U.S. Supreme Court, and these standards are now in place.

Aerosols are small enough to remain suspended in the atmosphere for long periods. Such small particles are easily breathable and can cause lung disease. Because of their relatively large surface area, aerosol particles have great capacities to *adsorb* and concentrate chemicals on their surfaces. Liquid aerosols or particles covered with a thin coating of water may also *absorb* air pollutants, thereby concentrating them and providing a medium in which reactions may occur.

Sulfur Dioxide

Sulfur dioxide (SO_2), the pollutant that is a major contributor to industrial smog and acid rain, is produced when sulfur or sulfur-containing compounds are burned in air. Most of the coal burned in the United States contains sulfur in the form of the mineral pyrite (FeS_2). The weight percent of sulfur in this coal ranges from 1 to 4%. The pyrite is oxidized as the coal is burned, producing sulfur dioxide.



Sulfur is also part of some of the organic compounds making up the coal itself.

EXERCISE 10.18 Calculating SO_2 Emissions from Burning Coal

Large quantities of coal are burned in the United States to generate electricity. A 1000-MW coal-fired generating plant will burn 3.06×10^6 kg of coal per hour. For coal that contains 4% sulfur by weight, calculate the mass of SO_2 released (a) per hour and (b) per year.

A table of the current NAAQS for many pollutants, including particulates, can be found at <http://epa.gov/air/criteria.html>.

To *adsorb* is to attract firmly to a surface. To *absorb* is to draw into the bulk of a solid or liquid.

Oil-burning electrical generation plants produce quantities of SO_2 comparable to coal-burning facilities, since fuel oils can also contain up to 4% sulfur. The sulfur in oil is in the form of smelly organic compounds in which sulfur atoms are bound to carbon and hydrogen atoms (the —SH functional group), such as $\text{CH}_3\text{CH}_2\text{SH}$. A mixture of such low-molar-mass compounds is used as an odorant in natural gas so that gas leaks can be detected by smell.

CHEMISTRY YOU CAN DO

Particle Size and Visibility

A common feature of all aerosols is that they decrease visibility. This problem can be observed in a city or along a busy highway, for example. Fog is an extreme example of disruption of visibility by aerosol particles. Here is a way to simulate the effect of air pollutants on visibility. You will need a flashlight, a little milk, a transparent container (if possible, with flat, parallel sides) full of water, and something with which to stir the water.

Turn off the room lights and shine the beam of the flashlight through the container perpendicular to the flat sides. What do you observe? Can you see the beam? Now add a couple of drops of milk to the container and stir. Can you see the flashlight beam now? How does the beam's appearance

change as the angle of viewing changes? What color is it? What color is the light that passes through the milky water? Keep adding milk dropwise, stirring and observing until the beam of the flashlight is no longer visible from the far side of the container.

1. Which wavelengths of light are scattered more by the particles? Which are scattered less?
2. Based on your observations of the milky water, devise an explanation of the fact that at midday on a sunny day the sun appears to be white or yellow, while at sunset it appears orange or red.

CHEMISTRY IN THE NEWS

Hazy Observations

Haze in the atmosphere can lead to a number of phenomena, both beautiful and unsightly—a polychrome sunset, the smoky bluish color of Tennessee's Great Smoky Mountains, limited visibility in national parks. Such haze forms naturally in many ways. For example, volatile organic compounds released by trees react with gases in the atmosphere to form small particles called aerosols. The largest source of aerosols is the ocean, which sends billions of metric tons of salt spray into the atmosphere each year. Types of aerosol particles include smoke, soot, smog, sea spray, dust, suspended powders, and water droplets with dissolved materials. Whatever their source, aerosol particles are small enough to diffract light, and they cause light scattering, which produces phenomena such as colorful sunsets.

One of the main manmade sources of aerosols is the combination of organic chemicals and sulfur dioxide, which can react in the atmosphere. A recent study¹ focused on aerosol formation chemistry as it could occur where both SO₂ and organic chemicals are released. The most abundant haze was observed when sulfur dioxide levels were elevated. Formation of haze resulted from the combination of acid, such as H₂SO₄ which comes from SO₂,

and organic compounds reacting on the surface of aerosol particles in the atmosphere.

The U.S. National Park Service has been studying the air quality in parks for decades, and one component of the study focuses on the decrease in visibility in the parks due to haze. A report of the most recent ten-year study² says that the “air quality is generally improving or remaining stable in more than half of the national parks monitored.” The national parks with the biggest impairment problems are located in the eastern United States: Mammoth Cave, Shenandoah, Great Smoky Mountains. Sulfate particles (SO₄²⁻ · x H₂O), a secondary pollutant formed from emitted SO₂, account for 60% to 80% of the visibility impairment in these parks.

Aerosol particles also play a major role in overall atmospheric chemistry. They scatter light back into space. They provide surfaces on which chemical reactions can take place. Droplets of water provide solvent for the dissolution of chemicals that can then undergo reactions in solution. Thousands of reactions can occur in the atmosphere, and sorting through them to find those that are most important is a daunting task. One goal of this area of research is to generate simulations that are realistic



Royalty-Free/Corbis

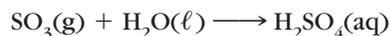
Red sky behind sea stacks at Sunset Beach, Oregon. The red sky results from light scattering due to aerosols in the atmosphere. The stacks are formed as water dissolves rock along lines of weakness, leaving behind a column strong enough to withstand wind and storm.

enough to be useful while simple enough to be manageable.

1. Jang, M., et al. “Heterogeneous Atmospheric Aerosol Production by Acid-Catalyzed Particle-Phase Reactions.” *Science*, October 25, 2002; p. 814.
2. National Park Service. “Air Quality in the National Parks.” Washington, DC, 2002. Available on the Internet at <http://www2.nature.nps.gov/ard/pubs/aqnps.htm>.

SOURCE: Perkins, S. “Solving Hazy Mysteries.” *Science News*, December 7, 2002; p. 360.

Once in the atmosphere, SO₂ can be oxidized by reactions with O₂ or ozone, for example, to form SO₃. SO₃ has a strong affinity for water and will dissolve in aqueous aerosol droplets to form sulfuric acid, which contributes to acid rain (Section 17.3).



Sulfur dioxide can be physiologically harmful to both plants and animals, although most healthy adults can tolerate fairly high levels of SO₂ without apparent lasting ill effects. Exposure to SO₂ levels exceeding 0.2 ppm (p. 431) more than 3% of the time leads to respiratory symptoms in a community of people. Exposure to SO₂ levels exceeding 0.3 ppm for 8 hours can cause vegetation damage. People with chronic respiratory difficulties such as bronchitis or asthma tend to be much more sensitive to SO₂, accounting for many of the deaths during episodes of industrial smog. To reduce the hazards, many facilities have installed equipment that removes SO₂ from emitted gases.

EXERCISE 10.19 Calculations Involving Air Pollutants

Suppose the air on a smoggy day contains 5 ppm SO₂. What volume percent is that?

Nitrogen Oxides

Most of the nitrogen oxides (NO_x) found in the atmosphere originate from nitrogen monoxide, NO, formed whenever nitrogen and oxygen—always present in the atmosphere—are raised to high temperatures, as in an internal combustion engine. This nitrogen monoxide reacts rapidly with atmospheric oxygen to produce NO₂.

Vast quantities of nitrogen oxides are formed each year throughout the world, resulting in a global atmospheric concentration of NO₂ of a few parts per billion or less. In the United States, most oxides of nitrogen are produced during fossil fuel combustion, including that of gasoline in automobile engines, with significantly less coming from natural sources such as the action of lightning. Elsewhere in the world, large amounts are produced by the burning of trees and other biomass. Most NO₂, either from human activities or from natural causes, eventually washes out of the atmosphere in precipitation. This process is one way green plants obtain the nitrogen necessary for their growth. In the troposphere, however, especially around urban centers, excessive NO₂ causes problems.

In laboratory studies, nitrogen dioxide in concentrations of 25 to 250 ppm inhibits plant growth and causes defoliation. Breathing NO₂ at a concentration of 3 ppm for 1 hour causes bronchial constriction in humans, and short exposures at high levels (150 to 220 ppm) causes changes in the lungs that can be fatal.

As you saw in Section 10.10, during the day nitrogen dioxide photodissociates to form nitrogen monoxide and free oxygen atoms. The oxygen atoms can then react to form ozone and regenerate NO₂. At night, reactions that lead to the formation of dinitrogen pentoxide, N₂O₅, predominate. The N₂O₅ can react with water to form nitric acid, HNO₃, a contributor to acid rain (Section 17.3).

The common oxides of nitrogen found in air, NO and NO₂, are collectively called NO_x.

Normally nitrogen dioxide has a lifetime of about three days in the atmosphere.

EXERCISE 10.20 Air Pollutant Stoichiometry

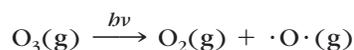
If 400 metric tons N₂ is converted to NO and then to HNO₃, what mass (in metric tons) of HNO₃ is produced?

Ozone: A Secondary Pollutant in the Troposphere

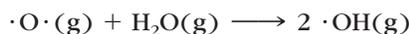
In a complex series of reactions involving O₂, NO₂, and oxygen-containing organic compounds, ozone is produced in the troposphere. Ozone is a **secondary pollutant**, one that is formed by reaction of a primary pollutant. Its pungent odor can be detected at concentrations as low as 0.02 ppm. We often smell the ozone produced by sparking electric appliances and photocopiers, or after a thunderstorm when lightning-caused ozone washes out with the rainfall. In the troposphere (the air we breathe), ozone is harmful because it is a component of photochemical smog and because it can damage human health and decompose materials such as plastics and rubber.

The most significant chemical reaction producing ozone in the atmosphere is the combination of molecular oxygen and atomic oxygen. In the troposphere the major source of oxygen atoms is the photodissociation of NO₂ (p. 462).

Ozone photodissociates at any altitude to give an oxygen atom and an oxygen molecule whenever it is struck by photons in the near-ultraviolet range (240 to 310 nm).



In the troposphere, oxygen atoms react with water to produce hydroxyl radicals ($\cdot\text{OH}$).



In the daytime, when they are produced in large numbers, hydroxyl radicals can react with nitrogen dioxide to produce nitric acid.



This three-step process is the primary means of removing NO_2 from the atmosphere. Summing the three steps gives the net reaction



Ozone is a very difficult pollutant to control because its formation depends on sunlight as well as NO_2 and hydrocarbons, which almost every automobile emits to some degree. In cities with high ozone concentrations, the cause is always related to emissions of nitrogen oxides from automobiles, buses, and trucks. Most major urban areas operate vehicle inspection centers for passenger automobiles in an effort to control emissions of nitrogen oxides as well as those of carbon monoxide and unburned hydrocarbons.

As difficult as they are to attain, established ozone standards may not be low enough for good health. Exposure to concentrations of ozone at or near 0.12 ppm has been shown to lower the volume of air a person breathes out per second; studies of children who were exposed to ozone concentrations slightly below the former EPA standard (0.12 ppm) showed a significant decrease in exhaled air volume. In 1997 the EPA lowered the ozone standard to 0.08 ppm for an eight-hour average exposure. No matter what the official standard, ozone concentrations in many urban areas represent health hazards to children at play, joggers, others doing outdoor labor or exercise, and older persons who may have diminished respiratory capabilities.



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Automobile emissions testing. Such testing is mandated in many cities that have failed to meet EPA's ozone standards. Cars that fail the emissions standards for hydrocarbons and carbon monoxide are required to be repaired. Often the local government will not reissue vehicle registration until satisfactory emissions levels are achieved.

EXERCISE 10.21 Photodissociation Reactions

Write the equations for the two photodissociation reactions that produce atomic oxygen. Then write the equation for a reaction in which ozone is formed.

Urban Air Pollution—Industrial Smog

The poisonous mixture of smoke (particulate matter), fog (an aerosol), air, and other chemicals was first called **smog** in 1911 by Dr. Harold de Voeux in his report on a London air pollution disaster that caused the deaths of 1150 people. The smog de Voeux identified is the *chemically reducing type* that is derived largely from the combustion of coal and oil and contains sulfur dioxide (a strong reducing agent) mixed with soot, fly ash, smoke, and partially oxidized organic compounds. This industrial smog is common in many cities in the world where heavy industry and power plants are found. Thanks to the U.S. Clean Air Act, industrial smog is becoming less common in the United States as more pollution controls are installed. It is, unfortunately, still a major problem in some cities of the world.

Urban Air Pollution—Photochemical Smog

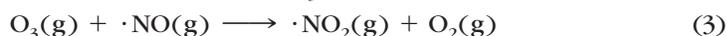
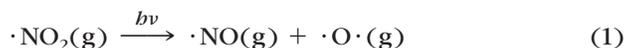
The other major kind of smog is the *chemically oxidizing type*, which contains strong oxidizing agents such as ozone and oxides of nitrogen, NO_x . It is known as

photochemical smog because light—in this instance sunlight—is important in initiating the reactions that cause it.

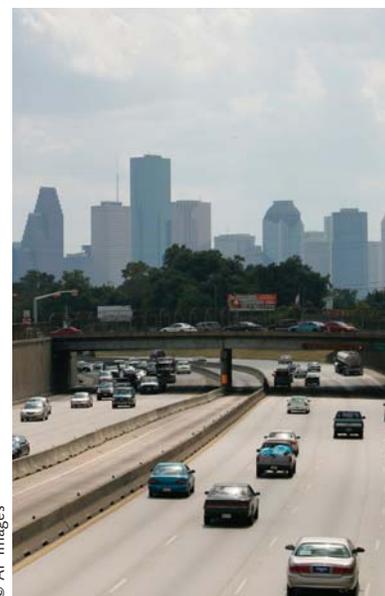
Photochemical smog is typical in cities where sunshine is abundant and internal combustion engines exhaust large quantities of pollutants to the atmosphere. Houston and Mexico City are examples (Figure 10.20). This type of smog is practically free of sulfur dioxide but contains substantial amounts of nitrogen oxides, ozone, the products of hydrocarbon oxidation, organic peroxides, and hydrocarbons of varying complexity. The concentrations of these substances vary during the day, building up in the morning hours and dropping off at night (Figure 10.21).

A city's atmosphere is an enormous mixing bowl of interrelated chemical reactions. Identifying the exact chemical reactions that produce photochemical smog was a challenge, but we now know that photochemical reactions are essential to the smog-making process and that aerosols serve to keep the primary pollutants together long enough to form secondary pollutants. Photons in the ultraviolet region of the spectrum are primarily responsible for the formation of photochemical smog.

The reaction scheme by which primary pollutants are converted into the secondary pollutants found in photochemical smog (Figure 10.22) is thought to begin with the photodissociation of nitrogen dioxide (Reaction 1). The very reactive atomic oxygen next reacts with molecular oxygen to form ozone, O_3 (Reaction 2), which is then consumed by reacting with nitrogen monoxide to form the original reactant—nitrogen dioxide (Reaction 3).



The net effect of these three reactions is absorption of energy without any net chemical change. If this were all that happened there would be no problem. Unfortunately, some of the reactive ozone molecules and oxygen atoms go on to react with other species in the atmosphere, which leads to photochemical smog formation.



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Figure 10.20 Photochemical smog over Houston.

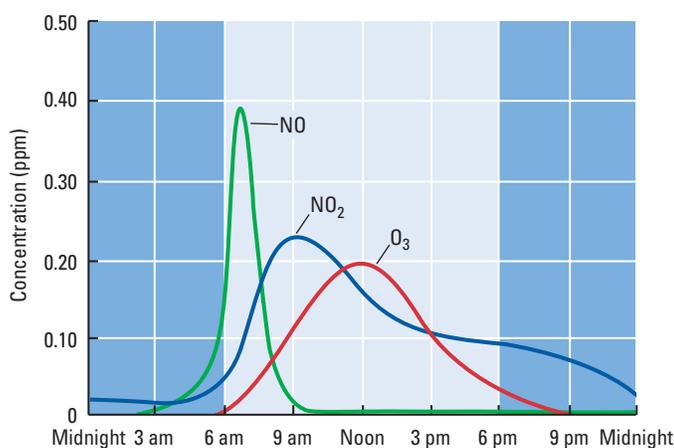


Figure 10.21 The average concentrations of the pollutants NO, NO₂, and O₃ on a smoggy day in Los Angeles, California. The NO concentration builds up during the morning rush hour. Later in the day the concentrations of NO₂ and O₃, which are secondary pollutants, build up.

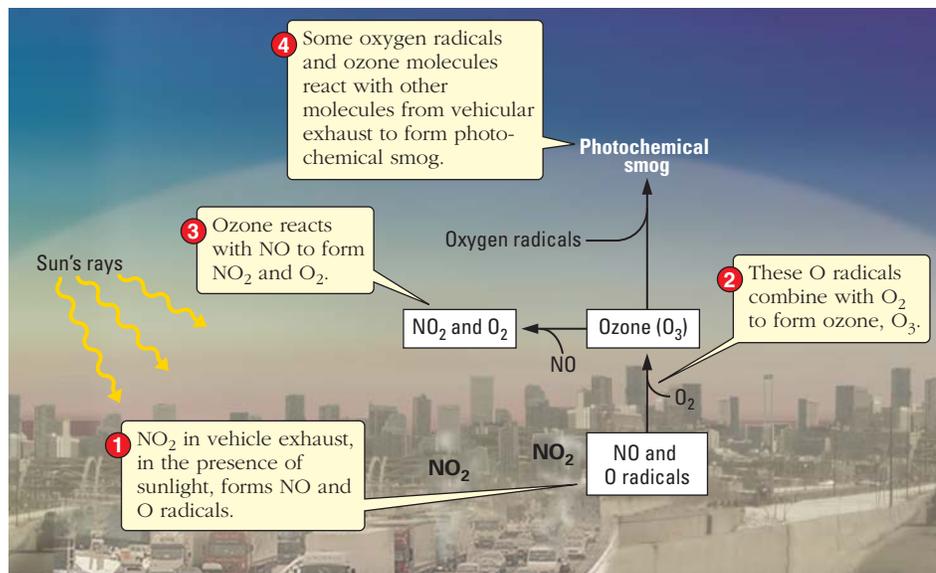


Figure 10.22 Photochemical smog formation.

The air in an urban environment contains unburned hydrocarbons released from car exhausts, evaporation, and spillage at filling stations. Atomic oxygen produced in Reaction 1 reacts with the more reactive of these hydrocarbons—unsaturated compounds and aromatics—to form other free radicals. These radicals, in turn, react to form yet other radicals and secondary pollutants such as aldehydes (for example, formaldehyde, HCHO). In addition, reactions of $\cdot\text{OH}$ (hydroxyl radical), $\cdot\text{NO}$, O_2 , and other species can produce other compounds that contribute to the smog. Some of those compounds stabilize NO_2 so that it can be carried over great distances by prevailing winds. Through a variety of chemical reactions coupled with wind, urban pollution in the form of NO_2 can be carried to outlying areas, where it may do additional damage to vegetation, human tissue, and fabrics.

EXERCISE 10.22 Smog Ingredients

Write the formulas and give sources for three ingredients of photochemical smog.

Where Do We Stand on Air Quality Now?

Average air quality across the United States is improving. Under the Clean Air Act, the U.S. Environmental Protection Agency establishes air quality standards for six principal air pollutants: NO_2 , O_3 , SO_2 , PM (particulate matter), CO, and Pb. The EPA measures the levels of these pollutants at thousands of monitoring stations. Yearly summaries of current air pollution status are provided. Data show that these six primary pollutants are declining in the United States (see the following table). For example, over the period from 1990 to 2004, NO_x emissions declined by 25%, SO_2 emissions by 34%, CO emissions by 39%, lead emissions by 40%, and particulate matter by 17%. The EPA has concluded that “the Clean Air Act has resulted in many improvements in the quality of air in the United States.”

Principal Pollutants	Percent Decrease in Emissions	
	(1980–2004)	(1990–2004)
CO	51	39
Pb	96	40
NO _x	31	25
SO ₂	41	34
Particulates, < 2.5 μm	—	17

Source: <http://www.epa.gov/airtrends/2005/econ-emissions.html>.

10.13 Atmospheric Carbon Dioxide, the Greenhouse Effect, and Global Warming

Previous sections in this chapter have discussed how earth's atmosphere screens out harmful ultraviolet radiation and makes the surface habitable. The atmosphere also performs another function by moderating the earth's surface temperature.

The Greenhouse Effect

The energy that heats the earth comes from the sun as electromagnetic radiation. Some of the electromagnetic radiation from the sun is reflected by the atmosphere back into space, and some is absorbed by the atmosphere. The remainder reaches the earth, warming its surface and oceans. The warmed surfaces then reradiate this energy into the troposphere as infrared radiation (☞ p. 273). Carbon dioxide, water vapor, methane, and ozone all absorb radiation in various portions of the infrared region. By absorbing this reradiated energy they warm the atmosphere, creating what is called the **greenhouse effect** (Figure 10.23). Thus, all four are “greenhouse gases.” Such gases constitute an absorbing blanket that reduces the quantity of energy radiated back into space. Thanks to the greenhouse effect, the earth's average temperature is a comfortable 15 °C (59 °F). By comparison, the moon, with no moderating atmosphere, has a surface mean daytime temperature of approximately 107 °C and –153 °C at night.

Earth has such a vast reservoir of water in the oceans that human activity has a negligible influence on the concentration of water vapor in the atmosphere. In addition, methane is produced by natural processes in such large quantities that human contributions are negligible. Ozone is present in such small concentrations that its contribution to the greenhouse effect is small. So among the four greenhouse gases, most attention is focused on CO₂.

Carbon dioxide is a greenhouse gas because it absorbs infrared radiation, causing C=O bonds in the molecule to stretch and bend, much like springs attached to balls (Figure 10.24). Stretching and compressing the C=O bonds requires more energy (shorter wavelength) than does bending them. Thus, C=O stretching and compressing occurs when infrared radiation with a wavelength of 4.257 μm is absorbed, whereas the C=O bending vibrations occur at lower energy (longer wavelength) when the molecule absorbs 15.000-μm infrared radiation.

Each year fossil fuel combustion worldwide puts about 6.2 billion metric tons of carbon into the atmosphere as CO₂. About 45% is removed from the atmosphere by natural processes—some by plants during photosynthesis and the rest by dissolving in rainwater and the oceans to form hydrogen carbonates and carbonates.

The greenhouse effect derives its name by analogy with a botanical greenhouse. However, the warming in a botanical greenhouse is much more dependent on the glass reducing convection than on blocking infrared radiation from leaving through the glass.

Radiation from objects on Earth to outer space answers the question, “Why does frost form on top of a parked car in winter, but not on the sides?” that was posed in Chapter 1 (☞ p. 2).

$$1 \mu\text{m} = 1 \times 10^{-6} \text{ m} = 1 \times 10^3 \text{ nm}$$

Recall from Section 7.1 that energy and wavelength are inversely related.

Worldwide, nearly one third of all atmospheric CO₂ is released as a by-product from fossil fuel-burning electric power plants.