OZONE (O₃)

Ozone is a form of elemental oxygen. In its most stable form, elemental oxygen exists as diatomic molecules (O₂). The molecules of ozone contain three oxygen atoms (O₃) and are unstable relative to O₂. Ozone is a very reactive gas, and even at low concentrations it is irritating and toxic. It occurs naturally in small amounts in the Earth's upper atmosphere and in the air of the lower atmosphere after a lightning storm. At room temperature, ozone is a pale blue gas with a sharp odor, characteristic of the air after a thunderstorm or near an old electric motor. It condenses to a dark blue liquid at –112°C and freezes at –193°C.

Ozone is much more reactive than O₂. It is a very powerful oxidizing agent, second among elements only to fluorine. It can oxidize many organic compounds and is used commercially as a bleach for waxes, oils, and textiles, and as a deodorizing agent. Because it is a powerful germicide, it is also used to sterilize air and drinking water. Ozone is usually manufactured by passing an electrical discharge through O₂ gas or through dry air. The resulting mixture of ozone and O₂ or air is usually suitable for most industrial applications of ozone. Because ozone is very unstable and reactive, the preparation of pure ozone is both difficult and hazardous and is seldom attempted.

Ozone can be formed when a mixture of O₂ and NO₂ is exposed to bright light. Such mixtures occur in the polluted air of large cities. The concentration of NO₂ in air is usually very low because N₂ and O₂ do not react at normal temperatures. However, in the hot cylinders of internal combustion engines, nitrogen and oxygen react.

\[
\text{N}_2(g) + \text{O}_2(g) \xrightarrow{\text{heat}} 2 \text{NO}(g)
\]

The NO formed inside automobile engines reacts spontaneously with O₂ in air to form NO₂.

\[
2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g)
\]

Nitrogen dioxide is a red-brown gas that dissociates when it is irradiated with bright light.

\[
\text{NO}_2(g) \xrightarrow{\text{light}} \text{NO}(g) + \text{O}(g)
\]

The oxygen atom formed in this process is extremely reactive and attaches to a molecule of O₂, forming ozone.

\[
\text{O}(g) + \text{O}_2(g) \rightarrow \text{O}_3(g)
\]

On sunny days where NO₂ pollution from traffic is high, the concentration of ozone in the air can reach levels that are dangerous for plants and animals. The U.S. Environmental Protection Agency characterizes ozone levels as “unhealthful” when they exceed the National Ambient Air Quality Standard of 125 parts per billion (ppb). In the state of Wisconsin, an “ozone alert” is issued when the average concentration of ozone over a four hour period is over 100 ppb. An “ozone warning” is announced when the this level reaches 300 ppb. An “ozone emergency” is declared when it exceeds 350 ppb. In addition to posing a threat to health, ozone in the air also damages polymeric materials such as rubber and plastics, causing them to deteriorate prematurely.

In contrast to the harmful effects of ozone in the air we breathe, the effects of ozone in the upper atmosphere are essential to the survival of life on Earth. In the upper atmosphere (specifically, the stratosphere, 15-55 km above the Earth's surface), ozone filters harmful ultraviolet radiation from sunlight. This ultraviolet radiation is highly energetic and would damage both plants and animals exposed to it. Diatomic oxygen absorbs the highest-energy ultraviolet radiation from the sun; namely, all radiation with wavelengths shorter than 240 nm. However, there is a great deal of ultraviolet radiation between 240 nm and 290 nm that is not absorbed by O₂ molecules. This radiation is absorbed by ozone.

The ozone in the stratosphere is produced by photochemical reactions involving O₂. When diatomic oxygen in the stratosphere absorbs ultraviolet radiation with wavelengths less than 240 nm, it breaks apart into two oxygen atoms.

\[
\text{O}_2(g) \xrightarrow{\text{uv light}} 2 \text{O}(g) \quad \text{(light wavelength < 240 nm)}
\]

The resulting oxygen atoms combine with O₂ molecules to form ozone.
This reaction is exothermic, and the net effect of the previous two reactions is the conversion of three molecules of \( \text{O}_2 \) to two molecules of ozone with the simultaneous conversion of light energy to heat. Ozone absorbs ultraviolet radiation with wavelengths as long as 290 nm. This radiation causes the ozone to decompose into \( \text{O}_2 \) molecules and oxygen atoms.

\[
\text{O}_3(g) + \text{uv light} \rightarrow \text{O}_2(g) + \text{O}(g) \quad \text{(light wavelength < 290 nm)}
\]

This, too, is an exothermic reaction. The overall effect of this reaction and the previous reaction is the conversion of light energy into heat. Thus, ozone in the stratosphere prevents highly energetic radiation from reaching the Earth's surface and converts the energy of this radiation to heat.

The 1995 Nobel Prize in Chemistry (http://nobelprize.org/nobel_prizes/chemistry/laureates/1995/) was awarded to three scientists for their research on the chemistry that controls the amount of ozone in the stratosphere. Paul Crutzen, director of the Department of Atmospheric Chemistry at the Max Plank Institute for Chemistry in Germany, showed in 1970 that nitrogen oxides could participate in the decomposition of ozone.

\[
\text{O}_3 + \text{uv light} \rightarrow \text{O}_2 + \text{O}
\]

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
\]

\[
\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2
\]

Net: \( 2 \text{ O}_3 \rightarrow 3 \text{ O}_2 \)

Because NO is regenerated in the third step, a single molecule of NO can assist in the destruction of many ozone molecules. Crutzen described how \( \text{N}_2\text{O} \) released from soil rises unchanged in the lower atmosphere until it is decomposed by UV radiation in the stratosphere. A fraction of the \( \text{N}_2\text{O} \) is converted to the NO that catalytically destroys ozone.

A few years later, F. Sherwood Rowland, Chemistry Professor at the University of California at Irvine, and Mario Molina, Professor of Environmental Studies at the Massachusetts Institute of Technology, described the similar activity of chlorofluorocarbons (compounds containing chlorine, fluorine, and carbon). These compounds are so inert that they, like \( \text{N}_2\text{O} \), survive in the atmosphere until they eventually reach the stratosphere, where intense UV radiation from the sun liberates chlorine atoms from them. The chlorine atoms, like NO, catalytically destroy ozone.

\[
\text{O}_3 + \text{uv light} \rightarrow \text{O}_2 + \text{O}
\]

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2
\]

\[
\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2
\]

Net: \( 2 \text{ O}_3 \rightarrow 3 \text{ O}_2 \)

Chlorofluorocarbons (CFCs) are quite unreactive chemically; they are nontoxic, noncorrosive, nonflammable, and very stable. For these reasons they have been used in fire extinguishers, as propellants in aerosols, solvents in electronics manufacture, and as foaming agents in plastics. Notable among the physical properties of some CFCs are boiling points near room temperature, so they are readily liquefied under pressure. This made them ideally suited for use as the coolant in refrigerators and air conditioners. However, because of the damage CFCs cause to the stratospheric ozone layer, an international agreement reached in 1987, the Montreal Protocol on Substances that Destroy the Ozone Layer phased out their production as of 2000.

An annual ozone “hole” has been documented over Antarctica every spring since the early 1980s. Rather than being a literal hole through the layer, the ozone hole is a large area of the stratosphere with extremely low amounts of ozone. Ozone depletion is focused mainly over Antarctica, and to a lesser degree the North Pole, because ozone destruction is most vigorous when extremely frigid temperatures create clouds of ice particles in the stratosphere that speed up the chemical reaction. You can find more information about ozone depletion from the U.S. Environmental Protection Agency (http://www.epa.gov/ozone/) and from the National Aeronautics and Space Administration (http://www.nasa.gov/missions/earth/f-ozone.html).