

Learn About ...

OZONE



Ozone is a form of elemental oxygen. In its most stable form, elemental oxygen exists as diatomic molecules (O_2). The molecules of ozone contain three oxygen atoms (O_3) and are unstable relative to O_2 . (Diatomic oxygen and ozone are examples of *allotropes*, different forms of the same element.) 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 (stratosphere) and in the air of the lower atmosphere (troposphere) 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 (161 K) and freezes at -193°C (80 K).

Use as an oxidizing agent

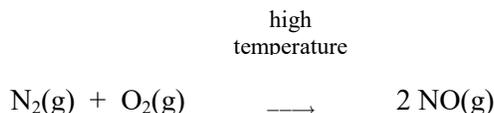
Under normal conditions, ozone is much more reactive than O_2 . It is a very powerful oxidizing agent, second among elements only to fluorine. It can oxidize many organic compounds and is used commercially to bleach waxes, oils, and textiles, and as a deodorizing agent. Because it is a powerful germicide, it is also used to sterilize air and drinking water. Ozone is usually manufactured by passing an electrical discharge through O_2 gas or through dry air. The resulting mixture of ozone and O_2 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.

Location, Location, Location

In the real estate business, these are sometimes a humorous description of the three most important characteristics that determine the value of a property. For ozone, these are seriously the three most important characteristics that determine its importance to life on Earth. Ozone in the troposphere is a danger to life. Ozone in the stratosphere is essential for life. Let's see why.

Tropospheric ozone

Ozone can be formed when a mixture of O_2 and NO_2 (nitrogen dioxide) is exposed to bright light. Such mixtures occur in the polluted air of large cities. The concentration of NO_2 in air is usually very low because N_2 and O_2 do not react at normal temperatures. However, in the hot cylinders of internal combustion engines, nitrogen and oxygen react.



The NO (nitric oxide) formed inside automobile engines reacts spontaneously with O_2 in air to form NO_2 .

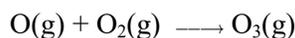


Nitrogen dioxide is a red-brown gas (often seen in smoggy cities) that dissociates when it is irradiated with bright light (sunlight).

sunlight



The oxygen atom formed in this process is very reactive and reacts with a molecule of O_2 , forming ozone. (Note that the NO product can also react with O_2 to reform NO_2 and continue these ozone-forming reactions.)



On sunny days in locations where NO_2 pollution from traffic is high, the concentration of ozone in the air can reach levels that are dangerous for plants and animals (humans with respiratory problems are particularly at risk). 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 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.

Stratospheric ozone

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. Figure 1 is a schematic representation of the absorption of harmful ultraviolet (UV) radiation from sunlight by oxygen and ozone in the upper atmosphere (the stratosphere, about 15-55 km above the Earth's surface). Ultraviolet radiation is highly energetic and will damage both plants and animals exposed to it.

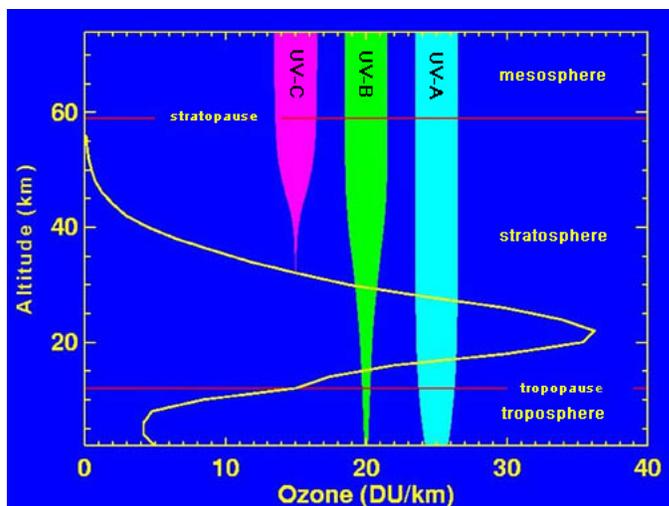
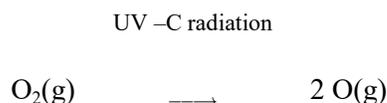


Figure 1. Schematic representation of absorption of UV radiation overlaid on a plot of the concentration of ozone (horizontal axis) in Earth's atmosphere as a function of altitude (vertical axis). The DU, Dobson unit, is a measure of the amount of ozone, named for Gordon Dobson, inventor of the instrument used to measure the amount of ozone in a column of air.

Source: NASA.

Diatomic oxygen absorbs the highest-energy ultraviolet radiation from the sun, light with wavelengths shorter than 240 nm. This is part of the UV spectrum usually called UV-C radiation, 100 nm to 280 nm. The remainder of the UV-C radiation, as well as the UV-B, 280 nm to 315 nm, is almost all absorbed by ozone. Most of the remaining ultraviolet radiation, UV-A wavelengths between 315 nm and 400 nm, reaches the Earth's surface and is responsible for human suntans, sunburns, and DNA damage that can lead to skin cancers.

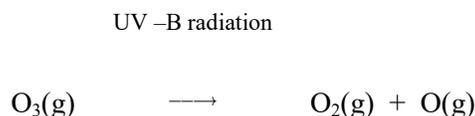
The ozone in the stratosphere is produced by the photochemical dissociation reaction of O₂. When diatomic oxygen in the stratosphere absorbs UV-C radiation, it breaks apart into two oxygen atoms.



The resulting oxygen atoms combine with O₂ molecules to form ozone.

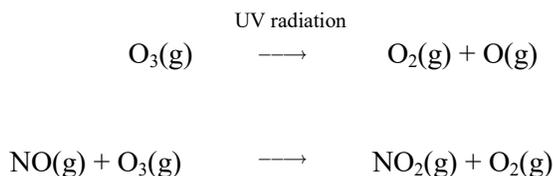


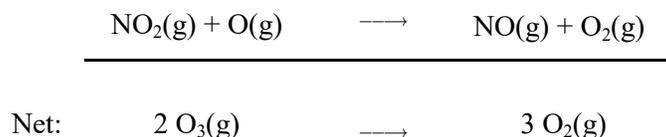
This reaction is exothermic, and the net effect of these two reactions is the conversion of three molecules of O₂ to two molecules of ozone with the simultaneous conversion of light energy to heat. Ozone absorbs UV-B radiation that causes the ozone to decompose into O₂ molecules and oxygen atoms.



This, too, is an exothermic reaction. The overall effect of this reaction and the previous reactions 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. This is why the temperature of the stratosphere increases with altitude. In the troposphere, air temperature decreases with altitude; it's colder at the top of a mountain than at its base. At the tropopause, the decreasing temperature profile in the troposphere reverses and the atmosphere (stratosphere) warms with altitude. Similarly, at the stratopause, the temperature profile again reverses and temperatures in the mesosphere decrease with altitude.

[The 1995 Nobel Prize in Chemistry](#) was awarded to three scientists for their research on the chemistry of natural and human emissions that affect 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.

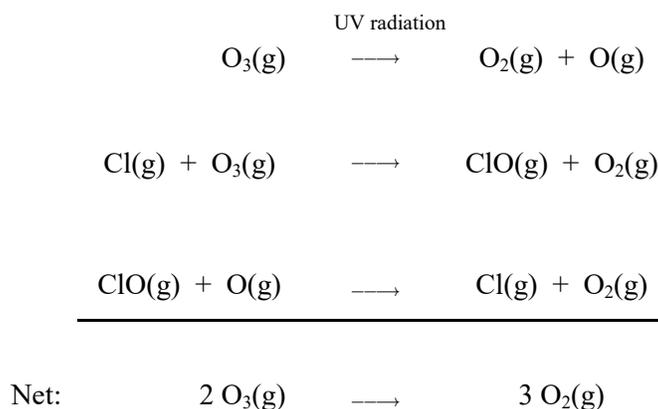




Because NO is regenerated in the third step, a single molecule of NO can cause the destruction of many ozone molecules; NO is a catalyst for ozone depletion. Crutzen described how N₂O released from soil rises unchanged in the troposphere until it is decomposed by UV radiation in the stratosphere. A fraction of the N₂O is converted to the NO that catalytically destroys ozone. The amount of atmospheric N₂O has increased by about 33% as the agricultural use of nitrogen-containing fertilizers has grown.

At the time knowledge of catalytic ozone destruction was growing, some nations were planning fleets of supersonic passenger aircraft flying in the stratosphere (where they meet less atmospheric drag). Several scientists spoke out about the possible disastrous effect of injecting their exhaust nitrogen oxides directly into the ozone layer. Although two modest fleets of supersonic transports (SSTs) were built, they were very expensive to build and maintain and were essentially a niche market for those able to afford the fares. Following a horrendous crash on a takeoff from Paris, SSTs were grounded and are no longer in operation.

A few years after the discovery of the effect of NO on stratospheric ozone, F. Sherwood Rowland, Chemistry Professor at the University of California at Irvine, and postdoctoral fellow Mario Molina, now professor in the Department of Chemistry and Biochemistry, University of California San Diego and the Center for Atmospheric Sciences at the Scripps Institution of Oceanography, described the similar activity of chlorofluorocarbons (compounds containing chlorine, fluorine, and carbon). These compounds are so inert that they, like N₂O, survive in the atmosphere until they eventually reach the stratosphere, where they absorb UV radiation from the sun and photodissociate, producing chlorine atoms. The chlorine atoms, like NO, catalytically destroy ozone.



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 working fluid in refrigerators and air conditioners, which is why these compounds, also

called "freons", were first developed. 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.

Eventually, the CFCs humans have released will reach the stratosphere where they will finally be destroyed photochemically, while continuing ozone depletion until they are gone by about the middle of the century. Figure 2 shows the amount of stratospheric ozone from the 1920s (when Dobson invented his ground-based ozone-monitoring instrument) to the early 21st century. The decrease in the ozone concentration beginning in about 1970 coincides with the surge in the use of CFCs, especially the more volatile ones used in aerosol sprays and as foaming agents that are released into the atmosphere. The largest decrease over most of the Earth was about six percent and is now about four percent. The Montreal Protocol has successfully prevented further loss from CFCs (and other ozone-destroying compounds) and put the stratosphere on the road to recovery.

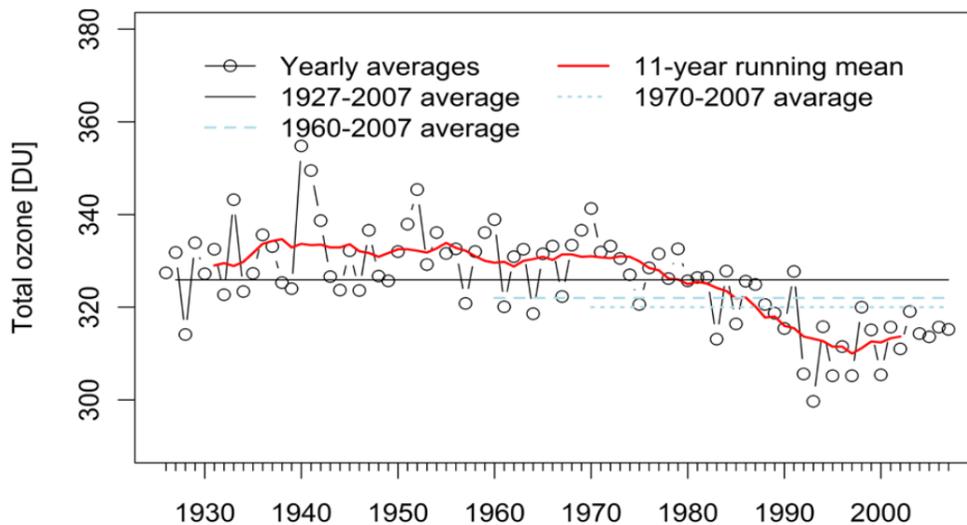


Figure 2.

These are the annual average total ozone concentrations above a weather station in Switzerland for about the past 90 years. The solid horizontal black line is the average of all the years. To better see trends in the scattered data, the red curve shows the 11-year running mean values. Each annual point on this curve is the average of the year in question plus the five previous and five subsequent years. That's why the curve begins five years after the beginning and ends five years before the end of the data points.

Source: J. Staehelin, S. Brönnimann, T. Peter, R. Stübi, P. Viatte and F. Tummon, "The value of Swiss long-term ozone observations for international atmospheric research," in *From Weather Observations to Atmospheric and Climate Sciences in Switzerland - celebrating 100 years of the Swiss Society for Meteorology*, S. Willemse and M. Furger (eds.), vdf Hochschulverlag AG an der ETH Zürich 2016, pp. 325-349 (Chapter 16).

The ozone “hole”

In contrast to the relatively small decreases in ozone over most of the Earth, a decrease of about 40% between 1975 and 1984 was observed and reported from ground-based measurements of ozone over a British experiment station in Antarctica in the spring (September-November in the southern hemisphere). Satellite measurements have documented an annual ozone “hole” over all of Antarctica every spring since at least the late 1970s. The ozone hole is not an actual hole through the layer but a large area of the stratosphere with very low amounts of ozone, Figure 3.

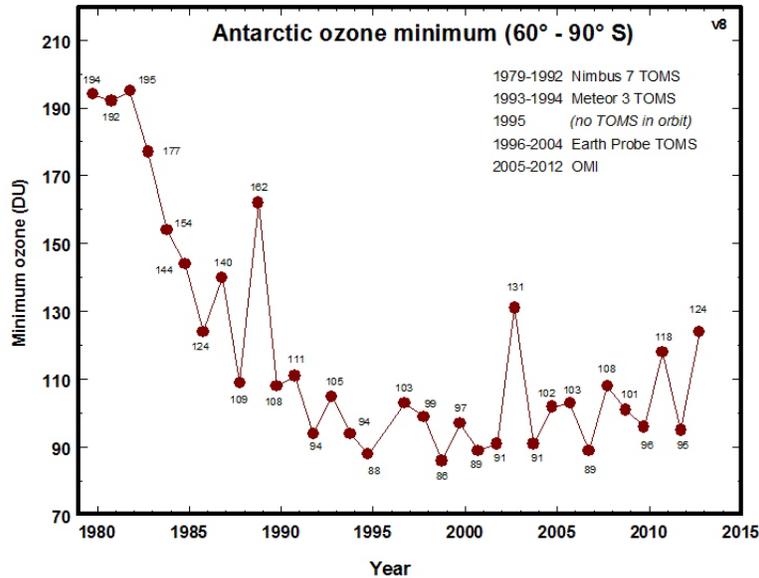


Figure 3. These are the lowest annual values for the Antarctic ozone concentration (most often in October) measured by a series of satellites with Total Ozone Mapping Spectrometers (TOMS).
Source: NASA

There is a cautionary tale here for experimenters tempted to throw out data that do not fit their expectations. When the ground-based observations were published in 1985, there were objections that measurements of ozone from satellite instruments had seen no such depletion in the Antarctic ozone. However, reexamination of the satellite results showed that the computer program used to analyze the “raw” data was designed to account for possible instrument malfunction by disregarding values that were outside the expected range. Thus, very low values over Antarctica were simply discarded. When the raw data were reevaluated without filtering out these values, the ozone hole appeared and could have been discovered years earlier, when satellite measurements began.

The puzzle was why there is such a large effect on the ozone over Antarctica (and, at times, a much smaller similar effect over the Arctic). The answer is provided by a mechanism proposed by NOAA atmospheric chemist, Susan Solomon, now Professor of Atmospheric and Climate Science at Massachusetts Institute of Technology, which involves chemistry on the surface of ice and the unique weather over Antarctica that greatly enhances catalytic ozone destruction. The key components are formation of clouds of ice crystals in the extreme cold of the stratosphere over the continent during the dark (almost totally sunless) polar winter, a vortex of wind that

encircles the continent and holds the clouds and reactants over it, and the catalytic photochemical reactions enhanced by chemistry on the surface of the ice crystals when sunlight returns in the spring. Fortunately, nowhere else on Earth, except above the poles, is the stratosphere cold enough to produce the clouds of ice crystals required for this rapid ozone destruction. Although dramatic, the ozone hole represents only a small amount of total ozone depletion and there are signs that the hole is now “healing”. It will be decades before ozone levels recover (assuming no more ozone depleting substances reach the stratosphere).

You can find more information about ozone depletion from the [U.S. Environmental Protection Agency](#) and from the [National Aeronautics and Space Administration](#).