INFRALiGHT
Technology

Address: 4 Vera St, Helensburgh
NSW 2508 Australia
E-mail: iruv@infralight.com.au
Web: www.infralight.com.au

Tel: +61 2 4294 2779
Fax: +61 2 4294 2779

ABN: 68 514 847 616

Excellence in Ultraviolet Solutions

Ozone Chemistry

Ozone is a form of elemental oxygen. In its most stable form, elemental oxygen exists as a diatomic molecule (O_2). The molecules of ozone contain three oxygen atoms (O_3) and are unstable with respect to O_2. 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 odour, 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 O_2. It is a very powerful oxidising agent, second among elements only to fluorine. It can oxidise many organic compounds and is used commercially as bleach for waxes, oils, and textiles, and as a deodorising agent. Because it is a powerful germicide, it is also used to sterilise 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.

Ozone can be formed when a mixture of O_2 and NO_2 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, reacting gases inside the cylinders of internal combustion engines, nitrogen and oxygen can react.

$$N_2(g) + O_2(g) \xrightarrow{\text{heat}} 2\,NO(g)$$

The **NO** formed inside automobile engines reacts spontaneously with O_2 in air to form NO_2.

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$

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

$$NO_2(g) \xrightarrow{\text{light}} NO(g) + O(g)$$

The oxygen atom formed in this process is extremely reactive and readily attaches to a molecule of O_2, forming ozone.

$$O(g) + O_2(g) \longrightarrow O_3(g)$$

On sunny days 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. Health organisations around the world characterise ozone levels as "unhealthy" when they exceed the 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 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, 15-55km 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 240nm.
However, there is a great deal of ultraviolet radiation between 240nm and 290 m that is not absorbed by O_2 molecules. This radiation is absorbed by ozone.

The ozone in the stratosphere is produced by photochemical reactions involving O_2. When diatomic oxygen in the stratosphere absorbs ultraviolet radiation with wavelengths less than 240nm, it breaks apart into two oxygen atoms.

$$O_2(g) \xrightarrow{\text{UV light}} 2\,O(g) \qquad \text{(light wavelength < 240nm)}$$

The resulting oxygen atoms combine with O_2 molecules to form ozone. $O(g) + O_2(g)$ $O_3(g)$
This reaction is exothermic, and the net effect of the previous two reactions is the conversion of three molecules of 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 290nm. This radiation causes the ozone to decompose into O_2 molecules and oxygen atoms.

$$O_3(g) \xrightarrow{\text{UV light}} O_2(g) + O(g) \qquad \text{(light wavelength < 290nm)}$$

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 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.

$$O_3 \xrightarrow{\text{UV light}} O_2 + O$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + O \longrightarrow NO + O_2$$

$$\text{Net:}\quad 2\,O_3 \longrightarrow 3\,O_2$$

Because **NO** is regenerated in the third step, a single molecule of **NO** can assist in the destruction of very many ozone molecules. Crutzen described how **N_2O** released from soil rises unchanged in the lower atmosphere until it is decomposed by UV radiation in the stratosphere.

A fraction of the **N_2O** 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 as 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 **N_2O** 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.

$$\begin{aligned}
& O_3 \xrightarrow{\text{UV light}} O_2 + O \\
& Cl + O_3 \longrightarrow ClO + O_2 \\
& ClO + O \longrightarrow Cl + O_2 \\
\text{Net:}\quad & 2\,O_3 \longrightarrow 3\,O_2
\end{aligned}$$

Chlorofluorocarbons (CFCs) have chemical and physical properties that make them valuable in industry. CFCs are quite unreactive chemically: they are nontoxic, non-corrosive, 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 makes 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, calls for the phaseout of their manufacture, which is to have ceased as of 1996. Therefore, industries are engaged in an intensive search for replacements. However, even if CFC use were to be immediately terminated worldwide, the depletion of the ozone layer would still increase as a result of the large quantity of CFCs already released into the atmosphere.

The hole in the ozone layer that opens over Antarctica each southern spring formed earlier and grew bigger in 2000 than at any time since satellites have been monitoring the polar atmosphere. In early September, the hole expanded to a record 17.1 million square miles, an expanse larger than North America. By comparison, in 1981 it covered just 900,000 square miles. This record ozone hole has renewed suspicions among atmospheric scientists that global warming may aid ozone destruction. 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. The link with global warming comes because while a build up of carbon dioxide and other heat-trapping industrial gases warms the lower atmosphere, it acts in an opposite way in the stratosphere, causing it to radiate more heat to space and to grow colder than it otherwise would. Ozone loss itself also causes stratospheric cooling, because energy arriving from the sun as ultraviolet radiation is not absorbed. More ice clouds mean CFCs and other ozone destroying chemicals can more efficiently react to deplete the ozone layer.