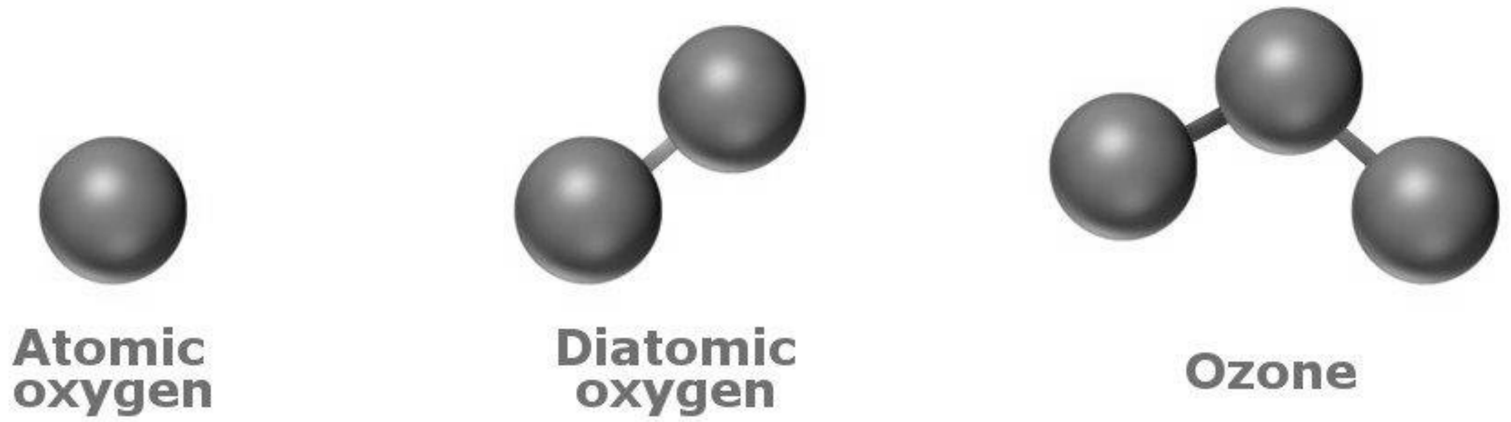
OZONE DEPLETION

Ozone is a gas that is naturally present in our atmosphere and it has the chemical formula O_3 because an ozone molecule contains three oxygen atoms.



Good Ozone vs. Bad Ozone

Good ozone (Stratospheric ozone): Stratospheric ozone is considered good for humans and other life forms because it absorbs ultraviolet-B (UV-B) radiation from the Sun. If not absorbed, UV-B radiation would reach Earth's surface in amounts that are harmful to a variety of life forms. In humans, increased exposure to UV-B radiation increases the risks of;

- Skin cancer
- Cataracts
- Suppressed immune system

UV-B radiation exposure before adulthood and cumulative exposure are both important health risk factors. Excessive UV-B exposure also can damage terrestrial plant life, single-cell organisms, and aquatic ecosystems. Other UV radiation, UV-A, which is not absorbed significantly by ozone, causes premature aging of the skin.

Bad ozone (Tropospheric ozone): Ozone near Earth's surface in excess of natural amounts is considered bad ozone. It is formed by reactions involving human-made pollutant gases. Increasing surface ozone above natural levels is harmful to humans, plants, and other living systems because ozone reacts strongly to destroy or alter many biological molecules. High ozone exposure reduces crop yields and forest growth.

In humans, exposure to high levels of ozone:

- can reduce lung capacity,
- cause chest pains,
- throat irritation,
- coughing,
- worsen preexisting health conditions related to the heart and lungs.

In addition, increases in tropospheric ozone lead to a warming of Earth's surface because ozone is a greenhouse gas. The negative effects of excess tropospheric ozone contrast sharply with the protection from harmful UV-B radiation afforded by an abundance of stratospheric ozone.

How is Ozone Formed in the Atmosphere?

- In the first step, solar ultraviolet radiation breaks apart one oxygen molecule (O_2) to produce two oxygen atoms (2 O).

- In the second step, each of these highly reactive atoms combines with an oxygen molecule to produce an ozone molecule (O_3).

<u>Step 1</u>

O_2 +UV Sunlight $\rightarrow O + O$

<u>Step 2</u>

$O + O_2 \rightarrow O_3$

<u>Overall reaction</u>

$$3O_2 \xrightarrow{Sunlight} 2O_3$$

- The ozone layer, in the stratosphere, protects the earth from the harmful radiations of the sun. It is very important and critical to the existence of life forms on earth.

- Pollutants like CFC's, oxides of nitrogen and hydrocarbons cause the depletion of ozone layer. This phenomenon of gradual depletion of the protective ozone layer in the stratosphere, is termed as ozone layer depletion.

Mechanism of Stratospheric Ozone Depletion

A catalytic cycle can destroy O_3 as follows:

$X + O_3 \rightarrow XO + O_2$

$XO + O \rightarrow X + O_2$

This cycle leads to the net reaction:

$O_3 + O \rightarrow 2O_2$

Role of NO, NO_2, N_2O

Paul Crutzen (1970) was the first to suggest the ozone destruction through the involvement of NOx. The latter were produced by the reaction of N_2O with $O(^1D)$. N_2O, which has a long lifetime, is released in the troposphere and passes into the stratosphere. In the NO_x cycle, ozone is destroyed by NO, which is formed through reactions below.

$$N_2O + O(^1D) \rightarrow NO + NO$$

$$N_2O + h\nu\ (\lambda < 4200\ \text{nm}) \rightarrow NO + N$$

These reactions are the most important source of NO in the stratosphere.

The catalytic cycle for ozone destruction is as follows.

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2$$

NO_x is the most important destroyer of ozone is 25-45 km altitude region.

Role of Chlorine Compounds

- Chlorofluorocarbons (CFCs) **have no natural source,** but were entirely synthesized for such diverse uses as refrigerants, aerosol propellants and cleaning solvents. Their creation was in 1928 and since then concentrations of CFCs in the atmosphere have been rising.
- Due to the discovery that they are able to destroy stratospheric ozone, a global effort to halt their production was undertaken and was extremely successful.
- So much so that levels of the major CFCs are now remaining level or declining. However, their long atmospheric lifetimes determine that some concentration of the CFCs will remain in the atmosphere for over 100 years.

Chlorine atoms, released from CFCs/CCl_4/other active chlorine compounds during photodissociation, react with ozone to form ClO and O_2.

$CF_2Cl_2 + h\nu \rightarrow Cl + CF_2Cl$

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

ClO can react as follows also.

$ClO + NO \rightarrow Cl + NO_2$

$ClO + h\nu \rightarrow Cl + O$

ClO reacts about six times faster than any NOx species. By far, Cl is the most important destroyer of O3. In the mechanism, destruction of an ozone molecule involves the consumption of an O atom, whose concentration is not high. To overcome this difficulty, Molina et al., (1987) suggested the following modified mechanism.

$Cl + O_3 \rightarrow ClO + O_2$

$2ClO + M \rightarrow Cl_2O_2 + M$

$Cl_2O_2 + h\nu \rightarrow Cl + ClOO$

$ClOO + M \rightarrow Cl + O_2 + M$