

# O Z O N E

*What is the fuss about these “ozone holes” over the Earth’s poles?*

*What’s so bad about auto emissions? and why do they make ozone?*

*What’s so bad about chlorofluorocarbons? and why do they destroy ozone?*

*If ozone is bad for your lungs, why are we concerned that levels of it are decreasing in some places?*

## The Chemical Ozone

Ozone is a slightly bluish colored gas with a pungent smell. In fact the word comes from the Greek word *ozon* ( $οζων$ ) meaning “smelling.” You may have noticed the smell after electric sparks are produced (as in an electric train set) or sometimes when lightning strikes nearby. Ozone can also form from oxygen in the presence of ultraviolet light.

Ozone is a molecule made up of three atoms of oxygen, or  $O_3$ . The oxygen we breathe is actually molecular oxygen, or  $O_2$ . Normally at ground level there is very much less ozone than oxygen.

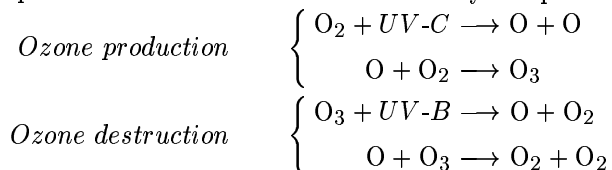
ATMOSPHERIC COMPOSITION		
Gas	Percentage	PPB
Nitrogen ( $N_2$ )	78.084	780,840,000
Oxygen ( $O_2$ )	20.946	209,460,000
Argon (Ar)	0.934	9,340,000
Carbon Dioxide ( $CO_2$ )	0.033	332,000
Neon (Ne)	0.002	18,000
⋮		
Carbon Monoxide (CO)	0.000010	100
⋮		
Ozone ( $O_3$ ) on surface	0.000004	40
Ozone ( $O_3$ ) in stratosphere	0.0003	3,000
⋮		

Ozone is, however, a much more powerful “oxidizing agent” than oxygen, meaning it can react chemically with various substances adding an atom of oxygen to their molecular structure. Ozone is used industrially as a bleach and disinfectant because of its strong oxidizing ability. Whereas oxygen also causes oxidation, it is a much more stable molecule than ozone, which can more freely break apart to give up one of its atoms to another molecule. Oxidation in its rapid form is called combustion, so the “burning feeling” you get in your lungs when you breathe too much ozone is more or less just that—burning.

## Ozone in the Stratosphere

One of the reasons ozone is normally so rare at the Earth’s surface is that it reacts very rapidly with many different substances and is quickly destroyed. However, in the upper atmosphere, the air is thinner and there are fewer chemicals to react with, so ozone can persist in larger quantities for longer periods of time. Levels of ozone in the stratosphere (about 20 to 50 km up) can reach several parts per million.

The basic photochemical process was worked out in the 1930’s by Chapman:



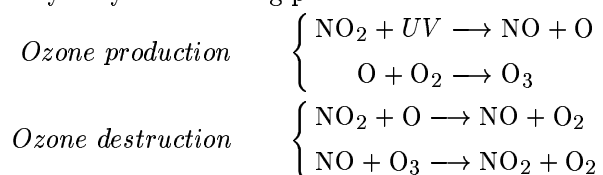
When the production and destruction rates are balanced, an equilibrium concentration of ozone is reached.

The ultraviolet photons come from the Sun, which emits about 10% of its power in ultraviolet photons. In fact the oxygen and ozone absorb so much energy in the stratosphere that it is warmer than most of the air except right at the surface. The ultraviolet photons that destroy oxygen and ozone in the photochemical reactions have different energies. Oxygen is so tightly bound together that it requires a very high energy *UV-C* photon. These are sometimes call *UV-C* photons. Such energetic photons are extremely dangerous to living organisms, but fortunately there’s plenty of oxygen in the atmosphere to make sure that none of these reach the surface.

Ozone absorbs *UV-B* photons, which are less energetic, but still damaging to living organisms. Fortunately for life on Earth, the amount of ozone that normally exists in the stratosphere prevents most of the *UV-B* photons from reaching the surface. Remember, though, the level of ozone in the stratosphere depends on the balance of the production and destruction rates of the chemical reactions. If other destruction mechanisms begin to operate, the amount of ozone available to absorb the *UV-B* photons will decrease.

## Photochemical Smog

At ground level, ozone can be created as a secondary byproduct of our combustion engines and even from fertilizers. When fossil fuels are burned at high temperatures (as in an auto engine), various levels of nitrogen dioxide ( $\text{NO}_2$ ) and nitric oxide ( $\text{NO}$ ) are created as a byproduct. Nitrogen dioxide can react photochemically to create ozone, and nitric oxide can react to destroy it by the following processes:



Note that the ozone production is generally increased when there's more  $\text{NO}_2$  and its destruction is increased when there's more  $\text{NO}$ .

Combustion produces both oxides of nitrogen, therefore we would have to study all the possible formation and destruction processes for  $\text{NO}$  and  $\text{NO}_2$  to determine their equilibrium abundances in order to find the equilibrium concentration of ozone in turn. This is not a simple calculation! Results of detailed studies indicate that in the lower atmosphere ozone is increased by nitrogen oxide emissions, but in a more intense  $UV$  radiation field of the upper atmosphere, the balance may swing toward  $\text{NO}$  and hence to the destruction of ozone. This is why concerns were raised in the 1970's when it was proposed that we should build SST's that would fly in the stratosphere—there their nitrogen oxide emissions could *reduce* the ozone level.

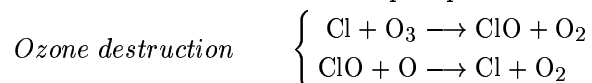
## Chlorofluorocarbons and Ozone

At last we come to the infamous hair spray problem. What have we done to change the balance of chemistry in the stratosphere?

The problem is a wonderful set of chemicals called chlorofluorocarbons (CFCs). As their lengthy name indicates, these are molecules that contain chlorine, fluorine, and carbon. Freon is a trade name for  $\text{CFCl}_3$  and  $\text{CF}_2\text{Cl}_2$ , which are common refrigerants. CFCs are also used as solvents, propellants, blowing agents for plastic foam, etc.

CFCs are unusual in that they are not soluble in water and are chemically inert, so instead of being destroyed on the Earth's surface like most other chemicals we release, they gradually rise into the stratosphere. There the molecules are broken apart by the high-energy  $UV$  photons present.

The problem is with the chlorine that is released in the stratosphere. Chlorine *catalyzes* the destruction of ozone. Normally, there would be no more than a few tenths of a part per billion of chlorine occurring naturally.



The net reaction is a double-whammy since it removes both ozone *and* free atomic oxygen which could otherwise react to create ozone. Worst of all, since  $\text{Cl}$  is a catalyst, it is not destroyed in the process, so it is free to continue destroying the ozone.

## The Antarctic (and Arctic) Ozone Holes

Why should the loss of stratospheric ozone show up in the arctic regions of Earth?

This is a complicated issue relating to several unusual aspects of the polar atmosphere. One aspect is the lower level of sunlight (on average) received at the poles. Normally, there is only about half as much ozone present in the polar stratosphere as over the equator. Also, after the long winter night, ozone levels are quite low because there has been so little sunlight for so long. Thus the polar atmosphere has a weaker (and more susceptible) ozone layer to begin with.

A second aspect of the polar atmosphere helps to increase the levels of free chlorine. Normally chlorine from CFCs can combine with hydrogen to form hydrochloric acid ( $\text{HCl}$ ) which can reduce the amount of free chlorine available to destroy ozone. But on the surface of ice crystals in stratospheric clouds, the  $\text{HCl}$  reacts to unbind the hydrogen, leaving free chlorine, *and then* the ice can precipitate down to the surface, leaving lots of free chlorine.

All through the polar winter, the levels of chlorine in the stratosphere build up so that even with the coming of sunlight in the arctic spring, the rate of ozone production by  $UV$  photons just can't keep up with the destruction rate caused by the chlorine. As spring progresses into summer, the  $UV$  levels continue to rise, and finally the ozone hole closes, although this seems to be taking longer and longer each year.

The question is, is this a phenomenon that will remain isolated to the poles, or is it just showing up there *first*?

## Further Reading

R. S. Stolarski, "The Antarctic Ozone Hole," *Scientific American*, January 1988

O. B. Toon and R. P. Turco, "Polar Stratospheric Clouds and Ozone Depletion," *Scientific American*, June 1991.