Chem Factsheet

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Depletion of the Ozone Layer

What is ozone?

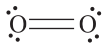
Ozone (molecular formula O_3) is the tri-atomic *allotrope* of oxygen (O). The more familiar allotrope is the diatomic form, O_2. Allotropes are different structural forms of the same element. O_2 is commonly referred to as just "oxygen" but they can be properly distinguished using the names dioxygen (O_2) and trioxygen (O_3).

Note: Diamond, graphite, fullerenes and carbon nanotubes are probably the most familiar examples of allotropes, all being forms of carbon but with different structures.

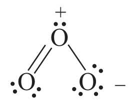
Ozone is a pale blue gas with a sharp smell. In past times it was considered to be "good for your health" and was associated with the "fresh" smell of sea air because, as a result of lightning activity over the sea, O_2 was thought to be converted to O_3 resulting in a higher than average presence of O_3 in the area. However, the "seaside smell of ozone" was later shown to be caused by dimethyl sulphide CH_3-S- CH_3] produced by plankton in the sea. It can however be detected in the vicinity of machines prone to electrical discharges such as photocopiers. Forget the myth about it being "healthy in small doses" – the European Union has set upper limits of only 120 µg (120×10^{-6}g) per cubic metre of air because its presence in higher concentrations is certainly associated with premature death, asthma, bronchitis, heart attacks, and many other cardiopulmonary problems!

Note: "Healthy" dimethyl sulphide is also toxic!

The dot-and-cross diagrams show the different structures of O_2 and O_3.

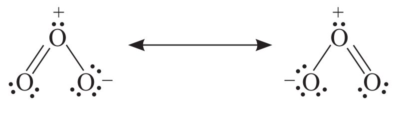


Dioxygen (O_2)



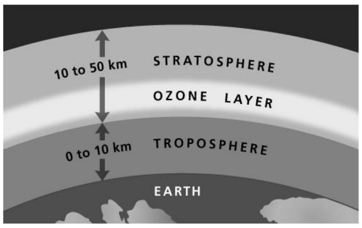
Trioxygen (O_3)

Note: The structure of ozone is better represented as a "resonance hybrid" – a "blend" of two or more valid dot-and-cross structures which represents overall delocalisation of some electrons.



What is the ozone layer?

The ozone layer was discovered in 1913 by the French physicists Charles Fabry and Henri Buisson. It is a layer in Earth's atmosphere which is responsible for absorbing most of the Sun's harmful ultra-violet radiation. It is mainly found in the lower portion of the stratosphere at about 20 to 30 kilometres above Earth's surface, although its thickness varies both seasonally (generally higher in spring) and geographically (generally higher above the poles).



It contains relatively high concentrations of ozone (O_3) – about ten parts per million whereas the average ozone concentration in the Earth's atmosphere is only about 0.6 parts per million.

More about ultra-violet radiation

The Sun produces radiations covering all the wavelengths in the entire electromagnetic spectrum. Amongst these is the ultra-violet (uv) region.

ir	red	orange	yellow	green	blue	indigo	violet	uv

Decreasing wavelengths →

The UV region is divided in terms of its tendency to cause harm to living plants and creatures.

1. The very short and most damaging UV wavelengths (10–100 nm). These are absorbed by nitrogen in the stratosphere and do not reach the surface of the Earth.
2. UV-C (100–280 nm wavelengths). These are very harmful to all living things but are entirely screened out by a combination of dioxygen and ozone (see later).
3. UV-B (280–315 nm wavelengths). These can be harmful to the skin and are the main cause of sunburn; excessive exposure can also cause genetic damage, resulting in problems such as skin cancer.
4. UV-A (315–400 nm wavelengths). These are significantly less harmful to DNA, although they may still potentially cause physical damage, indirect genetic damage and skin cancer.

How does the ozone get into the ozone layer?

It is formed by a "photochemical" or "photolytic" process – one involving a chemical change (bond breaking) arising from the use of energy derived from light. The process was first elucidated by the British physicist Sydney Chapman in 1930.

First of all, oxygen molecules (O_2) absorbing energy from short wavelength UV light (100-200 nm : part of the UV-C region) derived from the Sun. This causes the O_2 molecule to split into individual oxygen atoms (radicals). $O_2 \rightarrow 2O$

The atomic oxygen then rapidly combines with unbroken O_2 molecules to create ozone, O_3. $O_2 + O \rightarrow O_3$

The overall process can be represented by: $3O_2 \rightarrow 2O_3$

Most importantly, this process causes a significant proportion of the harmful UV-C wavelengths to be absorbed, preventing them reaching the surface of the Earth and causing damage.

What Does The Ozone In The Ozone Layer Do?

When "working properly", the ozone layer absorbs 97–99% of the Sun's medium-frequency ultraviolet radiation (240-310 nm wavelength ; much of the remainder of UV-C and nearly all of UV-B regions) reducing damage to life on Earth even more. This is achieved via the "oxygen-ozone cycle".

Note: Ozone and oxygen do not absorb UV-A, so most of this type of longer wavelength radiation reaches the surface of the Earth.

The oxygen-ozone cycle

Oxygen and ozone are continuously inter-converting in the stratosphere. This can be summarised in the following "oxygen-ozone cycle".

First of all, ozone is created from oxygen as described above.

i.e. $O_2 + \mathit{UV\text{-}C} \rightarrow 2O$ ---(1)

followed by $O_2 + O \rightarrow O_3$ ---(2)

The cycle proper then begins. The ozone molecules formed absorb UV-B radiation between 240 and 310 nm resulting in oxygen (O_2) plus a free oxygen atom

$O_3 + [240 \text{ nm} < \text{UV-B} < 310 \text{ nm}] \rightarrow O_2 + O$ ---(3)

The atomic oxygen produced quickly reacts with another oxygen molecule to reform ozone:

$O + O_2 \rightarrow O_3 + \text{Heat Energy}$ ---(4)

Reactions (3) and (4) together constitute the oxygen-ozone cycle - the overall effect is to convert harmful UV-B light into heat, without any net loss of ozone. The cycle keeps the ozone layer in a steady state while protecting the lower atmosphere from UV-B radiation.

This means that, in the absence of impurities, the concentrations of ozone (minor) and oxygen (major) will be constant with the added bonus that most harmful UV-B radiation is absorbed!

However, the cycle can be disrupted naturally by other processes leading to the removal of O_3 molecules and/or O atoms. Such processes include:

1. If an oxygen atom and an ozone molecule collide, they recombine to form two oxygen molecules: $O_3 + O \rightarrow 2O_2$ ---(5)
2. If two oxygen atoms collide to form one oxygen molecule: $2O \rightarrow O_2$ ---(6)

The overall amount of ozone in the stratosphere is determined by a balance between production by UV-C radiation [reactions (1) and (2)] and these removal processes [reactions (5) and (6)]. Fortunately, the removal rate is slow because the concentration of O atoms is very low and the activation energy of reaction (5) is relatively high.

How has the ozone layer been depleted?

The highly desirable balance where the rate of formation of ozone [(1) + (2)] equals the rate of loss of ozone [(5) + (6)] has been disturbed by the introduction of artificial substances into the stratosphere. In general, radicals have been introduced into the stratosphere (by humans!) which take the place of the O atom (also a radical) in reaction (5) and cause a faster decomposition of O_3 because the process happens to have a lower activation energy. This leads to a net loss of ozone and a reduced ability to absorb UV-B via the ozone-oxygen cycle. Hence, it gives rise to the notorious "hole in the ozone layer over the Antarctic" first identified in the 1970-80's – not so much a "hole" as a differential lowering of the ozone concentration in this region because the lower temperatures here produce ice particles which provide surfaces on which the depletion reaction can occur even more efficiently. The radicals cause ozone depletion throughout the ozone layer, just more in some places than others.

The main culprits are chlorofluorocarbons (a.k.a. "CFC's" – e.g. CF_3CFCl_2; 2,2-dichloro-1,1,1,2-tetrafluroethane) which were developed in the early 1900's as cheap propellants (for use in aerosols), plastic expanders (e.g. polystyrene) and refrigerants. Following intentional or accidental release into the atmosphere, these volatile compounds diffused into the stratosphere where they started to cause problems.

They cause problems because of the relatively weak C-Cl bonds present in the molecules.

Bond	C-C	C-Cl	C-F
Bond Enthalpy (/kJ mol-1)	+348	+328	+485

In the stratosphere, sufficient energy is available in the form of UV to allow the weaker C-Cl bonds to be broken, producing chlorine atoms (free radicals having an unpaired electron).

$C\text{-}Cl + [UV] \rightarrow C^\bullet + Cl^\bullet$

This is the "initiation" reaction of the following "chain" reaction.

The Cl atoms can then collide with an ozone molecule to form an O_2 molecule and another radical ($ClO^\bullet$)

$O_3 + Cl^\bullet \rightarrow O_2 + ClO^\bullet$ ---(7)

This radical can then react with another O_3 molecule to form more O_2 and regenerating the Cl atom

$O_3 + ClO^\bullet \rightarrow 2O_2 + Cl^\bullet$ ---(8)

These are the "propagation" stages of the reaction.

The regenerated Cl atom can then repeat reaction (7) followed by reaction (8) over and over again. As a result, just one Cl radical can be responsible for the loss of millions of O_3 molecules.

Note: If reactions (7) and (8) are added together to form an overall equation, the Cl and ClO radicals cancel.

$O_3 + \cancel{Cl^\bullet} \rightarrow O_2 + \cancel{ClO^\bullet}$

$O_3 + \cancel{ClO^\bullet} \rightarrow 2O_2 + \cancel{Cl^\bullet}$

Add $2O_3 \rightarrow 3O_2$

This shows that the Cl atom from the CFC acts as a catalyst for the decomposition of O_3. It must have a lower activation energy than the natural process [(5)] responsible for O_3 loss.

How is the ozone depletion by different substances assessed?

The "ozone depletion potential (ODP)" is the scale used to compare the abilities of various compounds to promote the depletion of ozone.

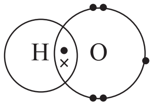
Note: The ODP of a given substance is defined as the global loss of ozone due to that substance compared to the global loss of ozone due to the same mass of trichlorofluoromethane ($CFCl_3$). $CFCl_3$ therefore has an ODP of 1.0.

Most other CFC's also have ODP values of 1.0 since they all contain the weaker C-Cl bond responsible for the initiation of the depletion process. However, related molecules which also contain H atoms (hydrochlorofluorocarbons [HCFC's]) such as chlorodifluoromethane (CHF_2Cl) have much lower ODP values (0.065 for CHF_2Cl). The presence of the C-H bond makes them susceptible to degradation by OH radicals present in the lower atmosphere (the troposphere). The degradation products are water soluble and are returned to earth in rain before most can reach the ozone layer.

Note: OH radicals arise from the photolysis of water molecules.

H_2O ----uv----> $HO^\bullet + H^\bullet$.

They are free radicals because of the unpaired electron on the O atom.



In contrast, related molecules which contain no Cl (hydrofluorocarbons (HFC's]) such as trifluoromethane (CHF_3) have zero ODP values because of the absence of the offending C-Cl bonds.

Note: Related bromo compounds have much higher ODP values (e.g. bromotrifluoromethane, $CBrF_3$; ODP = 9.2) because the C-Br bond is even weaker than a C-Cl bond and is more likely to produce radicals ($Br^\bullet$) to cause the depletion process.

How is the ozone layer being restored?

The protective role of the ozone layer in the upper atmosphere is so vital that scientists believe life on land probably would not have evolved - and could not exist today - without it! Consequently, from the 1980's when the depletion of ozone was confirmed by scientific investigation and finally acknowledged by governments, steps were taken in the Montreal Protocol (1987) to stop the depletion process. It took more than 10 years for western governments to respond to the scientific evidence! In brief, about 200 countries signed up to the Montreal Protocol and agreed to work to phase out the production and use of CFC's. This allowed for developed countries to phase out their use faster than more economically vulnerable developing countries.

It also allowed scientists time to develop and investigate alternative materials for use in aerosols, as refrigerants, as fire retardants etc. The protocol set a target of 2010 to eventually reduce manufacture and use of CFC's to zero.

Because of their much lower ODP values, HCFC's and HFC's were seen as suitable replacements for CFC's. However, their role as greenhouse gases has since been highlighted and scientists are now tasked with finding new compounds which have the same or better functionality without the disadvantages of ozone depletion and global warming.

Acknowledgements: *This Factsheet was researched and written by Mike Hughes*