

Stratospheric Chemistry

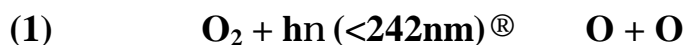
Some historical facts about ozone:

- 19th century discovery of ozone and its relevance for the Earth.
- in the beginning of 20th century first quantitative measurements of ozone by french scientists (Fabry and Buisson) by UV-spectroscopy.
- Dobson, a british scientist, developed a technique based on UV-measurements of ozone – the Dobson spectrometer, which is still in common use.
- in the 1930's Chapman proposed a mechanism for formation and destruction of ozone, later named after him Chapman mechanism.
- in the 1950's Bates and Nicolet proposed the contribution of water vapor to the ozone formation and destruction.
- in the 1960's researcher found due to accurate measurements that the Chapman mechanism predicts much more ozone as found in the Stratosphere and concluded that there must be more destruction mechanisms present!
- 1970 Crutzen discovered the role of NO_x as catalysator in the ozone destruction.
- 1974 Rowland and Molina discovered the role of CFC's in the ozone destruction.
- in 1985 first evidence was found for the Antarctic "ozone-hole".
- 1995 Crutzen, Molina and Rowland were awarded with the Nobel prize of Chemistry for their contribution in the field of atmospheric chemistry.

Chapman Mechanism:

The ozone formation and destruction (cycle) takes place between 25 and 30km altitude and needs UV-radiation with wavelength smaller than 242nm.

Start reaction:

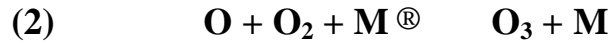


- slow and time determining

No.7

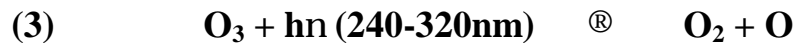
- only source of "odd oxygen"
- rate = $j_{O_2} [O_2]$

Cycle reaction:



- M usually O_2 or N_2
- fast reaction
- rate = $k[O] [O_2] [M]$
- only production way of O_3 in the Troposphere and Stratosphere

Cycle reaction:



- fast
- rate = $j_{O_3} [O_3]$
- cycles with (2)

Destruction:



- slow
- only sink of "odd oxygen"
- competes with (3), but (2) and (3) much faster and cycle many times before reaction (4) can take place
- rate = $k_1 [O_3] [O]$

The net rate for ozone formation is composed from the different step rates. Putting equations (2), (3) and (4) together gives us the production rate of ozone. The rate constants j and k are standing for the different processes with j dependent on absorption efficiency, light intensity etc.

$$\frac{d[O_3]}{dt} = k[O][O_2][M] - j_{O_3}[O_3] - k_1[O_3][O]$$

Due to the cycling between reaction (2) and (3), which is a rapid conversion between ozone and atomic oxygen (O and O₃), both species together are thought as a single species and are called "odd oxygen" or O_x.

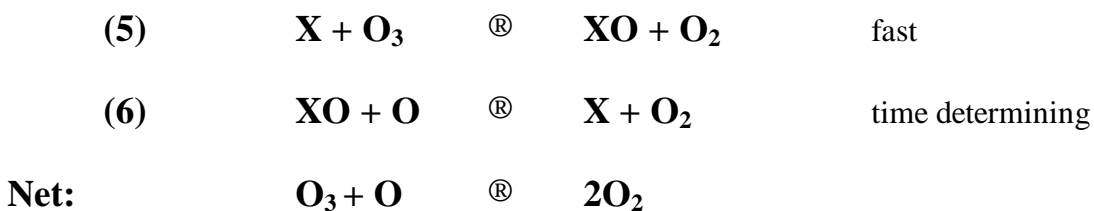
Since reactions (2) and (3) are much faster than reactions (1) and (4), there exists a pseudo steady-state concentration of O atoms governed by reactions (2) and (3).

$$\frac{[O]}{[O_3]} = \frac{J_{O_3}}{k[O_2][M]}$$

The formation of O is favoured at high altitudes, whereas the formation of O₃ is favoured at lower altitudes. The ozone production is highest near the equator and increases with increasing altitude. The highest concentrations of ozone, however, are found at higher latitudes. This disagreement between ozone production and highest concentration has its source in the horizontal and vertical transport patterns and the redistribution of stratospheric air masses. An occurrence of the highest concentration of ozone at higher latitudes suggests that the ozone molecule must have sufficient life time to be transported such far. The transport time from the equator to the poles is approximately 3 to 4 months. The lifetime of the ozone molecule varies with altitude: it is at 15km altitude (equator) about 3 years and at 40km altitude (equator) about 1 day. At altitudes lower than 20km at the equator and about 40km at the poles the lifetime of ozone would be enough to be transported intact.

In the 1960's accurate measurements of the rate constant for reaction (4) –the destruction of ozone- showed that the reaction is significantly slower as expected, thus the Chapman mechanism predicts a much higher ozone concentration as actually observed. As a conclusion there must be other pathways of ozone destruction present in the Stratosphere.

General Reaction for additional pathways:

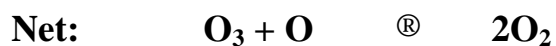
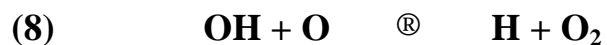


X: free radical: NO, H, OH, Cl, Br

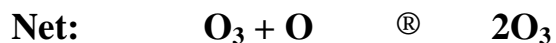
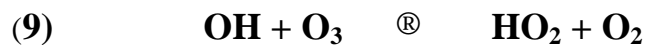
HO_x-Cycles

The first catalytic cycle identified for ozone involves the hydrogen containing radicals: H, OH and HO₂. Together they are called HO_x.

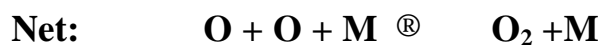
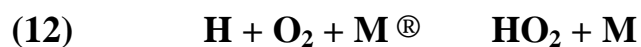
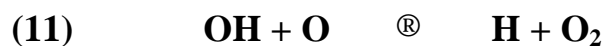
Cycle 1:



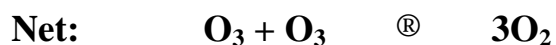
Cycle 2:



Catalytic *cycle 3* removes O from the system:



Cycle 4:



Whether Cycle 1, 2, 3, or 4 are active depends on the altitude as O, OH, HO₂ and also ozone have different mixing ratios at different altitudes.

OH mixing ratios: 1ppt at 16km 3ppt at 25km 400ppt at 45km.

HO₂ mixing ratios: 10ppt at 25km 200ppt at 45km

H mixing ratios: significant only >40km.

Cycle 1: important only above >40km altitude.

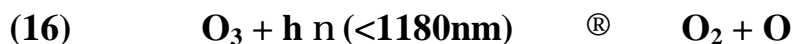
Cycle 2: is effective below <40km altitude.

Cycle 3: only important in the upper stratosphere.

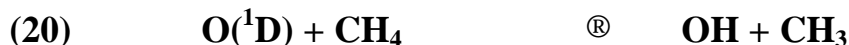
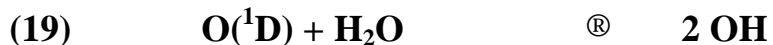
Cycle 4: important below <30km altitude.

Production of OH-radicals:

Atmospheric sources for the production of OH radicals are water vapor and methane. The whole process is only initiated by photolysis of O₃:



Most of the singlet D oxygen is quenched back by collision with O₂ and N₂, but the remaining part can react with H₂O and CH₄ to form OH:



NO_x-Cycles

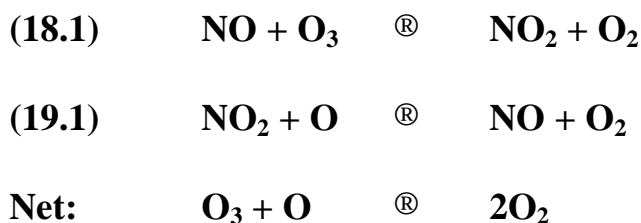
The only natural source of NO_x in the Stratosphere is the long-living species N₂O, transported by convective mixing from the Troposphere into the Stratosphere. N₂O can be activated by the following reactions in the Stratosphere:



The loss rates of N₂O are highest at the lower latitudes between 0 and 30degree at about 25-35km altitude.

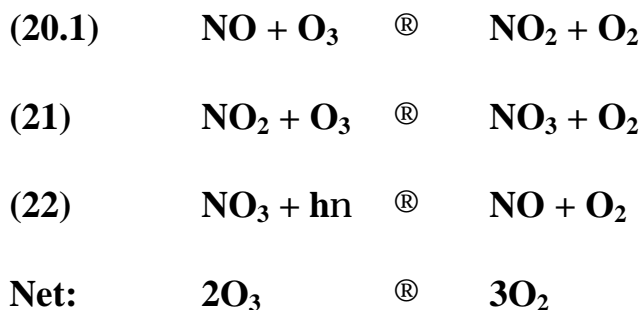
Two cycles are possible for the reaction of NO/NO₂ with O₃/O:

Cycle 1:

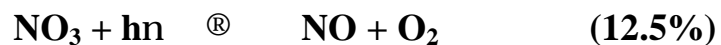


Reaction (18.1) is fast and has a characteristic time of 100s for an O₃-concentration of 5*10¹² molecules/cm³ at an altitude of 25km. If sufficient O is present reaction (19) controls the concentration of NO₂ relative to NO. Assumed there is O-concentration of 10⁸ molecules/cm³, the characteristic time for reaction (19) would be 870s thus exceeding reaction (18) and controlling the overall rate of in cycle 1.

Cycle 2:



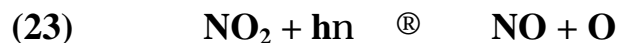
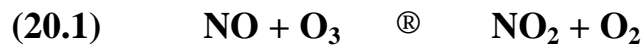
Reaction (22) happens very fast (0.2/s) during the day and has two possible pathways:



loss of odd nitrogen

A *null cycle* with respect to odd nitrogen exists, where NO_2 is temporarily not available for other reactions.

Null Cycle:



Odd nitrogen can be temporarily fixed as the reservoir species N_2O_5 , which experiences an equilibrium reaction with NO_2 and NO_3 , but can be transformed back to NO_2 and NO_3 by photolysis. The photolysis rate depends strongly on the presence of O_3 as both species absorb at the same wavelength. The lifetime of N_2O_5 is at 40km altitude about hours, but at 30km altitude several days (O_3 peaks here).



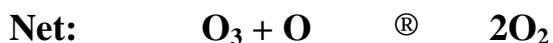
ClO_x-Cycles

The third group involved in O₃ destruction are the CFC's. CFC's were found in the early 1970's to be in equal concentration in the atmosphere as the amounts ever produced. Since they don't have any tropospheric sinks they diffuse into the stratosphere and are photolysed there by UV-radiation to active Cl or Br.



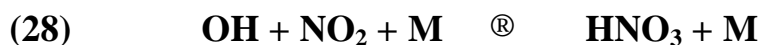
The maximum production of Cl appears to be at 23km altitude in the tropics due to the higher photolysis rate. The only natural source of Cl comes from CH₃Cl, released from the oceans to the atmosphere. Its lifetime is about 1.5 years. The following cycle is dominant above 20kms altitude for the destruction of ozone.

ClO_x-Cycle 1:



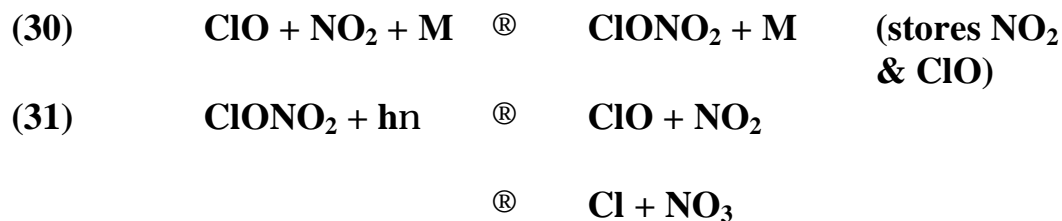
Reservoir Species and Coupling

Cycles 1&2 for HO_x and cycle 1 of NO_x and ClO_x (e.g. runs about 10⁵ times before Cl or ClO are removed ultimately) would continue forever, if not one of the active species is removed from the reaction by another pathway. The removal can be ultimately or temporarily as reservoir species. The removal is permanent when the species exits the Stratosphere and enters the Troposphere:



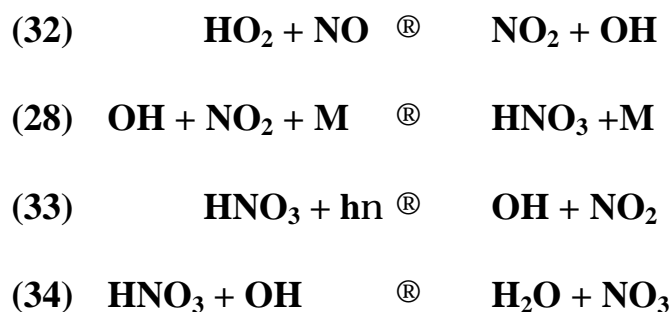
Both HCl and HNO₃ are rather stable in the Stratosphere thus able to diffuse down into the Troposphere and are there removed by wet-deposition.

Temporary removal happens via certain reservoir species, with ClONO₂ as the most important ones.

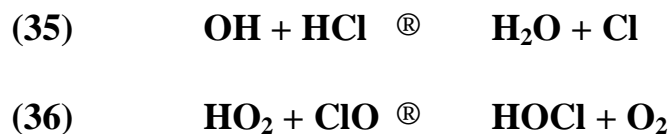


As we can see in equations (30) and (31) the ClO_x and NO_x cycles are coupled. Indeed HO_x, NO_x and ClO_x cycles are all coupled with each other in one or the other way and their interrelationship governs strongly the stratospheric ozone chemistry.

Coupling of NO_x and HO_x cycles:



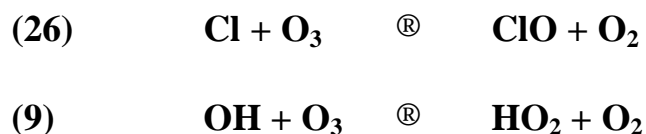
Coupling between HO_x and ClO_x-cycles:

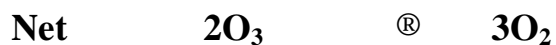
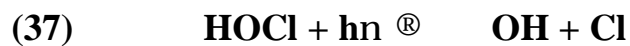


The reservoir species HCl and ClONO₂ store together about 99% of the active Cl-species.

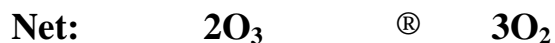
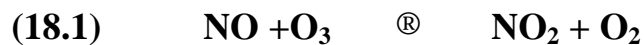
Above 20km altitude ClO_x-cycle 1 is responsible for ozone destruction, whereas below 20km altitude cycles involving coupling become dominant.

HO_x/ClO_x-cycle:

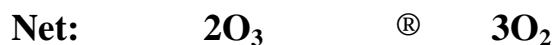
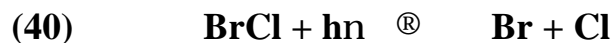
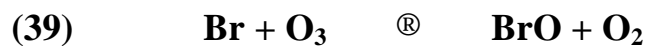
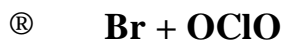




Coupling of NO_x/ClO_x-cycles:



A BrO_x-cycle exists similar to the ClO_x-cycle. Coupling of both cycles produces free Cl and Br atoms:



Despite the lower Br-concentrations in the atmosphere relative to Cl, the Br-species react much more efficient in removing O₃ as the two reservoir species BrONO₂ and HBr are much less abundant due to high photolysis rates for BrONO₂ and the endothermic reaction of forming HBr.

From all reactions it turns out that reaction (32) is extremely relevant for stratospheric chemistry as it governs the distribution of NO and NO₂ as well as the OH free radicals, which in turn influence several other reactions.

Reaction (32):



Observations and Predictions

In situ measurements by balloons and aircrafts showed that at latitudes <46 degree the ozone production exceeds the ozone loss. This is due to the photolysis of O₂, which does not occur until the sun stands higher than 45 degree above the horizon. Thus the ozone production is interrupted between fall and spring in the higher latitudes as the incoming radiation is not enough to photolyse O₂. The net-removal during this times is largest, however, since the radiation penetrating to the Earth at this latitudes is enough to drive the catalytic cycles.

The chemical destruction of ozone is rather slow in the lower Stratosphere as most of the radical are short lived and produced photochemically, with the exception of NO₂, which is cycled into HNO₃ during the *day* by:

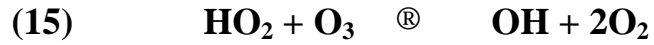


and during the *night* by



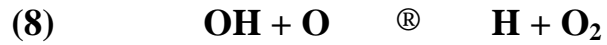
HO_x-cycle 4 accounts for about 30-50% of the total ozone loss in the lower Stratosphere:





whereas cycle 1 and 5 are responsible for a high loss of ozone in the upper Stratosphere:

Cycle 1:



Cycle 5:



The NO_x-cycles 2 & 4 account for about 20% loss of ozone in the lower Stratosphere, whereas the remaining part is destroyed by ClO_x and BrO_x- mechanisms.

Ozone hole

In 1985 British scientists discovered a massive annual decrease of stratospheric ozone over Antarctica in the polar spring (September/October). Despite routine satellite measurements were carried out, the findings came as surprise. The satellite measurements could not confirm these results on the first view, but after careful looking into the satellite measurements it turned out that also there a steep decrease was detected, but systematically rejected as out of the reasonable range of data. After revision, the satellite data confirmed the ozone depletion over Antarctica. The measurement showed that the monthly mean column of ozone over Halley Bay, Antarctica, decreased from 350DU in the mid 70's to about 100DU in 1985. Balloon borne instruments detected the region of ozone depletion between 10-20km altitude.

Situation:

The Antarctic has some of the highest ozone concentrations throughout much of the year due to the transport of ozone and other species from the tropics by large-scale air motions. The production of ozone at the Antarctic itself is very low because of the absence of sunlight. In winter the air cools down and descends, developing a westerly circulation, which is called the polar vortex. This polar vortex develops a core of very cold air, which is very stable in winter and early spring and sealing efficiently off the air from outside. The vortex keeps high levels of ozone trapped over Antarctica, sufficient to block of the UV-radiation from space. By return of the sun in September the temperature increases, weakening the polar vortex, which breaks up some time in November and allows transport of ozone and other species to the Antarctic. Under normal circumstances the ozone amount in the vortex decreases at the end of the winter in late August-beginning of September. After the sun is back, it levels off in October to be increasing in November. However, the observations from 1985 showed that something is disturbing this mechanism destroying obviously much more ozone as before. Several different theories involving oxygen atoms were developed and rejected as not applicable in the polar regions. Finally an explanation might be found by involving polar stratospheric clouds.

Polar Stratospheric Clouds

Molina discovered that a mechanism involving the ClO-dimer Cl_2O_2 might be responsible for ozone depletion, but the amount and reactions happening in the gas-phase are not sufficient to explain the high decrease.

The Stratosphere is extremely dry and cloudless, but during the polar night the temperatures drop to 183K at about 15-20km altitude allowing even the smallest amount of water to be condensed. This condensed water forms so-called polar stratospheric clouds (PSC). The PSC's can remain a long time very stable as the polar vortex is also

extremely stable in this region. In the Stratosphere is a natural aerosol layer present consisting of small H_2SO_4 -droplets at an altitude of 12-30km. In the midlatitude Stratosphere at 16km at $T=220\text{K}$ the aerosols consists of about 70-75 weight% H_2SO_4 and rest water. Decreases the temperature the particles absorb more water to keep the equilibrium and at about 195K they contain only about 40 weight% H_2SO_4 . At such low temperatures the aqueous sulfuric acid aerosol can absorb quantities of HNO_3 to form ternary solutions of $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$. With further temperature drop, more HNO_3 and H_2O can be absorbed, forming PSC-particles composed almost entirely of $\text{HNO}_3/\text{H}_2\text{O}$. PSC are generally distinguished in two different categories: Type I consists of $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ (NAT) crystals and the ternary mixture of $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$. Type II is composed of only frozen water. The exact mechanism how PSCs form is still unresolved!

Table1: Types of PSCs

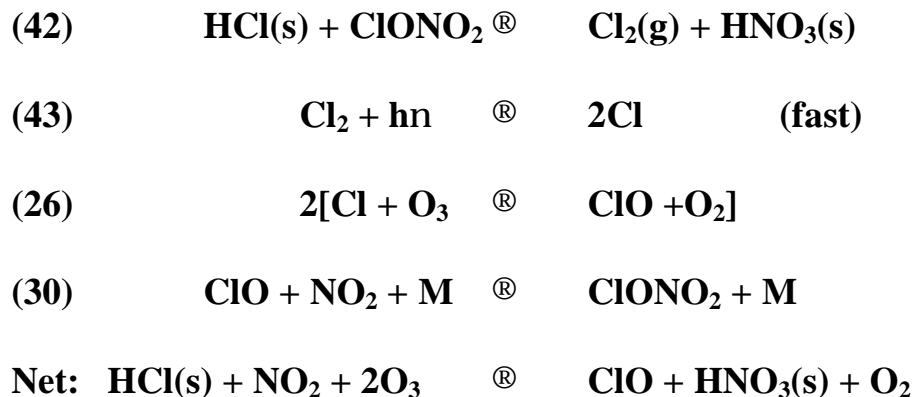
Class	Composition	Structure	Temperature of formation
Type Ia	$\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ (NAT)	non-spherical, crystalline	~190-195K
Type Ib	$\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$	spherical liquid	~190-195K
TypeII	H_2O ice	non-spherical, crystalline	~188-190K

Heterogenous reactions happening onto the PSC's play a key role in ozone destruction. Both the ozone hole and the PSC's appear in 10-25km altitude and the heterogenous surfaces promote the process of releasing active Cl from the reservoir species HCl and ClONO_2 .

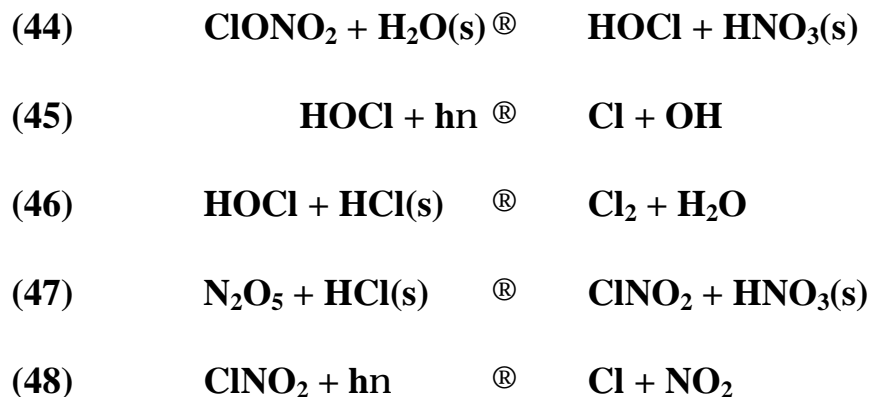


With reaction (41) HCl gas is absorbed by PSCs. This heterogenous surface can react with the other reservoir species to form in reaction $\text{Cl}_2(\text{g})$ and $\text{HNO}_3(\text{s})$ retained on ice. Reaction (42) is the most chlorine-activating reaction in the polar Stratosphere, since when temperatures drop below 200K the stratospheric particles absorb water and HCl to maintain in equilibrium. With reaction (42) HNO_3 is trapped on the ice and nitrogen compounds efficiently removed from the Stratosphere enhancing therefore the destruction by ozone. Remember: $\text{NO}_2 + \text{ClO} \rightarrow \text{ClONO}_2(\text{reservoir})$

The following reactions take place further:



Other reactions releasing active Cl can occur:

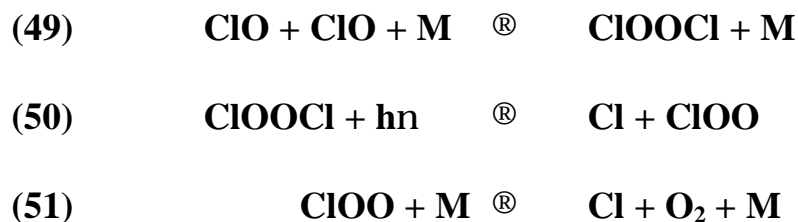


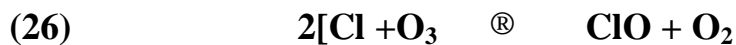
In all cases the start reaction occurs on the PSC and without this most of the reactions would be extremely slow or never happening. To bring it to the point, the conditions, which favour ozone destruction in the polar regions are *cold temperatures and sunlight*.

Cold temperature to form polar stratospheric clouds acting as surface for heterogenous reactions.

Sunlight to photolyze the formed reactive Cl-species Cl_2 , HOCl and ClNO_2 and release Cl, which in turn destroys ozone.

Reaction of the ClO with ozone:



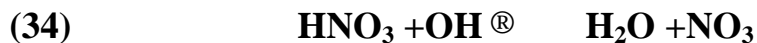
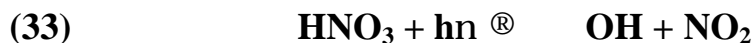


Since most of the NO_x is trapped in the ice of the PSC's, reaction (30) cannot take place to moderate the effect and remove ClO from the system:



Within the polar vortex and out of it the transport is extremely slow, much slower as the characteristic time needed to destroy ozone. ClO concentrations of about a factor of 100 higher as normal were found in 12-24km altitude to confirm this theory.

As soon as the sun is back and the temperature rises enough the PSCs evaporate releasing HNO_3 into the Stratosphere.



The arctic ozone hole

In the last years measurements showed that also in the arctic ozone is dramatically decreasing. The situation in the arctic is not such critical as at the Antarctic as the winter temperatures are about 10K higher there. This means that the polar vortex is far less stable and still parcels of transported air can supply ozone and other species. Furthermore the occurrence of PSC's is much more rarely thus lacking the surfaces for heterogenous reactions. In March 95 however, an extremely cold winter was experienced and ozone levels dropped to about 50% of their usual values.