

Q7

What are the reactive halogen gases that destroy stratospheric ozone?

The chlorine- and bromine-containing gases that enter the stratosphere arise from both human activities and natural processes. When exposed to ultraviolet radiation from the Sun, these halogen source gases are converted to more reactive gases that also contain chlorine and bromine. Some reactive gases act as chemical reservoirs which can then be converted into the most reactive gases, namely ClO and BrO. These most reactive gases participate in catalytic reactions that efficiently destroy ozone.

Halogen-containing gases present in the stratosphere can be divided into two groups: *halogen source gases* and *reactive halogen gases* (see **Figure Q7-1**). The source gases, which include ozone-depleting substances (ODSs), are emitted at Earth's surface by natural processes and by human activities (see Q6). Once in the stratosphere, the halogen source gases chemically convert at different rates to form the reactive halogen gases. The conversion occurs in the stratosphere instead of the troposphere for most gases because solar ultraviolet radiation (a component of sunlight) is more intense in the stratosphere (see Q2). Reactive gases containing the halogens chlorine and bromine lead to the chemical destruction of stratospheric ozone.

Reactive halogen gases. The chemical conversion of halogen source gases, which involves solar ultraviolet radiation and other chemical reactions, produces a number of reactive halogen gases. These reactive gases contain all of the chlorine and bromine atoms originally present in the source gases. The most important reactive chlorine- and bromine-containing gases that form in the stratosphere are shown in Figure Q7-1. Throughout the stratosphere, the most abundant are typically hydrogen chloride (HCl) and chlorine nitrate (ClONO₂). These two gases are considered important *reservoir* gases because, while they do not react directly with ozone, they can be converted to the *most reactive* forms that do chemically destroy ozone. The most

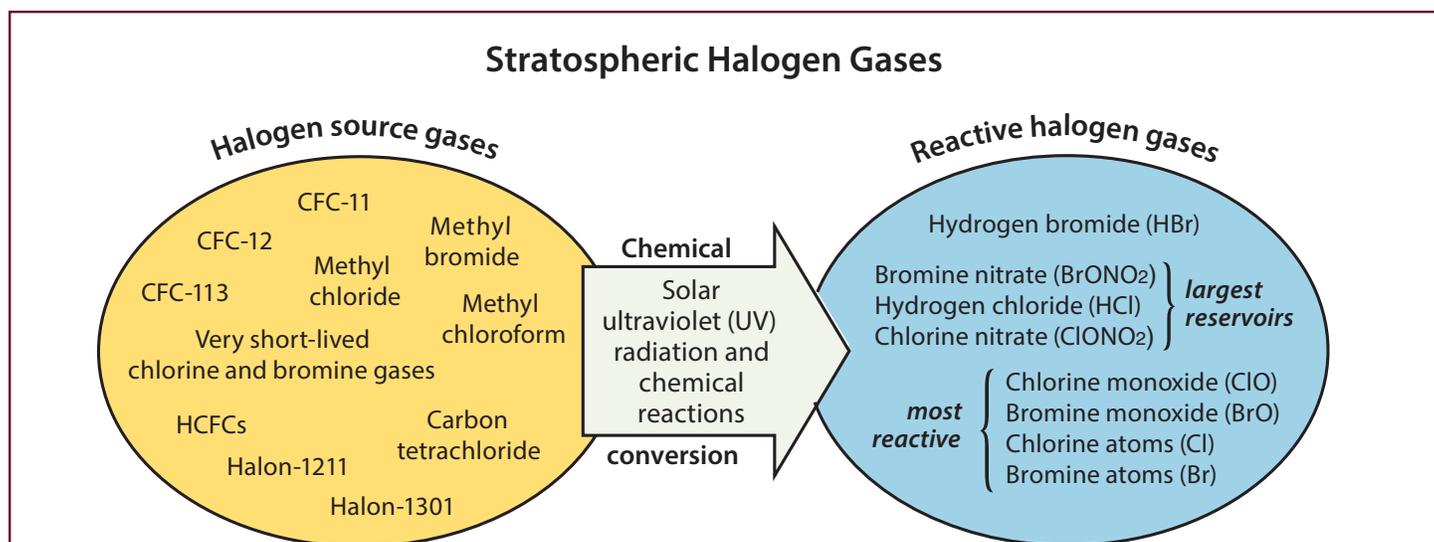


Figure Q7-1. Conversion of halogen source gases. Halogen source gases containing chlorine and bromine are chemically converted to reactive halogen gases, primarily in the stratosphere. Most of the halogen source gases are ozone-depleting substances. The conversion requires solar ultraviolet radiation and a few chemical reactions. The shorter-lived gases undergo partial conversion in the troposphere. The reactive halogen gases contain all the chlorine and bromine originally present in the source gases before conversion. The reactive gases can be grouped into the reservoir gases, which do not directly destroy ozone, and the most reactive gases, which participate in ozone destruction cycles (see Q8). A principal reactive gas, ClO, is formed by reactions of the reservoir gases HCl and ClONO₂ that occur on the surfaces of liquid and solid polar stratospheric clouds (PSCs) (see Q9).

reactive forms are chlorine monoxide (ClO) and bromine monoxide (BrO), and chlorine and bromine atoms (Cl and Br). A large fraction of total reactive bromine is generally in the form of BrO, whereas usually only a small fraction of total reactive chlorine is in the form of ClO. The special conditions that occur in the polar regions during winter cause the reservoir gases HCl and ClONO₂ to undergo nearly complete conversion to ClO in reactions on polar stratospheric clouds (PSCs) (see Q9).

Reactive chlorine at midlatitudes. Reactive chlorine gases have been observed extensively in the stratosphere using both local and remote measurement techniques. The measurements from space displayed in **Figure Q7-2** are representative of how the amounts of chlorine-containing gases change between the surface and the upper stratosphere at middle to high latitudes. Total available chlorine (see red line in Figure Q7-2) is the sum of chlorine contained in halogen source gases (e.g., CFC-11, CFC-12) and in the reactive gases (e.g., HCl, ClONO₂, and ClO). Available chlorine is constant to within about 10% from the surface to above 50 km (31 miles) altitude. In the troposphere, total chlorine is contained almost entirely in the source gases described in Figure Q6-1. At higher altitudes, the source gases become a smaller fraction of total available chlorine as they are converted to the reactive chlorine gases. At the highest altitudes, available chlorine is all in the form of reactive chlorine gases.

In the altitude range of the ozone layer at midlatitudes, as shown in Figure Q7-2, the reservoir gases HCl and ClONO₂ account for most of the available chlorine. The abundance of ClO, the most

reactive gas in ozone depletion, is a small fraction of available chlorine. The low abundance of ClO limits the amount of ozone destruction that occurs outside of polar regions.

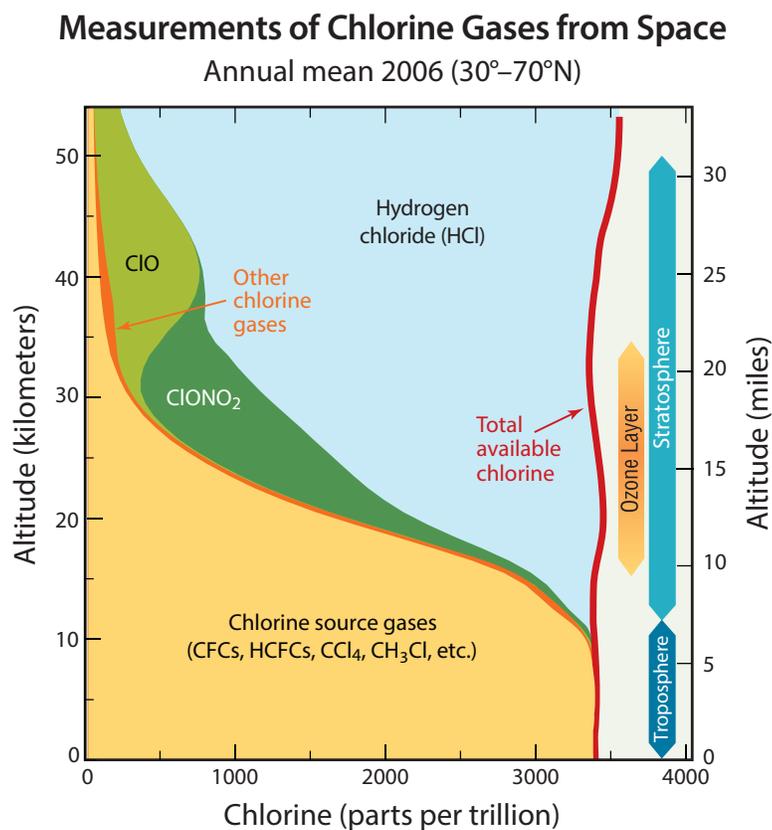
Reactive chlorine in polar regions. Reactive chlorine gases in polar regions undergo large changes between autumn and late winter. Meteorological and chemical conditions in both polar regions are now routinely observed from space in all seasons. Autumn and winter conditions over the Antarctic are contrasted in **Figure Q7-3** using seasonal observations made near the center of the ozone layer (about 18 km (11.2 miles) altitude; see Figure Q11-3).

Ozone values are high over the entire Antarctic continent during autumn in the Southern Hemisphere. Temperatures are mid-range, HCl and nitric acid (HNO₃) are high, and ClO is very low. High HCl indicates that substantial conversion of halogen source gases has occurred in the stratosphere. In the 1980s and early 1990s, the abundance of reservoir gases HCl and ClONO₂ increased substantially in the stratosphere following increased emissions of halogen source gases. HNO₃ is an abundant, primarily naturally-occurring stratospheric compound that plays a major role in stratospheric ozone chemistry by both moderating ozone destruction and condensing to form PSCs, thereby enabling conversion of chlorine reservoir gases to ozone-destroying forms. The low abundance of ClO indicates that little conversion of the reservoir gases occurs in the autumn, thereby limiting catalytic ozone destruction.

Figure Q7-2. Reactive chlorine gas observations.

The abundances of chlorine source gases and reactive chlorine gases as measured from space in 2006 are displayed as a function of altitude for a range of latitudes. In the troposphere (below about 12 km), all of the measured chlorine is contained in the source gases. In the stratosphere, the total chlorine content of reactive gases increases with altitude as the amount of chlorine source gases declines. This is a consequence of chemical reactions initiated by solar ultraviolet radiation that convert source gases to reactive gases (see Figure Q7-1). The principal reactive chlorine gases formed are HCl, ClONO₂, and ClO. Adding up the source gases with the reactive gases gives “Total available chlorine”, which is nearly constant with altitude throughout the stratosphere. In the ozone layer (15–35 km), chlorine source gases are still present and HCl and ClONO₂ are the most abundant reactive chlorine gases at midlatitudes.

(The unit “parts per trillion” is defined in the caption of Figure Q6-1.)



By late winter (September), a remarkable change in the composition of the Antarctic stratosphere has taken place. Low amounts of ozone reflect substantial depletion at 18 km altitude over an area larger than the Antarctic continent. Antarctic ozone holes arise from similar chemical destruction throughout much of the altitude range of the ozone layer (see altitude profile in Figure Q11-3). The meteorological and chemical conditions in late winter, characterized by very low temperatures, very low HCl and HNO_3 , and very high ClO, are distinctly different from those found in autumn. Low stratospheric temperatures occur during winter, when solar heating is reduced. Low HCl and high ClO reflect the conversion of the reactive halogen reservoir compounds, HCl and ClONO_2 , to the most reactive form of chlorine, ClO. This conversion occurs selectively in winter on PSCs, which form at very low temperatures (see Q9). Low HNO_3 is indicative of its condensation to form PSCs, some of which subsequently descend to lower altitudes through gravitational settling. High ClO abundances generally cause ozone depletion to continue in the Antarctic region until mid-October (spring), when the lowest ozone values usually are observed (see Q10).

As temperatures rise at the end of the winter, PSC formation is halted, ClO is converted back into the reservoir species HCl and ClONO_2 (see Q9), and ozone destruction is curtailed.

Similar though less dramatic changes in meteorological and chemical conditions are also observed between autumn and late winter in the Arctic, where ozone depletion is less severe than in the Antarctic.

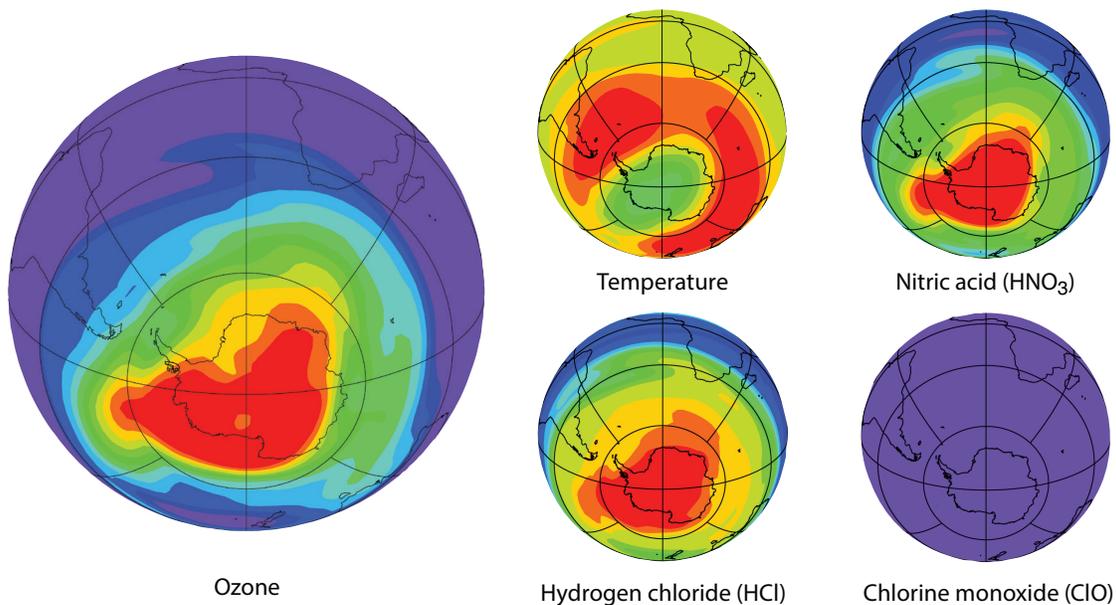
Reactive bromine observations. Fewer measurements are available for reactive bromine gases in the lower stratosphere than for reactive chlorine. This difference arises in part because of the lower abundance of bromine, which makes quantification of its atmospheric abundance more challenging. The most widely observed bromine gas is BrO, which can be observed from space. Estimates of reactive bromine abundances in the stratosphere are larger than expected from the conversion of the halons and methyl bromide source gases, suggesting that the contribution of the very short-lived bromine-containing gases to reactive bromine must also be significant (see Q6).

Figure Q7-3. Chemical conditions in the ozone layer over Antarctica. Observations of the chemical conditions in the Antarctic region highlight the changes associated with the formation of the ozone hole. Satellite instruments have been routinely monitoring ozone, reactive chlorine gases, and temperatures in the global stratosphere. Results are shown here for autumn (May) and late winter (September) seasons in the Antarctic region, for a narrow altitude region near 18 km (11.2 miles) within the ozone layer (see Figure Q11-3). Ozone has naturally high values in autumn, before the onset of ozone destruction reactions that cause widespread depletion. The high ozone is accompanied by moderate temperatures, high values of HCl and HNO_3 , and very low amounts of ClO. When the abundance of ClO is low, significant ozone destruction from halogens does not occur. Chemical conditions are quite different in late winter when ozone undergoes severe depletion. Temperatures are much lower, HCl has been converted to ClO (the most reactive chlorine gas), and HNO_3 has been removed by the gravitational settling of polar stratospheric cloud particles. The abundance of ClO closely surrounding the South Pole is low in September because formation of ClO requires sunlight, which is still gradually returning to the most southerly latitudes. The high values of ClO in late winter cover an extensive area that at times exceeds that of the Antarctic continent and can last for several months, leading to efficient destruction of ozone in sunlit regions in late winter/early spring. Ozone typically reaches its minimum values in early to mid-October (see Q11). Note that the first and last colors in the color bar represent values outside the indicated range of values.

(The unit “parts per billion,” abbreviated “ppb,” is used here as a measure of the relative abundance of a substance in dry air: 1 part per billion equals the presence of one molecule of a gas per billion ($=10^9$) total air molecules (compare to ppt in Figure Q6-1).)

Chemical Conditions Observed in the Ozone Layer Over Antarctica

Normal ozone amounts in autumn (1 May 2008) at 18 km altitude



Large ozone depletion in late winter (15 September 2008) at 18 km altitude

