Toward the theory of ozone hole

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The presented theory of the ozone hole has been developed based on four fundamental physical-chemical factors: (1) the technogenic-freon impact on the ozone layer started in the past century; (2) the presence in the atmosphere of photochemical equilibrium of families of odd constituents at daytime, proved by the calculations and permitted the concentrations of atomic oxygen, chlorine, ozone, and other components in the ozone hole to be calculated correctly without the use of heterogeneous reactions; (3) the action of catalytic cycles in the stratosphere, depleting and generating ozone; (4) a new physical insight into the atmospheric front, including polar stratospheric front (PSF) in Antarctic as an air shield preventing different air masses from turbulent horizontal mixing and forming a dynamically isolated part of the atmosphere inside the polar stratospheric cyclone (PSC) in Antarctic. The theory development is based on readily reproducible calculations, which rest on derived formulas and data of satellite, aircraft, and balloonsonde measurements of concentration of atmospheric minor constituents. The developed theory does not contradict the experimental facts and explains all known features of the ozone hole.

Introduction

At the end of the twentieth century, a non-predicted large-scale ecological catastrophe had occurred in the Earth's atmosphere, continuing each spring until presently and resulting in the damage of a considerable part of the earth's ozone shield in Antarctic and adjacent regions.[1–7,18,32] Simultaneously, there occurred significant changes in the atmospheric chemical composition, optical properties, and radiation regime in these regions. The destruction of the ozone layer in Antarctic (ozone hole) was first discovered in 1984 by Japanese scientists during ground-based and balloonborne observations at Syowa station but has not been given a due attention,[8] and in 1985 (independently and with a larger array of data) by English scientists at Halley Bay and Argentina Island,[9] who pointed out to possible anthropogenic origin and ecological danger of this phenomenon. Later on, the springtime ozone depletion was confirmed by other researchers, including those at the Main Geophysical Observatory and Institute of the Arctic and Antarctic, Russian Federation,[1,2,33,34] dealing with measurements and analysis of variations of atmospheric ozone in Antarctic. As the result of the balloonsonde and satellite measurements, it has been found that the total ozone (TO) in the ozone hole decreases by 50–70%, the ozone concentration at a height of 15–20 km – by 95–97% (Ref. 10), and the ozone hole size corresponds to the area of Europe.[5]

Despite 18 years elapsed since the discovery of the ozone hole and much work was done to interpret this dangerous phenomenon, no generally accepted theory of the ozone hole still exists. This prevents answering correctly a number of questions on actual causes of the ozone hole formation, growth, intensification of ozone depletion in the ozone hole, possibility of ozone holes development in other regions of the globe, as well as on well grounded methods of preventing anthropogenic destruction of the ozone layer, protecting all living matters on the Earth from harmful effect of the solar short-wave ultraviolet radiation.

Because the ozone catastrophe can serve as a warning against further large-scale stratospheric pollution and great expenses are required to its rapid elimination, this phenomenon needs for manifold responses from the scientific community including a creation of the generally accepted theory of the ozone hole.

After detection of the ozone hole, a few hypotheses were proposed to explain its origin,[2,3,32] almost all of which being subsequently rejected, except for the freon-heterogeneous one.[6,7,13,18,19] Briefly, it is based on two key factors:

1) a doubtless factor that chlorine-containing gaseous compounds of the anthropogenic origin (primarily chlorofluorocarbons or freons CFC-11 ($CFCl_3$), CFC-12 (CF_2Cl_2), and CFC-10 (CCl_4)), whose production permanently grew in 1930s – 1980s, lifting in the atmosphere and propagating around the globe through turbulent mixing, photodissociate due to shortwave solar ultraviolet radiation in the lower stratosphere, and release atomic chlorine. The latter reacts with ozone to produce the chlorine monoxide ClO, whose concentration grows with time under daytime conditions. Chlorine oxide, interacting day and night with nitrogen dioxide NO_2, has formed for the indicated period relatively chemically stable chlorine nitrate $ClONO_2$, which increases from year to year in concentration,[16,17] and this increase takes place during polar night (Table 1). At daytime, the chlorine nitrate participates in the first catalytic cycle (Table 5) as a catalyst, and in the spring season

its concentration remains unchanged. At the same time, in Antarctic and, partly, in Arctic, in the daytime lower stratosphere, the nitrogen-containing species NO_2 and NO (Table 2), as well as related to them HNO_3 decrease in concentration at the cost of increasing concentration of ClO. In spring, August, and September, under daytime conditions, due to absence of the photochemical equilibrium of the O_x family, the atomic chlorine, chlorine monoxide, and atomic oxygen participate as catalysts (and, hence, do not change in concentration) in the 1st and 2nd catalytic cycles (Tables 5 and 7), which rapidly destruct ozone in the lower stratosphere without any marked compensation by the 3rd cycle. In addition, the atomic chlorine interacts with methane (much slower than with O_3) and produces hydrochloric acid HCl, which is relatively inactive in the stratosphere and, unlike $ClONO_2$, is capable to dissolve in particles of polar stratospheric clouds (PSC) and aerosol and can be slowly removed from the stratosphere through the particle coagulation and gravitational settling, thereby influencing the chlorine budget in the stratosphere and the process of the ozone hole degradation.

As a whole, from the data of observations and calculations, in the last quarter of the twentieth century the anthropogenic activity has led to increase of the chlorine-containing species and decrease of the nitrogen-containing ones in the Antarctic stratosphere with a simultaneous ozone decrease in spring, as is seen from Table 2. Note that the calculated data on concentrations of constituents in Table 2 and the tendency of their variations are given not on the basis of freon-heterogeneous hypothesis (the correct data on the species concentrations calculated according to this hypothesis, are unavailable), but they are based on the theory presented below;

2) Erroneous factor, which arises from some underestimation of daytime concentrations of atomic chlorine and oxygen in the lower stratosphere,[12,23] and which, as will be shown below, can be omitted in the development of the ozone hole theory; its essence is that during polar night at low temperatures in the Antarctic stratosphere, a quite serious complex of heterogeneous reactions is hypothesized to occur on the surface of PSC and aerosol particles, namely[13]

$$ClONO_2 + \underline{H_2O} \rightarrow HOCl + \underline{HNO_3}$$

$$ClONO_2 + \underline{HCl} \rightarrow Cl_2 + \underline{HNO_3}$$

$$N_2O_5 + \underline{H_2O} \rightarrow \underline{2HNO_3}$$

$$N_2O_5 + \underline{HCl} \rightarrow ClNO_2 + \underline{HNO_3}$$

$$HOCl + \underline{HCl} \rightarrow Cl_2 + \underline{H_2O},$$

where non-underlined species are in the gas-phase state, while underlined ones are in solution. The efficiency of these reactions increases with decreasing stratospheric temperature.

With chlorine-containing species, too abundant in recent decades, in the winter Antarctic stratosphere, due to heterogeneous destruction of $ClONO_2$ and HCl, the above reactions result in formation of gaseous species Cl_2, HOCl, and $ClNO_2$, which later, under exposure to spring sun, rapidly photodissociate to produce atomic chlorine, which destructs ozone. It is erroneously assumed that there is no photochemical equilibrium of the odd oxygen family including ozone in the lower stratosphere (10–25 km) throughout the year. This assumption is based on widely known but incorrect estimates,[23,12] as argued in Ref. 20, that the chemical lifetime of the odd oxygen family at altitudes of 10–25 km at daytime exceeds 70 days, which is much larger than the maximum permissible limit for establishment of photochemical equilibrium equal to one day.[12]

Like any other hypothesis, in order to be widespread, the freon-heterogeneous hypothesis, namely its main principles and conclusions, should not contradict the experimental facts and should explain all specific features of the ozone hole. However, upon careful examination, this hypothesis is in conflict with a number of available experimental facts.

Table 1 presents average data of satellite and balloonsonde measurements of the $ClONO_2$ concentration at a height of about 20 km, close to the altitude of the ozone maximum; the data were obtained in winters of 1992–1993 in Antarctic and Arctic,[13] i.e., when the ozone hole was already regular in spring.

Table 1. Results of measurements of area-average $ClONO_2$ and HNO_3 concentrations (molecule · cm^{-3})* in near-pole regions of Antarctic and Arctic in the period of polar night at a height of about 20 km according to satellite and balloon measurements[13]

Antarctic		Arctic	
Date	Concentration	Date	Concentration
Satellite measurements ($ClONO_2$)		Satellite measurements ($ClONO_2$)	
06/02/92	$5.4 \cdot 10^8$	12/03/92	$9.0 \cdot 10^8$
08/17/92	$2.7 \cdot 10^9$	02/22/93	$2.6 \cdot 10^9$
Satellite measurements (HNO_3)		Balloon measurements ($ClONO_2$), Sweden, Kiruna (68°N)	
06/02/92	$6.3 \cdot 10^9$	01/13/92	$5.0 \cdot 10^8$
08/17/92	$1.5 \cdot 10^9$	03/14/92	$3.6 \cdot 10^9$

* Further we present concentrations of atmospheric constituents mostly without designation of the dimensions.

It follows from Table 1 that there was an increase, and not a decrease, of the $ClONO_2$ concentration in the lower stratosphere in Antarctic and Arctic in winter of 1992–1993, that contradicts the freon-heterogeneous hypothesis of the ozone hole. In spring during day the growth of $ClONO_2$ concentration is impossible due to action of catalytic cycle (Tables 5 and 9), because of which the rates of $ClONO_2$ destruction and formation become identical (such as equal to $2.1 \cdot 10^5$ molecules · $cm^{-3} \cdot s^{-1}$ at height of 20 km). At the same time, nearly identical

$ClONO_2$ concentrations and their variations were observed in Arctic and Antarctic, despite 20–30°K higher stratospheric temperatures in Arctic than in Antarctic, that again contradicts the freon-heterogeneous hypothesis. In addition, Table 1 presents the data of measurements of area-average concentrations of HNO_3 in the central part of Antarctic in 1992, from which it follows that in winter the HNO_3 concentration has decreased, once again contradicting the action of the complex of heterogeneous reactions (or at least signifying their low efficiency).

In addition, a disadvantage of the freon-heterogeneous hypothesis of the ozone hole is the absence of correct physical model of dynamics of the Antarctic stratosphere, having a direct bearing on formation and evolution of the ozone hole.

1. Formulation of the problem and key factors of the ozone hole theory

The present paper is devoted to creation of the ozone hole theory which does not contradict the available experimental data, is able to explain the features of the phenomenon under study, has no obscuring disadvantages, and can allow correct calculation of concentrations of atmospheric constituents of the ozone hole including ozone.

The foundation of the ozone hole theory are four factors:

1) The above-mentioned factor, used in the freon-heterogeneous hypothesis and taking into account the anthropogenic freon emissions to the stratosphere in the second part of the past century. In this development, all calculations use only homogeneous chemical reactions.

2) It is assumed that in Antarctic stratosphere, with increased concentration of chlorine-containing constituents at daytime in spring, the photochemical equilibrium is established for families of odd constituents

oxygen $(O_x) = (O) + (O'_D) + (O_3)$,
nitrogen $(NO_x) = (NO) + (NO_2) + (NO_3)$,
hydrogen $(HO_x) = (H) + (OH) + (HO_2)$,
chlorine $(Cl_x) = (Cl) + (ClO) + (ClOO) + (OClO) + (HOCl) + (ClONO_2) + (ClNO) + (ClONO) + (HCl)$,
bromine $(Br_x) = (Br) + (BrO)$,

and individual constituents – (Cl_2O_2) and (Cl_2), which is confirmed by calculations of their chemical lifetime presented in Table 3 (for O_x family, the equilibrium is established in October, and remains practically unchangeable in other periods in spring).

3) To calculate the ozone concentration decrease in the stratosphere, three well-known powerful catalytic cycles[27] are used, which destruct (cycles 1–2, Table 5) and form (cycle 3, Table 5) ozone in the atmosphere with increased concentration of chlorine-containing species.

4) A physical model is used of stratospheric dynamics in Antarctic for winter-spring period.[21,22,26] This model is based upon a new concept of atmospheric front as a dynamic system inhibiting the horizontal turbulent exchange (DSITE), obtained from a combined analysis of fields of ozone, temperature, pressure, wind, and other atmospheric variables. In this case, DSITE is a relatively narrow vertical or slant atmospheric layer with maximal along-front velocity of wind, identified with a well-known physical phenomenon, namely, air curtain (which, moreover, has a practical use as a permanently open door in public buildings in winter period, which prevents mixing of warm and cold air from inside and outside of the building). The role of the DSITE air curtain is played in this case by the polar stratospheric front (PSF), surrounding the near-pole region, inhibiting the horizontal turbulent mixing of polar and midlatitude air masses in the stratosphere, and forming in the winter–spring period the dynamically isolated part of the stratosphere in the inner part of Antarctic polar stratospheric cyclone (PSC), bounded by PSF and being the territory of the ozone hole. Because of the presence of DSITE (or PSF in this case), there is almost no supply of ozone and other constituents to the central part of Antarctic region and no large-scale horizontal exchange of gas constituents with surrounding stratosphere at lower stratospheric heights in the winter–spring period.

2. The order of constituent parts of the ozone hole theory and calculation results

The logical order of constituent parts of the ozone hole theory is as follows.

1) Chemical lifetimes τ_A for the above-mentioned atmospheric constituents and τ_{A_x} for families are calculated for conditions of increased concentration of chlorine-containing species observed in the ozone hole (Table 2). Values of τ_A are calculated by a well-known method from Ref. 12; the τ_{A_x} calculations use the method developed by the author.[20] To do this, the well-known chemical and photochemical reactions (160 in all) of atmospheric constituents are used, as well as constant reaction rates k_i (numbered by the author in Ref. 20) and photodissociation rate coefficients J_A from Refs. 6, 12–14, 24, 25, and 27. As the initial data, the $ClONO_2$, ClO, HNO_3, BrO, and O_3 concentrations are used measured from satellites, aircrafts, and ozonesondes at a height of about 20 km in the ozone hole[10,13,14] and presented in Table 2.

The τ_{A_x} value was calculated by the following formula derived by the author[20]

$$\tau_{A_x} = \frac{0.632(A_x)_0}{L_{A_x}}. \qquad (1)$$

The calculated τ_A and τ_{A_x} values are presented in Table 3. Physical contents of formula (1) is that it determines τ_{A_x}, during which a e-fold decrease of the initial concentration of $(A_x)_0$ family takes place (for this, the coefficient $0.632 = 1 - \frac{1}{2.72}$ is introduced), which is a part of the total time required for complete decrease of the $(A_x)_0$ concentration; this time is determined as the ratio of the $(A_x)_0$ concentration to the rate of its decrease L_{A_x}.

Table 3 shows that all τ_A and τ_{A_x} values are less than 5.2 h, that satisfies the criterion of the presence of photochemical equilibrium at daytime[12]:

$$\tau_{A_x} \text{ and } \tau_A < 24 \text{ h}, \qquad (2)$$

where 24 h is the time constant of zonal transport in the atmosphere at heights of 15–30 km.[12]

2) Assuming that all the above-mentioned atmospheric constituents and families (Table 3) in the ozone hole under daylight conditions in the second half of spring are at the state of photochemical equilibrium, the formulas for calculation of (NO_2), (Cl_2), (Cl_2O_2), $(OClO)$, $(HOCl)$, (Cl), $(ClOO)$, (O), and (O_3) concentrations have been derived, using the satellite, aircraft, and balloonsonde measurements of $(ClONO_2)$, (ClO), (HNO_3), (BrO), and (O_3) concentrations as the initial data[10,13,14] (Table 2).

Table 2. Area-average daily concentrations (molecule · cm^{-3}) of atmospheric constituents at a height of 20 km, obtained from measurements at different latitudes in the period 1965–1984 and calculated; and for the period after 1984 – calculated by spring satellite data for the ozone hole in Antarctic

Species	$ClONO_2$	ClO	HCl	HNO_3	NO_2	NO	NO_3	CH_4	Cl_2O_2
Concentration before 1984	$3.0 \cdot 10^8$ Ref. 12	$5.4 \cdot 10^6$ Ref. 12	$1.4 \cdot 10^9$ Ref. 12	$6.0 \cdot 10^9$ Ref. 12	$1.8 \cdot 10^9$ Ref. 12	$7.2 \cdot 10^8$ Ref. 12	$2.1 \cdot 10^5$ by Eq. (f. 18)	$4.0 \cdot 10^{12}$ Ref. 12	$1.9 \cdot 10^3$ by Eq. (f. 2)
Concentration after 1984 in the ozone hole	$2.5 \cdot 10^9$ Ref. 13	$3.0 \cdot 10^9$ Ref. 13	$2.0 \cdot 10^9$ Ref. 13	$1.7 \cdot 10^9$ Ref. 13	$7.3 \cdot 10^7$ by Eq. (f. 1)	$1.1 \cdot 10^7$ by Eq. (f. 17)	$1.7 \cdot 10^6$ by Eq. (f. 18)	$2.0 \cdot 10^{12}$ Ref. 13	$5.9 \cdot 10^8$ by Eq. (f. 2)

Species	Cl_2	BrO	Br	OH	HO_2	Cl	O	O_3	$OClO$	$ClOO$	$HOCl$
Concentration before 1984	$1.6 \cdot 10^2$ by Eq. (3)	$1.5 \cdot 10^7$ Ref. 12	$2.0 \cdot 10^5$ Ref. 12	$8.0 \cdot 10^5$ Ref. 12	$4.0 \cdot 10^6$ Ref. 12	$\approx 3.6 \cdot 10^3$ Ref. 12	$9.4 \cdot 10^5$ Ref. 12*	$2.9 \cdot 10^{12}$ Ref. 12	$1.9 \cdot 10^5$ by Eq. (10a)	$1.5 \cdot 10^4$ by Eq. (10)	$2.3 \cdot 10^6$ by Eq. (6)
Concentration after 1984 in the ozone hole	$4.9 \cdot 10^7$ by Eq. (f. 3)	$1.3 \cdot 10^7$ Ref. 14	$1.0 \cdot 10^5$ Ref. 29	$5.0 \cdot 10^5$ by Eq. (f. 5)	$7.5 \cdot 10^6$ by Eq. (f. 4)	$4.0 \cdot 10^4$ by Eq. (f. 9)	$4.4(015) \cdot 10^7$ by Eq. (f. 11) in October	$8.7 \cdot 10^{10}$ Ref. 10 by Eq. (f. 13) in October	$9.4 \cdot 10^7$ by Eq. (f. 10a)	$1.6 \cdot 10^5$ by Eq. (f. 10)	$1.4 \cdot 10^9$ by Eq. (f. 6)

* According to calculations in Refs. 12 and 27 using the condition $d(O)/dt = 0$ only from data on (O_3). When the condition $d(O_x)/dt = 0$ is used at height 20 km outside ozone hole, the average $(O) = 3.0 \cdot 10^8$ (Ref. 20).

Table 3. List of formulas derived from photochemical theory for calculation of concentrations of atmospheric constituents under conditions of photochemical equilibrium at a height of 20 km at $T = 217$ K, and estimates of the corresponding chemical lifetimes of constituents and members of the families. Formulas and estimates are derived for the case of increased concentrations of chlorine-containing constituents in the lower daytime stratosphere, observed in the ozone hole (Table 2)

No.	Formulas for estimation of concentrations of atmospheric constituents	Conditions assumed on derivation of formulas	Chemical lifetimes
1	2	3	4
(f. 1)	$(NO_2) = \dfrac{J_{ClONO_2}(ClONO_2)^{**}}{K_{37}(ClO)(M)}$	$\dfrac{d(NO_x)}{dt} = 0,$ $(NO_x) = (NO) +$ $+ (NO_2) + (NO_3)$	$\tau_{NO_x} = 3.6$ min
(f. 2)	$(Cl_2O_2) = \dfrac{K_{39}(ClO)^2(M)}{J^{1+2}_{Cl_2O_2}}$	$\dfrac{d(Cl_2O_2)}{dt} = 0$	$\tau_{Cl_2O_2} = 10$ min
(f. 3)	$(Cl_2) = \dfrac{K_{121}(ClO)^2}{J_{Cl_2}}$	$\dfrac{d(Cl_2)}{dt} = 0$	$\tau_{Cl_2} = 17$ min
(f. 4)	$(HO_2) = \dfrac{K_{14}J_{HNO_3}(HNO_3)}{(NO_2)(M)(K_{14}K_{51} + K_{16}K_{48})}$	$\dfrac{d(HO_x)}{dt} = 0,$ $(HO_x) = (H) +$ $+ (OH) + (HO_2)$	$\tau_{\mathrm{No_x}} = 1.4$ h

Table 3 continued

1	2	3	4
(f. 5)	$(\mathrm{OH}) = \frac{J_{\mathrm{HNO_3}}(\mathrm{HNO_3}) - K_{51}(\mathrm{NO_2})(\mathrm{HO_2})(M)}{K_{48}(\mathrm{NO_2})(M)}$	$\frac{\mathrm{d}(\mathrm{HO_x})}{\mathrm{d}t} = 0$	$\tau_{\mathrm{HO_x}} = 1.4$ h
(f. 6)	$(\mathrm{HOCl}) = \frac{K_{18}(\mathrm{ClO})(\mathrm{HO_2})}{J_{\mathrm{HOCl}}}$	$\frac{\mathrm{d}(\mathrm{HOCl})}{\mathrm{d}t} = 0$	$\tau_{\mathrm{HOCl}} = 50$ min
(f. 7)	$(\mathrm{Cl}) = \frac{2J^{1+2}_{\mathrm{Cl_2O_2}}(\mathrm{Cl_2O_2}) - 2K_{39}(\mathrm{ClO})^2(M) + 2J_{\mathrm{Cl_2}}(\mathrm{Cl_2}) - 2K_{121}(\mathrm{ClO})^2 +}{2K_{64}(\mathrm{HOCl}) + 2K_{133}(\mathrm{ClNO})}\ldots$ $\ldots\frac{+K_{118}(\mathrm{Br})(\mathrm{Cl_2O_2})}{2K_{64}(\mathrm{HOCl}) + 2K_{133}(\mathrm{ClNO})}$	$\frac{\mathrm{d}(\mathrm{Cl_x})}{\mathrm{d}t} = 0,$ $(\mathrm{Cl_x}) =$ $(\mathrm{Cl}) + (\mathrm{ClO}) +$ $+ (\mathrm{ClOO}) +$ $+ (\mathrm{OClO}) + (\mathrm{HOCl})$ $+$ $+ (\mathrm{ClONO_2}) +$ $+ (\mathrm{ClONO}) +$ $+ (\mathrm{ClNO}) + (\mathrm{HCl})$	$\tau_{\mathrm{Cl_x}} = 50.8$ min
(f. 8)	$(\mathrm{Cl}) = \frac{K_{118}(\mathrm{Br})(\mathrm{Cl_2O_2})}{2K_{64}(\mathrm{HOCl}) + 2K_{133}(\mathrm{ClNO})}$	$\frac{\mathrm{d}(\mathrm{Cl_x})}{\mathrm{d}t} = 0$	$\tau_{\mathrm{Cl_x}} = 50.8$ min
(f. 9)	$(\mathrm{Cl}) = \frac{K_{118}(\mathrm{Br})(\mathrm{Cl_2O_2})}{2K_{64}(\mathrm{HOCl})}$	$\frac{\mathrm{d}(\mathrm{Cl_x})}{\mathrm{d}t} = 0$	$\tau_{\mathrm{Cl_x}} = 50.8$ min
(f. 10)	$(\mathrm{ClOO}) = \frac{K_7(\mathrm{Cl})(\mathrm{O_2})}{K_{112}}$	$\frac{\mathrm{d}(\mathrm{ClOO})}{\mathrm{d}t} = 0$	$\tau_{\mathrm{ClOO}} = 0.001$ s
(f. 10a)	$(\mathrm{OClO}) = \frac{K_{99}(\mathrm{ClO})(\mathrm{BrO})}{J_{\mathrm{OClO}}}$	$\frac{\mathrm{d}(\mathrm{OClO})}{\mathrm{d}t} = 0$	$\tau_{\mathrm{OClO}} = 3.3$ min
(f. 11)	$(\mathrm{O}) = \frac{J_{\mathrm{OClO}}(\mathrm{OClO}) + J_{\mathrm{ClO}}(\mathrm{ClO}) + J_{\mathrm{NO_2}}(\mathrm{NO_2}) + J_{\mathrm{BrO}}(\mathrm{BrO}) + 2J_{\mathrm{O_2}}(\mathrm{O_2})}{K_5(\mathrm{ClO})}\ldots$ $\ldots\frac{-K_{19}(\mathrm{O_3})(\mathrm{Br}) - K_4(\mathrm{O_3})(\mathrm{Cl})}{K_5(\mathrm{ClO})}$	$\frac{\mathrm{d}(\mathrm{O_x})}{\mathrm{d}t} = 0,$ $(\mathrm{O_x}) = (\mathrm{O}) +$ $+ (\mathrm{O'D}) + (\mathrm{O_3})$	$\tau_{\mathrm{O_x}} = 5.2$ h
(f. 12)	$(\mathrm{O}) = \frac{J_{\mathrm{ClO}}(\mathrm{ClO}) + J_{\mathrm{NO_2}}(\mathrm{NO_2}) + 2J_{\mathrm{O_2}}(\mathrm{O_2}) - K_4(\mathrm{O_3})(\mathrm{Cl})}{K_5(\mathrm{ClO})}$	$\frac{\mathrm{d}(\mathrm{O_x})}{\mathrm{d}t} = 0$	$\tau_{\mathrm{O_x}} = 5.2$ h
(f. 13)	$(\mathrm{O_3}) = \frac{J_{\mathrm{OClO}}(\mathrm{OClO}) + J_{\mathrm{ClO}}(\mathrm{ClO}) + J_{\mathrm{NO_2}}(\mathrm{NO_2}) + J_{\mathrm{BrO}}(\mathrm{BrO}) + 2J_{\mathrm{O_2}}(\mathrm{O_2}) -}{K_4(\mathrm{Cl}) + K_{19}(\mathrm{Br})}\ldots$ $\ldots\frac{-K_5(\mathrm{ClO})(\mathrm{O})}{K_4(\mathrm{Cl}) + K_{19}(\mathrm{Br})}$	$\frac{\mathrm{d}(\mathrm{O_x})}{\mathrm{d}t} = 0$	$\tau_{\mathrm{O_x}} = 5.2$ h
(f. 14)***	$(\mathrm{O_3}) = \frac{J_{\mathrm{ClO}}(\mathrm{ClO}) + J_{\mathrm{NO_2}}(\mathrm{NO_2}) + 2J_{\mathrm{O_2}}(\mathrm{O_2}) - K_5(\mathrm{ClO})(\mathrm{O})}{K_4(\mathrm{Cl})}$	$\frac{\mathrm{d}(\mathrm{O_x})}{\mathrm{d}t} = 0$	$\tau_{\mathrm{O_x}} = 5.2$ h
(f. 15)	$(\mathrm{BrO}) = \frac{J_{\mathrm{BrONO_2}}(\mathrm{BrONO_2})}{K_{42}(\mathrm{NO_2})(M)}$	$\frac{\mathrm{d}(\mathrm{Br_x})}{\mathrm{d}t} = 0,$ $(\mathrm{Br_x}) = (\mathrm{Br}) +$ (BrO)	$\tau_{\mathrm{Br_x}} = 44$ min
(f. 16)	$(\mathrm{ClO}) = \frac{J_{\mathrm{ClONO_2}}(\mathrm{ClONO_2})}{K_{37}(\mathrm{NO_2})(M)}$	$\frac{\mathrm{d}(\mathrm{NO_x})}{\mathrm{d}t} = 0$	$\tau_{\mathrm{NO_x}} = 3.6$ min
(f. 17)	$(\mathrm{NO}) = \frac{J_{\mathrm{NO_2}}(\mathrm{NO_2})}{K_{36}(\mathrm{ClO})}$	$\frac{\mathrm{d}(\mathrm{NO})}{\mathrm{d}t} = 0$	$\tau_{\mathrm{NO}} = 1.7$ min
(f. 18)	$(\mathrm{NO_3}) = \frac{J_{\mathrm{ClONO_2}}(\mathrm{ClONO_2})}{J^{1+2}_{\mathrm{NO_3}}}$	$\frac{\mathrm{d}(\mathrm{NO_{x1}})}{\mathrm{d}t} = 0,$ $(\mathrm{NO_{x_1}}) = (\mathrm{NO_3}) +$ $+ (\mathrm{N_2O_5})$	$\tau_{\mathrm{NO_{x1}}} = 4.7$ h

* Formulas and estimates are derived for the case of increased concentrations of chlorine-containing constituents in the lower daytime stratosphere, observed in the ozone hole (Table 2), for $(\mathrm{O_x})$ family – in the second half of spring.

** M is concentration of the third partner; concentrations of components are in parenthesis.

*** (O) value for formula (f. 14) is calculated by formula (f. 12).

The obtained formulas are presented in Table 3. They were derived by the method presented in Refs. 12 and 20 through equalizing the sums of rates of reactions destructing and generating the sought species or families, and following selection of dominating terms in the obtained equations, having for the families the form

$$\sum_{i=1}^{n}\left[\frac{\mathrm{d}(A_x)_i}{\mathrm{d}t}\right] = 0, \qquad (3)$$

with solving these equations for the sought species. The examples of such a derivation of formulas for (O) and (O_3), representing odd oxygen family under conditions of the cloudy atmosphere free of increased concentrations of chlorine-containing species, are given in Ref. 20. For the atmosphere in ozone hole with increased concentrations of chlorine-containing species, Eq. (3) under conditions of photochemical equilibrium for (O_x) families at a height of 20 km has the form:

$$J_{\mathrm{OClO}}(\mathrm{OClO}) + J_{\mathrm{ClO}}(\mathrm{ClO}) + J_{\mathrm{NO_2}}(\mathrm{NO_2}) + $$
$$+ J_{\mathrm{BrO}}(\mathrm{BrO}) + 2J_{\mathrm{O_2}}(\mathrm{O_2}) - [K_5(\mathrm{ClO})(\mathrm{O}) +$$
$$+ K_4(\mathrm{O_3})(\mathrm{Cl}) + K_{19}(\mathrm{O_3})(\mathrm{Br})] = 0, \qquad (4)$$

from which formulas (11)–(14) follow.

Derivation of expression (3) for Cl_x family is presented below.

Taking into account that[20]

$$\frac{\mathrm{d}(\mathrm{Cl_x})}{\mathrm{d}t} = \frac{\mathrm{d}(\mathrm{Cl})}{\mathrm{d}t} + \frac{\mathrm{d}(\mathrm{ClO})}{\mathrm{d}t} +$$
$$+\frac{\mathrm{d}(\mathrm{ClOO})}{\mathrm{d}t} + \frac{\mathrm{d}(\mathrm{OClO})}{\mathrm{d}t} + \frac{\mathrm{d}(\mathrm{HOCl})}{\mathrm{d}t} +$$
$$+\frac{\mathrm{d}(\mathrm{ClONO_2})}{\mathrm{d}t} + \frac{\mathrm{d}(\mathrm{ClONO})}{\mathrm{d}t} + \frac{\mathrm{d}(\mathrm{ClNO})}{\mathrm{d}t} + \frac{\mathrm{d}(\mathrm{HCl})}{\mathrm{d}t}, \qquad (5)$$

and using this expression and all the corresponding chemical and photochemical reactions from Ref. 24, obtain

$$\frac{\mathrm{d}(\mathrm{Cl_x})}{\mathrm{d}t} = 2J^{1+2}_{\mathrm{Cl_2O_2}}(\mathrm{Cl_2O_2})\{1.88\cdot10^6\} +$$
$$+ 2J_{\mathrm{Cl_2}}(\mathrm{Cl_2})\{8.8\cdot10^4\} + K_{115}(\mathrm{Cl_2O_2})(\mathrm{NO})\{2.6\cdot10^2\} +$$
$$+ K_{118}(\mathrm{Br})(\mathrm{Cl_2O_2})\{1.77\cdot10^2\} +$$
$$+ 2K_{119}(\mathrm{OH})(\mathrm{Cl_2})\{0.97\} + J_{\mathrm{CCl_4}}(\mathrm{CCl_4})\{0.18\} +$$
$$+ J_{\mathrm{CFCl_3}}(\mathrm{CFCl_3})\{0.10\} + J_{\mathrm{CF_2Cl_2}}(\mathrm{CF_2Cl_2})\{0.024\} -$$
$$- [2K_{39}(\mathrm{ClO})^2(M)\{1.88\cdot10^6\} + 2K_{121}(\mathrm{ClO})^2\{8.8\cdot10^4\} +$$
$$+ 2K_{64}(\mathrm{Cl})(\mathrm{HOCl})\{1.8\cdot10^2\} + 2K_{133}(\mathrm{Cl})(\mathrm{ClNO})\{20.0\} +$$
$$+ K_{132}(\mathrm{Cl})(\mathrm{CO})(M)\{3.3\} + 2K_{111}(\mathrm{Cl})(\mathrm{ClOO})\{0.8\} +$$
$$+ K_{134}(\mathrm{HCl})(\mathrm{ClONO_2})\{5.0\cdot10^{-2}\}$$
$$+K_{66}(\mathrm{Cl})(\mathrm{OCS})\{2.3\cdot10^{-3}\}], \qquad (6)$$

where in braces is given the estimate of reaction rates in molecule · $\mathrm{cm}^{-3}\cdot\mathrm{s}^{-1}$. Equation (6) includes the reactions[6,12,24,27]:

$$\mathrm{Cl_2O_2} + h\nu \rightarrow \mathrm{ClO} + \mathrm{ClO}\ (J^1_{\mathrm{Cl_2O_2}} = 8.0\cdot10^{-4})$$
$$\mathrm{Cl_2O_2} + h\nu \rightarrow \mathrm{ClOO} + \mathrm{Cl}\ (J^2_{\mathrm{Cl_2O_2}} = 8.0\cdot10^{-4})$$
$$\mathrm{Cl_2} + h\nu \rightarrow \mathrm{Cl} + \mathrm{Cl}\ (J_{\mathrm{Cl_2}} = 1.0\cdot10^{-3})$$
$$\mathrm{Br} + \mathrm{Cl_2O_2} \rightarrow \mathrm{BrCl} + \mathrm{ClOO}\ (K_{118} = 3.0\cdot10^{-12})$$
$$\mathrm{OH} + \mathrm{Cl_2} \rightarrow \mathrm{HOCl} + \mathrm{Cl}\ (K_{119} = 2.2\cdot10^{-14})$$
$$\mathrm{CCl_4} + h\nu \rightarrow \mathrm{CCl_3} + \mathrm{Cl}\ (J_{\mathrm{CCl_4}} = 9.0\cdot10^{-10})$$
$$\mathrm{CFCl_3} + h\nu \rightarrow \mathrm{CFCl_2} + \mathrm{Cl}\ (J_{\mathrm{CFCl_3}} = 5.0\cdot10^{-10})$$
$$\mathrm{CF_2Cl_2} + h\nu \rightarrow \mathrm{CF_2Cl} + \mathrm{Cl}\ (J_{\mathrm{CF_2Cl_2}} = 8.0\cdot10^{-11})$$
$$\mathrm{ClO} + \mathrm{ClO} + M \rightarrow \mathrm{Cl_2O_2} + M\ (K_{39} = 5.8\cdot10^{-32})$$
$$\mathrm{ClO} + \mathrm{ClO} \rightarrow \mathrm{Cl_2} + \mathrm{O_2}\ (K_{121} = 4.9\cdot10^{-15})$$
$$\mathrm{Cl} + \mathrm{HOCl} \rightarrow \mathrm{Cl_2} + \mathrm{OH}\ (K_{64} = 1.6\cdot10^{-12})$$
$$\mathrm{Cl} + \mathrm{ClNO} \rightarrow \mathrm{NO} + \mathrm{Cl_2}\ (K_{133} = 3.6\cdot10^{-11})$$
$$\mathrm{Cl} + \mathrm{CO} + M \rightarrow \mathrm{ClCO} + M\ (K_{132} = 4.4\cdot10^{-33})$$
$$\mathrm{Cl} + \mathrm{ClOO} \rightarrow \mathrm{Cl_2} + \mathrm{O_2}\ (K_{111} = 1.0\cdot10^{-10})$$
$$\mathrm{HCl} + \mathrm{ClONO_2} \rightarrow \mathrm{Cl_2} + \mathrm{HNO_3}\ (K_{134} = 1.0\cdot10^{-20})$$
$$\mathrm{Cl} + \mathrm{OCS} \rightarrow \mathrm{SCl} + \mathrm{CO}\ (K_{66} = 1.0\cdot10^{-16}).$$

From relation (6) at $\frac{\mathrm{d}(\mathrm{Cl_x})}{\mathrm{d}t} = 0$ we obtain expression (3) for (Cl_x) family, from which we derive the formulas for (Cl), presented in Table 3. When deriving equation (6), we excluded 48 reactions having equal numbers of odd chlorine-containing species in the right- and left-hand sides, namely:

$\mathrm{Cl} + \mathrm{NO_3} \rightarrow \mathrm{ClO} + \mathrm{NO_2}$
$\mathrm{Cl} + \mathrm{N_2O} \rightarrow \mathrm{ClO} + \mathrm{N_2}$
$\mathrm{ClO} + \mathrm{O} \rightarrow \mathrm{Cl} + \mathrm{O_2}$
$\mathrm{ClO} + \mathrm{NO} \rightarrow \mathrm{NO_2} + \mathrm{Cl}$
$\mathrm{HCl} + \mathrm{NO_3} \rightarrow \mathrm{HNO_3} + \mathrm{Cl}$
$\mathrm{Cl} + \mathrm{ClOO} \rightarrow \mathrm{ClO} + \mathrm{ClO}$
$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2}$
$\mathrm{Cl} + \mathrm{H_2} \rightarrow \mathrm{HCl} + \mathrm{H}$
$\mathrm{Cl} + \mathrm{CH_4} \rightarrow \mathrm{HCl} + \mathrm{CH_3}$
$\mathrm{Cl} + \mathrm{C_2H_6} \rightarrow \mathrm{HCl} + \mathrm{C_2H_5}$
$\mathrm{Cl} + \mathrm{C_3H_8} \rightarrow \mathrm{HCl} + \mathrm{C_3H_7}$
$\mathrm{Cl} + \mathrm{CH_3OH} \rightarrow \mathrm{CH_2OH} + \mathrm{HCl}$
$\mathrm{Cl} + \mathrm{CH_3Cl} \rightarrow \mathrm{CH_2Cl} + \mathrm{HCl}$
$\mathrm{Cl} + \mathrm{H_2CO} \rightarrow \mathrm{HCl} + \mathrm{HCO}$
$\mathrm{Cl} + \mathrm{H_2O_2} \rightarrow \mathrm{HCl} + \mathrm{HO_2}$
$\mathrm{Cl} + \mathrm{HO_2} \rightarrow \mathrm{HCl} + \mathrm{O_2}$
$\mathrm{Cl} + \mathrm{HO_2} \rightarrow \mathrm{OH} + \mathrm{ClO}$
$\mathrm{OH} + \mathrm{HOCl} \rightarrow \mathrm{H_2O} + \mathrm{ClO}$
$\mathrm{O} + \mathrm{HCl} \rightarrow \mathrm{OH} + \mathrm{Cl}$
$\mathrm{O} + \mathrm{HOCl} \rightarrow \mathrm{OH} + \mathrm{ClO}$
$\mathrm{Cl} + \mathrm{Cl_2O} \rightarrow \mathrm{Cl_2} + \mathrm{ClO}$
$\mathrm{Cl} + \mathrm{NO_2} + M \rightarrow \mathrm{ClONO} + M$
$\mathrm{Cl} + \mathrm{NO} + M \rightarrow \mathrm{ClNO} + M$
$\mathrm{Cl} + \mathrm{O_2} + M \rightarrow \mathrm{ClOO} + M$

$ClO + ClO \rightarrow ClOO + Cl$
$ClO + NO_2 + M \rightarrow ClONO_2 + M$
$ClO + HO_2 \rightarrow HOCl + O_2$
$ClO + HO_2 \rightarrow HCl + O_3$
$ClO + O_3 \rightarrow ClOO + O_2$
$ClOO + O_3 \rightarrow ClO + 2O_2$
$ClOO + M \rightarrow Cl + O_2 + M$
$OH + HCl \rightarrow Cl + H_2O$
$BrO + ClO \rightarrow Br + OClO$
$BrO + ClO \rightarrow Br + Cl + O_2$
$BrO + ClO \rightarrow Br + ClOO$
$SO + ClO \rightarrow + SO_2 + Cl$
$Cl + H_2S \rightarrow HCl + SH$
$ClONO_2 + h\nu \rightarrow Cl + NO_3$
$ClO + h\nu \rightarrow Cl + O$
$HOCl + h\nu \rightarrow Cl + OH$
$HCl + h\nu \rightarrow H + Cl$
$ClOO + h\nu \rightarrow ClO + O$
$OClO + h\nu \rightarrow O + ClO$
$OClO + O \rightarrow ClO + O_2$
$OClO + OH \rightarrow HOCl + O_2$
$OClO + NO \rightarrow NO_2 + ClO$
$Cl + OClO \rightarrow ClO + ClO$
$SO + OClO \rightarrow SO_2 + ClO.$

The first listed reaction was excluded from formula (6), for example, because the derivatives entering into equation (5), $\frac{d(Cl)}{dt} = -K_{53}(Cl)(NO_3)$ and $\frac{d(ClO)}{dt} = K_{53}(Cl)(NO_3)$, respectively, are mutually cancelled in relation (6), as are all the rest 48 reactions indicated above.

Also, all incomplete reactions presented in Table 4 (1st column) are excluded from equation (6), because after conversion of incomplete reactions to complete ones (2nd column of Table 4), they turned out to be thermodynamically possible through estimation of Gibbs free energy ΔG_R^0 (Ref. 12), calculated to be for all these complete reactions (as required for existence of the reactions) negative (3rd column of Table 4). All complete reactions in Table 4 have the same (mainly single) quantity of odd members of the (Cl_x) family in the left- and right-hand sides of reactions, as in the 48 reactions presented above; therefore, they are excluded from formula (6).

Expressions (4) and (6) in square brackets incorporate L_{O_x} and L_{Cl_x} entering formula (1). Formula (f. 7) (Table 3) is readily derived from relation (6) at $\frac{d(Cl_x)}{dt} = 0$, and dominating terms being taken into account. When taking into account formulas (f. 2) and (f. 3), formula (f. 7) simplifies, because in the case of photochemical equilibrium formula (f. 2) suggests that $2J^{1+2}_{Cl_2O_2}(Cl_2O_2) - 2K_{39}(ClO)^2(M) = 0$, and formula (f. 3) suggests that $2J^{1+2}_{Cl_2O_2}(Cl_2) - 2K_{121}(ClO)^2 = 0$; and substitution of these differences in (f. 7) leads to formula (f. 8).

In its turn, formula (f. 8) can be simplified by neglecting relatively small term $2K_{133}(ClNO)$ in denominator. As a result, formula (f. 8) will evolve into formula (f. 9) (see estimates of chemical reaction rates in relation (6)).

An important and, in this case, decisive circumstance is that formulas in Table 3 for the species, chemically related to many other species, are derived under conditions assumed for families of odd species NO_x, Cl_x, HO_x, O_x, while formulas for Cl_2O_2, Cl_2, HOCl, OClO, and ClOO, related only to one or two species, are derived under conditions adopted for individual species (see column 3 of Table 3).

Table 4. Incomplete and corresponding complete chemical reactions excluded from formula (6), and ΔG_R^0 estimates

Incomplete reactions (Ref. 24)	Corresponding compete reactions	ΔG_R^0, kcal/mol
$ClO + H_2CO \rightarrow$ Products	$ClO + H_2CO \rightarrow HOCl + CHO$	– 39.38
$ClO + H_2 \rightarrow$ Products	$ClO + H_2 \rightarrow Cl + H_2O$	– 53.14
$ClO + CO \rightarrow$ Products	$ClO + CO \rightarrow Cl + CO_2$	– 59.981
$ClO + N_2O \rightarrow$ Products	$ClO + N_2O \rightarrow ClOO + N_2$	– 23.48
	$ClO + N_2O \rightarrow ClNO + NO$	– 12.12
$ClO + NO_3 \rightarrow$ Products	$ClO + NO_3 \rightarrow ClOO + NO_2$	– 14.02
$Cl + Cl_2O_2 \rightarrow$ Products	$Cl + Cl_2O_2 \rightarrow ClO + Cl_2O$	≈ – 3
$O + ClONO_2 \rightarrow$ Products	$O + ClONO_2 \rightarrow ClO + NO_3$	≈ –19
	$O + ClONO_2 \rightarrow OClO + NO_2$	≈ – 24
	$O + ClONO_2 \rightarrow ClONO + O_2$	≈ – 55
$Cl + HNO_3 \rightarrow$ Products	$Cl + HNO_3 \rightarrow NO_3 + HCl$	– 2.38
$ClO + CH_4 \rightarrow$ Products	$ClO + CH_4 \rightarrow HCl + CH_3O$	– 29.927
$ClONO_2 + OH \rightarrow$ Products	$ClONO_2 + OH \rightarrow ClO + HNO_3$	– 17.37
	$ClONO_2 + OH \rightarrow ClONO + HO_2$	– 15.78
$ClONO_2 + Cl \rightarrow$ Products	$ClONO_2 + Cl \rightarrow ClO + ClONO$	≈ – 3
$ClO + OH \rightarrow$ Products	$ClO + OH \rightarrow Cl + HO_2$	– 2.29
$OClO + O_3 \rightarrow$ Products	$OClO + O_3 \rightarrow ClO + 2O_2$	– 44.12

Also given in Table 3 is formula (f. 13) derived from expression (4) for calculation of O_3 concentration in the ozone hole of the second half of spring for known Cl, ClO, O, NO_2, BrO, Br, and OClO concentrations. Formula (f. 13) can be simplified, because J_{OClO}(OClO) is relatively small, and J_{BrO}(BrO) and K_{19}(Br) are also relatively small, they are in numerator and denominator, and removal of the former decreases (O_3) and of the latter - increases it, yielding approximate formula (f. 14). In the same way, formula (f. 11), derived to calculate (O), simplifies and goes over to approximate formula (f. 12).

3) Formulas in Table 3 are given in the logical order, allowing the concentrations of atmospheric constituents in the ozone hole to be calculated without the use of extra data, just moving downward through the Table. Formulas in Table 3 are used to calculate the concentrations in the ozone hole in the 15–30-km atmospheric layer.

Results of some calculations of atmospheric constituent concentrations in ozone hole at a height of 20 km by the formulas from Table 3 are presented in Tables 2 (for period after 1984), 6, and 8. Note that the calculations of concentrations of species in ozone hole use as the initial data the satellite, aircraft, and balloonsonde measurements of $ClONO_2$, ClO, HNO_3, BrO, and O_3 concentrations presented in Table 2 together with literature sources. Using these initial data and formulas from Table 3, we calculated the NO_2, Cl_2O_2, Cl_2, OClO, HO_2, OH, HOCl, Cl, O, and ClOO concentrations (see Tables 2, 6, and 8).

As an example, we present the calculation of photochemically equilibrium concentration of atomic chlorine in ozone hole at a height of 20 km for October. From formula (f. 9) we obtain

$$(\mathrm{Cl}) = \frac{3.0 \cdot 10^{-12} \cdot 1.0 \cdot 10^{5} \cdot 5.9 \cdot 10^{8}}{2 \cdot 1.6 \cdot 10^{-12} \cdot 1.4 \cdot 10^{9}} = 4.0 \cdot 10^{4},$$

that is consistent with data of Tables 2, 6, and 8. Also, we present test calculation of photochemically equilibrium concentration of the atmospheric ozone in ozone hole at a height of 20 km for October using the data on (ClO), (OClO), (NO_2), (BrO), (O), (Cl), and (Br) (Table 2). We obtain from formula (f. 13)

$$(\mathrm{O_3})=[5.0\cdot10^{-3}\cdot9.4\cdot10^{7}+5.0\cdot10^{-4}\cdot3.0\cdot10^{9}+$$
$$+1.1\cdot10^{-2}\cdot7.3\cdot10^{7}+1.0\cdot10^{-2}\cdot1.3\cdot10^{7}+2\cdot5.0\cdot10^{-14}\cdot3.6\cdot10^{17}-$$
$$-2.2\cdot10^{-11}\cdot3.0\cdot10^{9}\cdot4.4(015)\cdot10^{7}]/(8.7\cdot10^{-12}\cdot4.0\cdot10^{4}+$$
$$+4.3\cdot10^{-13}\cdot1.0\cdot10^{5})=8.7\cdot10^{10},$$

coinciding with (O_3) in Table 2 and indicating a considerable, up to 3%, theoretical reduction of ozone concentration in ozone hole in October relative to the average value. The decreased (O_3) value is equal to that, measured at that time, in ozone hole at a height of 20 km.[10] A series of publications, including scientific ones, claim that at heights of 13–18 km in October, ozone is totally depleted. Of coarse, this is not the case. According to measurements,[10] 1–5% of the initial ozone concentration remains, which for the minimum in this range is $2.9 \cdot 10^{12} \cdot 0.01 = 22.9 \cdot 10^{10}$ molecule · cm^{-3}, that exceeds a summarized concentration of (NO_x), (Cl_x), (HO_x), and (Br_x)

4) Springtime rates of ozone destruction and formation in ozone hole due to 1–3 catalytic cycles are calculated. Table 5 presents the estimate of productivity of ozone destruction and formation cycles at a height of 20 km. To obtain it, data of Tables 2 and 6 were used to calculate reaction rates of cycles in ozone hole and to determine the productivity of the cycles. By the cycle productivity it is meant the rate of reaction (or reactions) participating in the cycle and depleting ozone (in this case, in the cycles 1 and 2, this is the reaction $Cl + O_3 \rightarrow ClO + O_2$) taking into account that two ozone molecules are formed or destructed every time (Table 6). The productivity of cycle 3 is determined by the reaction $O_2 + h\nu \rightarrow O + O$, whose rate is minimal. It is taken into account that components of the 1st and 2nd cycles are in photochemical equilibrium as opposite to the 3rd one.

From Table 5 it is seen that in the ozone hole the average total productivity of the ozone destruction cycles (1 and 2) is 110 times higher than the productivity of ozone formation cycle 3.

To evaluate the mean time-dependent productivity of 1 and 2 cycles (decade in this case) we calculated the mean (Cl) and (O) concentrations in winter period at a height of 20 km (Table 6). The (Cl) and (O) concentrations were calculated using formulas from Table 3 as a function of time (decade) and corresponding (O_3) values, obtained from the ozone sensing data.[10] The (Cl) concentration was calculated by formula (f. 9), (O) concentration – by formula (f. 11) for the condition of photochemical equilibrium of (O) concentration. It was assumed that the (O) concentration does not influence the productivity of the 1st and 2nd cycles (see Table 5). Given in parentheses (Table 6) are (O_3) values in percent of the mean value equal to $2.9\cdot10^{12}$ molecule·cm^{-3} (Ref. 12).

5) The decadally average theoretical rate of the ozone concentration decrease in ozone hole at a height of 20 km, caused by net effect of catalytic cycles (1 and 2), is calculated as a function of time (decade) and compared with the ozonesonde-observed[10] ozone depletion at the same altitude (Table 7). The ozone depletion rate (the number of ozone molecules in 1 cm^3 degraded during a conventional time unit – 5 light days, i.e., $5 \cdot 24 \cdot 3600 = 4.32 \cdot 10^5$ s) for the 1st and other cycles was calculated by the formula

$$\Delta(\mathrm{O_3})_{1,i} = P_{\mathrm{O}_{3,i}} t, \qquad (7)$$

where $P_{\mathrm{O}_{3,i}}$ is the calculated productivity of a catalytic cycle (molecule·$cm^{-3} \cdot s^{-1}$), t is the time (in s) during which the cycle acts (5 light days, in this case). It is assumed that, during five light days, which in spring by the level of total illumination, correspond to ten (decade) calendar days, the average productivity of the cycle does not change significantly. The productivity of the cycles was calculated using Table 5. Also, Table 7 presents chemical lifetimes of odd oxygen family τ_{O_x} as a function of time (decade) at a height of 20 km for estimating the possibility of establishment of photochemical equilibrium; these lifetimes are calculated by formula (1).

It follows from Table 7 that, when two first cycles act simultaneously, the calculated rate of ozone destruction for the first four decades exceeds the observed ozone depletion, whereas for the last two decades it is less than or close to the observed ozone decrease. At the same time, the τ_{O_x} estimate suggests that for the last two decades the photochemical equilibrium of (O_x) family is established while for the first three decades it is not observed. The exceed of the calculated ozone destruction rate in the first four decades over the observed ozone depletion means that during the corresponding decade, some compensation is possible for some temporal decrease of calculated productivity of the cycles, assumed to be constant in the calculations. Further decrease of ozone concentration under impact of catalytic cycles leads to reduction of chemical lifetime of (O_x) family (see Table 7), which will establish the photochemical equilibrium and stop the ozone decrease.

Table 5. Estimate of the average reaction rates of catalytic cycles and their productivity in ozone destruction and formation in the atmosphere at a height of 20 km in ozone hole. The concentrations of the species are as in Tables 2 and 6, (O_3) = $1.5{\cdot}10^{12}$

Cycle number	Catalytic cycle	Reaction rates and productivity of catalytic cycles in molecule·cm^{-3}·s^{-1}
1	$ClONO_2 + h\nu \rightarrow Cl + NO_3$	$2.1\cdot10^{5}$
	$NO_3 + h\nu \rightarrow NO + O_2$	$2.5\cdot10^{4}$
	$2(Cl + O_3 \rightarrow ClO + O_2)$	$1.0\cdot10^{6}$
	$NO + ClO \rightarrow Cl + NO_2$	$7.9\cdot10^{5}$
	$ClO + NO_2 + M \rightarrow ClONO_2 + M$	$2.1\cdot10^{5}$
	Outcome: $2O_3 \rightarrow 3O_2$ Productivity of ozone destruction cycle	$2.0\cdot10^{6}$
2	$ClO + ClO + M \rightarrow Cl_2O_2 + M$	$9.4\cdot10^{5}$
	$Cl_2O_2 + h\nu \rightarrow ClOO + Cl$	$4.7\cdot10^{5}$
	$ClOO + M \rightarrow Cl + O_2 + M$	$1.1\cdot10^{8}$
	$2(Cl + O_3 \rightarrow ClO + O_2)$	$1.0\cdot10^{6}$
	Outcome: $2O_3 \rightarrow 3O_2$ Productivity of ozone destruction cycle	$2.0\cdot10^{6}$
3	$O_2 + h\nu \rightarrow O + O$	$1.8\cdot10^{4}$
	$2(O + O_2 + M \rightarrow O_3 + M)$	$6.0\cdot10^{7}$
	Outcome: $3O_2 \rightarrow 2O_3$ Productivity of ozone formation cycle	$3.6\cdot10^{4}$
4	$Br + O_3 \rightarrow BrO + O_2$	$6.5\cdot10^{4}$
	$BrO + O_3 \rightarrow Br + 2O_2$	$1.2\cdot10^{4}$
	Outcome: $2O_3 \rightarrow 3O_2$ Productivity of ozone destruction cycle	$1.5\cdot10^{5}$
5	$BrO + ClO \rightarrow Br + Cl + O_2$	$5.1\cdot10^{4}$
	$Br + O_3 \rightarrow BrO + O_2$	$6.5\cdot10^{4}$
	$Cl + O_3 \rightarrow ClO + O_2$	$5.2\cdot10^{5}$
	Outcome: $2O_3 \rightarrow 3O_2$ Productivity of ozone destruction cycle	$1.2\cdot10^{6}$

Table 6. Estimate of decadally average, photochemically equilibrium concentrations of atmospheric constituents (Cl) and (O) at a height of 20 km (at T = 217 K) in ozone hole according to data of satellite and aircraft measurements of ($ClONO_2$), (ClO), (HNO_3) (Ref. 13), (BrO) (Ref. 14), and (O_3) (Ref. 10) concentrations

Species	Decade					
	3rd of August	1st of September	2nd of September	3rd of September	1st of October	2nd of October
O_3	$2.6\cdot10^{12}$ (90%)	$2.0\cdot10^{12}$ (70%)	$1.5\cdot10^{12}$ (50%)	$8.7\cdot10^{11}$ (30%)	$2.9\cdot10^{11}$ (10%)	$8.7\cdot10^{10}$ (3%)
Cl	$4.0\cdot10^{4}$	$4.0\cdot10^{4}$	$4.0\cdot10^{4}$	$4.0\cdot10^{4}$	$4.0\cdot10^{4}$	$4.0\cdot10^{4}$
O	–	–	–	–	$4.281\cdot10^{7}$	$4.4015\cdot10^{7}$

Table 7. Estimate of the average rate of $\Delta(O_3)_{1,i}$ and $\Delta(O_3)_{2,i}$ destruction in Antarctic in ozone hole at a height of 20 km, caused by effect of the 1st and 2nd catalytic cycles as a function of time (*i*th decade) and corresponding decadally average ozone concentration $(O_3)_i$, measured by ozonesondes[10]

Quantity	decade					
	3rd of August	1st of September	2nd of September	3rd of September	1st of October	2nd of October
$(O_3)_i$	$2.6\cdot10^{12}$	$2.0\cdot10^{12}$	$1.5\cdot10^{12}$	$8.7\cdot10^{11}$	$2.9\cdot10^{11}$	$8.7\cdot10^{10}$
$(O_3)_{i-1}-(O_3)_i$	$3.0\cdot10^{11}$	$6.0\cdot10^{11}$	$5.0\cdot10^{11}$	$6.3\cdot10^{11}$	$5.8\cdot10^{11}$	$2.0\cdot10^{11}$
$\Delta(O_3)_{1,i}$	$1.6\cdot10^{12}$	$1.2\cdot10^{12}$	$9.0\cdot10^{11}$	$5.2\cdot10^{11}$	$3.5\cdot10^{11}$	$5.2\cdot10^{10}$
$\Delta(O_3)_{2,i}$	$1.6\cdot10^{12}$	$1.2\cdot10^{12}$	$9.0\cdot10^{11}$	$5.2\cdot10^{11}$	$3.5\cdot10^{11}$	$5.2\cdot10^{10}$
$\Delta(O_3)_{1,i}+\Delta(O_3)_{2,i}$	$3.2\cdot10^{12}$	$2.4\cdot10^{12}$	$1.8\cdot10^{12}$	$1.0\cdot10^{12}$	$7.0\cdot10^{11}$	$1.0\cdot10^{11}$
τ_{O_x}, days	6.8	5.0	3.8	2.1	0.72	0.22

Note. $\Delta(O_3)$ is calculated by data from Tables 5 and 6. The quantity $(O_3)_{i-1}-(O_3)_i$ is the observed decrease of ozone concentration in ozone hole for 10 calendar days. The quantity $\Delta(O_3)_{1,i}+\Delta(O_3)_{2,i}$ is the calculated decrease of ozone concentration due to simultaneous action of 1st and 2nd catalytic cycles during 5 light days (or 10 calendar days) for each decade.

Table 8. Estimate of the mean concentrations of atmospheric constituents (molecule $\cdot$ cm^{-3}) in Antarctic in ozone hole at different altitudes

Constituents	Altitude, km				Sources or calculation techniques
	15	20	25	30	
$ClONO_2$	$5.4\cdot10^9$	$2.5\cdot10^9$	$1.1\cdot10^9$	$5.1\cdot10^8$	Constant concentration equal to measured value at 20 km altitude throughout the altitude range (Ref. 13)
ClO	$3.0\cdot10^9$	$3.0\cdot10^9$	$3.0\cdot10^9$	$3.0\cdot10^9$	Constant concentration equal to measured value at 20 km altitude throughout the altitude range (Ref. 13)
HNO_3	$1.9\cdot10^9$	$1.7\cdot10^9$	$1.0\cdot10^9$	$3.6\cdot10^8$	Concentration is proportional to model (Ref. 12), and at 20 km altitude it is set to the measured value (Ref. 13)
$HOCl$	$7.1\cdot10^8$	$1.4\cdot10^9$	$1.7\cdot10^9$	$1.9\cdot10^9$	By (f. 6)
$ClOO$	$3.1\cdot10^6$	$1.6\cdot10^5$	$5.0\cdot10^3$	$4.3\cdot10^2$	By (f. 10)
Br	$1.0\cdot10^5$	$1.0\cdot10^5$	$8.0\cdot10^4$	$1.1\cdot10^5$	By the model from Ref. 29
BrO	$1.5\cdot10^7$	$1.3\cdot10^7$	$1.0\cdot10^7$	$6.0\cdot10^6$	Concentration is proportional to model (Ref. 12) and aircraft measurements (Ref. 14)
NO_2	$6.9\cdot10^7$	$7.3\cdot10^7$	$8.1\cdot10^7$	$9.6\cdot10^7$	By (f. 1)
Cl_2O_2	$2.6\cdot10^9$	$5.9\cdot10^8$	$9.9\cdot10^7$	$2.1\cdot10^7$	By (f. 2)
HCl	$2.0\cdot10^9$	$2.0\cdot10^9$	$1.0\cdot10^9$	$5.0\cdot10^8$	Concentration is proportional to model (Ref. 12), and to the measured value (Ref. 13) at 20 km
OH	$2.4\cdot10^5$	$5.0\cdot10^5$	$6.9\cdot10^5$	$7.9\cdot10^5$	By (f. 5)
HO_2	$3.6\cdot10^6$	$7.5\cdot10^6$	$1.0\cdot10^7$	$1.3\cdot10^7$	By (f. 4)
Cl	$3.4\cdot10^5$	$4.0\cdot10^4$	$4.2\cdot10^3$	$9.8\cdot10^2$	By (f. 9)
O	$2.4\cdot10^3$	$1.8\cdot10^4$	$1.6\cdot10^5$	$1.8\cdot10^8$	By numerical value of J_{O_2} (O_2) at 20 km
O_3	$1.3\cdot10^{12}$	$1.5\cdot10^{12}$	$1.6\cdot10^{12}$	$1.6\cdot10^{12}$	By measurements at South Pole in September 1987 (Ref. 10)
NO	$1.1\cdot10^7$	$1.1\cdot10^7$	$1.3\cdot10^7$	$1.5\cdot10^7$	By (f. 17)
NO_3	$3.9\cdot10^6$	$1.7\cdot10^6$	$7.5\cdot10^5$	$3.5\cdot10^5$	By (f. 18)
Cl_2	$4.9\cdot10^7$	$4.9\cdot10^7$	$4.4\cdot10^7$	$4.4\cdot10^7$	By (f. 3)

From items 4 and 5 of this section it follows that the total productivity of ozone destruction through the 1st and 2nd catalytic cycles at a height of 20 km in ozone hole is sufficient to initiate the observed ozone depletion in the late August and September, and that this ozone depletion is not compensated for by the action of the 3rd catalytic cycle. In October, the photochemical equilibrium of the oxygen family (and hence ozone) is established in the ozone hole. The photochemically equilibrium ozone concentration and for the observed ($ClONO_2$), (ClO), (BrO), (CH_4), (HCl), and (HNO_3) concentrations, given calculated photochemically equilibrium ($HOCl$), (O), and (Cl) concentrations (Tables 2, 6, and 8), reaches observed small values, as measured by satellites and ozonesondes in October (Table 2).

In the same way as it was done for the 20 km altitude in this section, we can calculate the ozone destruction rates under impact of the 1st and 2nd catalytic cycles at other altitudes in the ozone hole.

6) Estimates of stratospheric altitude variations of reaction rates of catalytic cycles and their productivity in ozone hole are presented in Table 9. To calculate these variations, we compiled Table 8 giving estimates of mean concentrations of atmospheric constituents at different altitudes in the layer at 15–30 km; this estimate is based on measurements of concentrations of the above-mentioned initial constituents and model calculations whose sources are indicated in the Table.

It follows from Table 9 that in the layer 15–25 km the total rate of ozone destruction due to the 1st and 2nd catalytic cycles is markedly higher than the rate of ozone formation in this layer due to the 3rd cycle. At a height of 30 km, the productivity of ozone formation (3rd cycle) exceeds the net productivity of ozone destruction (1st and 2nd cycles).

It follows from Table 9 that in the layer situated at 15–20 km the total rate of ozone destruction under action of the 1st and 2nd catalytic cycles is noticeably higher than the rate of ozone generation due to action of the 3rd cycle. An opposite pattern is observed at the 30 km altitude.

The above-mentioned results concerning the combined effect of catalytic cycles 1–3, (Table 9) determine a well-known shape of the curves of vertical ozone distribution observed in Antarctic in October[2,5,10] with abrupt decrease of ozone concentration at 15–25 heights and slowly varying concentration at a height of 30 km, characteristic of the ozone hole. The main reason for this regularity is a rapid increase of photodissociation coefficient J_{O_2} and the term $J_{O_2}(O_2)$ with height in the lower stratosphere (Table 9, 3rd cycle), which results in exceeding generation of ozone over its destruction at the 30 km height as compared to lower altitudes. According to available calculations, this tendency holds above 30 km at heights 35–40 km.

Table 9. Estimate of the average reaction rates of catalytic cycles (molecule·cm^{-3}·s^{-1}) and productivity of ozone destruction/formation rates in ozone hole at different altitudes in the Antarctic atmosphere in the first part of spring

Cycle number	Catalytic cycle	Altitude, km			
		15	20	25	30
1	$ClONO_2 + h\nu \rightarrow Cl + NO_3$	$4.5\cdot10^5$	$2.1\cdot10^5$	$1.0\cdot10^5$	$5.1\cdot10^4$
	$NO_3 + h\nu \rightarrow NO + O_2$	$5.8\cdot10^4$	$2.5\cdot10^4$	$1.1\cdot10^4$	$5.2\cdot10^3$
	$2(Cl + O_3 \rightarrow ClO + O_2)$	$1.8\cdot10^6$	$1.0\cdot10^6$	$1.2\cdot10^5$	$2.7\cdot10^4$
	$NO + ClO \rightarrow Cl + NO_2$	$7.9\cdot10^5$	$7.9\cdot10^5$	$9.2\cdot10^5$	$1.0\cdot10^6$
	$ClO + NO_2 + M \rightarrow ClONO_2 + M$	$4.5\cdot10^5$	$2.1\cdot10^5$	$1.0\cdot10^5$	$5.1\cdot10^4$
	Outcome: $2O_3 \rightarrow 3O_2$ Productivity of ozone destruction cycle:*	$\frac{3.6\cdot10^6}{120}$	$\frac{2.0\cdot10^6}{57.6}$	$\frac{2.4\cdot10^5}{6.5}$	$\frac{5.4\cdot10^4}{1.5}$
2	$ClO + ClO + M \rightarrow Cl_2O_2 + M$	$2.1\cdot10^6$	$9.4\cdot10^5$	$4.0\cdot10^5$	$1.7\cdot10^5$
	$Cl_2O_2 + h\nu \rightarrow ClOO + Cl$	$1.0\cdot10^6$	$4.7\cdot10^5$	$2.0\cdot10^5$	$8.4\cdot10^4$
	$ClOO + M \rightarrow Cl + O_2 + M$	$1.8\cdot10^8$	$1.1\cdot10^8$	$1.1\cdot10^7$	$3.1\cdot10^6$
	$2(Cl + O_3 \rightarrow ClO + O_2)$	$1.8\cdot10^6$	$1.0\cdot10^6$	$1.2\cdot10^5$	$2.7\cdot10^4$
	Outcome: $2O_3 \rightarrow 3O_2$ Productivity of ozone destruction cycle:*	$\frac{3.6\cdot10^6}{120}$	$\frac{2.0\cdot10^6}{57.6}$	$\frac{2.4\cdot10^5}{6.5}$	$\frac{5.4\cdot10^4}{1.5}$
Net productivity of the 1st and 2nd ozone destruction cycles:*		$\frac{7.2\cdot10^6}{240}$	$\frac{4.0\cdot10^6}{115}$	$\frac{4.8\cdot10^5}{13}$	$\frac{1.1\cdot10^5}{3.0}$
3	$O_2 + h\nu \rightarrow O + O$	$2.4\cdot10^3$	$1.8\cdot10^4$	$1.6\cdot10^5$	$1.8\cdot10^6$
	$2(O + O_2 + M \rightarrow O_3 + M)$	$4.0\cdot10^7$	$6.1\cdot10^7$	$1.0\cdot10^7$	$2.6\cdot10^8$
	Outcome: $3O_2 \rightarrow 2O_3$ Productivity of ozone formation cycle:*	$\frac{4.8\cdot10^3}{0.2}$	$\frac{3.6\cdot10^4}{1.0}$	$\frac{3.2\cdot10^5}{11}$	$\frac{3.6\cdot10^6}{98}$

* In numerator, the variation of ozone concentration in molecule · cm^{-3} · s^{-1} is given, and the same is in denominator but in percent of ozone concentration existing at a given altitude for the cycle during 5 light days. The concentrations of the constituents, used for calculation, are taken from Table 8.

3. Analysis and conclusions

To estimate, how the developed ozone hole theory meets the main requirements for such a theory, namely, whether or not the underlying factors and conclusions of the theory are hand in hand with available experimental facts and the theory adequately describes all known features of ozone hole, let us answer some questions ensuing from the theory.

– Whether or not the observed rapid and considerable ozone variations in the lower stratosphere contradict the photochemical equilibrium of (O_x) family and ozone?

Rapid and strong ozone variations in the lower stratosphere arise due to wavelike horizontal motions of atmospheric fronts, intimately linked to jet flows and observed in the stratosphere, which result in a change of stratospheric air masses over observation points.[21,22,26,28] Each air mass contains its own atmospheric constituents (and, in particular, those considered here) with specific concentrations, reported in Ref. 20 and Table 3 to be at photochemical/near-photochemical equilibrium during day. Therefore, if some high-altitude atmospheric front has passed over the observation site, and a new stratospheric air mass has come, it will bring a new concentration of ozone being at a state of photochemical equilibrium with concentrations of atmospheric constituents contained in this air mass. Hence, owing to (and not despite) the photochemical equilibrium and to regularities of the lower stratosphere dynamics, it experiences considerable and rapid ozone variations observed at the observation sites. The same dynamics may be and is a cause for rapid ozone variations inside the ozone hole,[32] when PSF passes over the observation site. The ozone concentration in the ozone hole in the lower stratosphere can also be decreased photochemically in the first half of spring when ozone is intensively destructed via the 1st and 2nd catalytic cycles (Table 7).

– Why the ozone layer, and, in particular, the ozone of the lower stratosphere, is at a steady state for many tens of years?

As it is stated by the theory developed in Ref. 20 and in the present paper, and as opposed to misunderstanding that there is no photochemical equilibrium between (O_x) family and ozone in the lower stratosphere,[12,23] the odd oxygen family and ozone, including those in the lower stratosphere, are presently and were in the past, at least since the beginning of instrumental observations, at or near the state of photochemical equilibrium during day, whereas at night the chemical ozone variations are insignificant because of long chemical lifetimes of ozone and (O_x) family. At the same time, according to Ref. 30, the deviations of annually mean values of total ozone from the multiyear average concentration, judging from the world ozonometric network data, did not exceed 2% for 1958–1980. The photochemical equilibrium of the ozone layer holds until presently (Table 3), despite the anthropogenic-freon impact on this layer, giving rise to ozone hole at spring time in Antarctic, characterized by a low level of photochemically equilibrium ozone concentration, which is gradually decreasing during the first half of the spring (when the photochemical equilibrium of the (O_x) family is absent) under influence of catalytic cycles 1 and 2 extending out to early October. After springtime switching of stratospheric circulation and changing air masses in Antarctic, the ozone concentration in the lower stratosphere, where the ozone hole was located, increases up to values close to the pre-hole level.

– Why ozone hole is observed only in Antarctic and only in spring?

First, only in wintertime and springtime, there is a relatively stable, dynamically isolated part of the stratosphere in Antarctic, bounded by PSF which prevents moderate and polar air masses, containing, respectively, low and high ozone concentrations at this time of year, from horizontal turbulent mixing.[21,26,28] In Arctic, in late winter or early spring, the PSC is deformed (it is divided into two parts), loses its efficiency as a dynamical system preventing turbulent mixing (with weaker along-PSF wind velocity),[4] and the internal part of PSC becomes incapable of functioning as a dynamically isolated system suitable for existence of such a hole as is observed in Antarctic. At the same time, Antarctic PSC, in contrast to Arctic one, holds until late spring.

Second, only during the long polar night, only the interior of Antarctic, i.e., dynamically isolated part of PSC (but not other parts of the atmosphere) accumulates a considerable amount of chlorine nitrate (see Table 1), which in spring, when the sun appears, photodissociates and forms the increased Cl and ClO concentrations, which, in turn, rapidly destruct ozone via catalytic cycles 1 and 2. The increase of $ClONO_2$ concentration, at appearance of sun, leads to the daytime photochemically equilibrium ClO concentration (see (f. 16)), in which the NO_2 concentration, low during the polar night in Antarctic,[15] is close to springtime daylight NO_2 concentration in the ozone hole (see formula (f. 1) and Table 2). An increase of ClO concentration leads to increase of chemically-equilibrium concentration of Cl_2O_2 (f. 2) and associated concentration of Cl (f. 9). This activates the action of catalytic cycles 1 and 2 and the decrease of O_3 concentration (see Table 5 and formula (f. 13)). As a result of the anthropogenic-freon impact on the atmosphere, the ClONO2 increases and accumulates in periods of polar nights in Antarctic, and remains unchanged in spring–summer periods during day because of action of catalytic cycle 1, which results in formation of ozone hole.

– Why a high negative correlation between ozone and chlorine oxide concentrations is observed in ozone hole in the lower stratosphere?

As the ClO concentration increases under conditions of photochemical equilibrium, the Cl_2O_2

concentration also increases. This leads to photochemical increase of the Cl concentration, with (Cl_2O_2) increasing faster than (HOCl) at building up (ClO); the more (Cl) concentration the greater the productivity of catalytic cycles 1 and 2 depleting ozone. As a result, O_3 concentration decreases in the same part of the ozone hole, where ClO increases. In the absence of photochemical equilibrium, the main part in the high negative correlation plays reaction $Cl + O_3 \rightarrow Cl_3 + O_2$ demonstrating that the O_3 destruction proceeds simultaneously with the ClO formation.

– Do the atmospheric constituents* BrO *and* Br *influence ozone concentration in ozone hole?

Yes, they do. It follows from formula (f. 9) that, all other factors being the same, an increase of Br concentration leads to a proportional increase of Cl concentration. At the same time, from formula (f. 13) it follows that the Cl increase causes O_3 reduction. For instance, doubling of Br concentration results in decrease of the O_3 concentration at a height of 20 km in mid-October from $8.7{\cdot}10^{10}$ to $4.35{\cdot}10^{10}$, i.e., by a factor of 2. According to Table 5, the bromine and chlorine-bromine catalytic cycles (4 and 5) influence insignificantly the ozone concentration in ozone hole as compared to the effect of chlorine catalytic cycles 1 and 2.

– Do the variations of atmospheric temperature influence ozone hole?

Yes, they do, though weakly. The temperature effects are most important for the rate of reaction $Cl + O_3 \rightarrow ClO + O_2$ in catalytic cycles 1 and 2. If, for example, the atmospheric temperature at a height of 20 km in ozone hole in mid-October decreases by 20 K, the reaction rate will decrease by 11%.

– Do vertical motions in the stratosphere affect the ozone concentration in ozone hole?

Had the Antarctic PSF possessed a stable upwelling (ascent of air in the upper troposphere and lower stratosphere), the vertical motions in the stratosphere could reduce the ozone concentration in ozone hole. However, the observations of American researchers[32] suggest that no upwelling, but rather descent of air, is observed in the stratosphere in PSL.

– Why the occurrence of ozone hole is accompanied by the decrease of total ozone in some subpolar and midlatitude regions outside the ozone hole?

First, the PSF has irregular wavelike shape with moving altitude troughs and ridges. If some region under discussion lies in such a trough, extending farther than the average boundaries of the ozone hole and oriented with northward component in Antarctic (southward component in Arctic), then this region will have a lower total ozone because of its location within the ozone hole (or non-developed ozone hole in the Northern Hemisphere). Second, the springtime change of atmospheric circulation at polar latitudes is accompanied by large-scale horizontal mixing of polar and midlatitude air masses, i.e., those with low (from region of the ozone hole) and, on average, normal (from midlatitude regions) ozone content. As a whole, this leads to dilution of ozone and reduction of total ozone in some regions of subpolar and middle latitudes.

Are there other catalytic cycles (except those from Table 5) destructing ozone?

Yes, for example, the 6th cycle:

$$\begin{array}{ll}
HOCl + h\nu \rightarrow Cl + OH & 4.6\cdot10^{5} \\
Cl + O_3 \rightarrow ClO + O_2 & 5.2\cdot10^{5} \\
OH + O_3 \rightarrow HO_2 + O_2 & 1.6\cdot10^{4} \\
ClO + HO_2 \rightarrow HOCl + O_2 & 4.7\cdot10^{5} \\
\hline
\text{Outcome: } 2O_3 \rightarrow 3O_2 &
\end{array}$$

The cycle's productivity is $1.1\cdot10^{6}$ molecule$\times$ $\times$cm$^{-3}\cdot$ s^{-1}. Neglected by calculations, the total productivity of the 5th and 6th cycles makes $2.3\cdot10^{6}$ molecule $\cdot$ cm$^{-3}\cdot$ s^{-1}, that exceeds the productivity of the 2nd cycle (Table 5). Depletion of ozone through 1, 2, 5, and 6 cycles is sufficiently fast even, possibly, without accounting for duplication of the calculated resultant ozone concentration.

This paper and the answers to the posed questions clarify the actual causes for origin of the ozone hole in Antarctic. Main causes of the ozone hole appearance are the anthropogenic-freon impact on the ozone layer dating back to the past century and following ozone destruction through the catalytic cycles. It also becomes clear why negative answer can be given to the question on the possibility of occurrence of ozone holes in other regions on the globe; regions with dynamically stable isolated part of the stratosphere cannot be found anywhere but in Antarctic. As for the question on the ozone hole increase in size and the intensity of ozone destruction in ozone hole, it is directly connected with the possibility of increase of the average sizes of PSL in Antarctic, not confirmed by observations during the last 40 years. The intensity of the ozone depletion in ozone hole depends on the growth of freon emissions into the atmosphere and, hence, on increase of $ClONO_2$, ClO, and Cl concentrations in ozone hole, which is quite possible if international agreements, including the Montreal Protocol adopted in 1989 and its 1990 London amendments,[5,6] are violated.

So, we can conclude that the presented theory of ozone hole well agrees with the available experimental facts and explains all known peculiarities of ozone hole.

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