

On chemical lifetime of atmospheric constituents and concentration of atomic oxygen in the atmosphere

G.P. Gushchin

Affiliate of the Main Geophysical Observatory, Voeikovo, St. Petersburg

Received January 14, 2002

A method is developed for calculation of the chemical lifetime of atmospheric constituents, in particular, of the odd oxygen family τ_{O_X} . The values of τ_{O_X} calculated at different altitudes in the atmosphere are presented and compared with the results calculated by other authors. A significant discrepancy in the calculated results is found for the altitudes below 30 km. The new values of τ_{O_X} turned out to be 20–8000 times smaller than the previous ones. Causes for such a discrepancy are discussed, and it is found that the main causes are the neglect of the effect of nitrogen oxides on τ_{O_X} in the previous calculations and unclear formulation and solution of the problem on τ_{O_X} calculation. It is concluded that at the altitudes of 10–50 km the odd oxygen family, including atmospheric ozone, in daytime is in the state of photochemical equilibrium or the state close to photochemical equilibrium. A new method is proposed for theoretical calculation of the concentration of atomic oxygen in the atmosphere taking into account the photochemical equilibrium of the odd oxygen family and the presence of nitrogen oxides in the atmosphere. An equation is derived for calculation of the vertical ozone distribution taking into account the photochemical equilibrium of the odd oxygen family and the presence of nitrogen and chlorine oxides and other constituents in the atmosphere.

Introduction

This paper considers briefly three related results of the photochemical theory, namely, the new method and calculated results on the chemical lifetime of the family of atmospheric constituents, the new method and calculation of the ozone and atomic oxygen concentrations at different altitudes in the atmosphere, and the problem on the effect of nitrogen oxides on the odd oxygen family. Unlike other works and works reviewed in Refs. 1, 2, and 5, in which calculations were performed for individual atmospheric constituents or mixed systems consisting of individual constituents and families, here the calculations deal with families of constituents interacting with each other and having a short chemical lifetime. The calculated results obtained in this work are compared with the results of previous calculations.

The chemical lifetime τ_A of an atmospheric constituent A (or a family of constituents A_X) is, as known,^{1,2} the period, during which the constituent (or family) concentration decreases by $e = 2.72$ times with respect to the initial value under the effect of all chemical and photochemical reactions destroying this constituent (or family). This definition concerns only the reactions destroying the given constituent (or family), while other reactions generating this constituent (or family) are ignored. The initial concentration of the constituent (or family) is taken to be equal to the photochemically equilibrium value or, in special cases, its other value at the given altitude in the atmosphere. Unless otherwise indicated, it is believed that the values of τ_A (or τ_{A_X}) correspond to the daytime conditions. From the definition of τ_A and τ_{A_X} , it follows that they depend on

the constituent A (or A_X) and, in the case of a family, on the composition of A_X .

The chemical lifetime τ_A (or τ_{A_X}) is one of the most important aeronomic characteristics of an atmospheric constituent (or family), and it is of primary significance for determining the stability of the chemical composition of the atmosphere, as well as calculating the constituent concentrations at different altitudes in the atmosphere and developing the theory and models of atmospheric constituents.

If $\tau_A < 10$ days (or $\tau_{A_X} < 10$ days), then, according to the criterion accepted in Ref. 1, the constituent A (or family A_X) is in photochemical equilibrium and the transport process in the atmosphere almost do not affect its concentration. If $\tau_A > 100$ days (or $\tau_{A_X} > 100$ days), then the concentration of the constituent A (or A_X) is determined by the transport processes. At $10 < \tau_A < 100$ days (or $10 < \tau_{A_X} < 100$ days) the concentration of the constituent A (or A_X) is determined by both photochemical and dynamic processes. According to another, more strict criterion published in Ref. 2, the constituent A (or family A_X) is in photochemical equilibrium at a given altitude in the atmosphere, if τ_A (or τ_{A_X}) is less than the time constant of zonal transport in the atmosphere, which does not exceed 1 day at the altitudes of 10–35 km and 5 h at the altitudes of 40–50 km.

The concentration of the family of, e.g., odd oxygen (O_X) is understood^{1,2} as a sum of concentrations

$$(O_X) = (O_3) + (O'_D) + (O^3_P), \quad (1)$$

where (O_3) is the concentration of ozone molecules; (O'_D) is the concentration of oxygen atoms in the first excited

state; (O) is the concentration of oxygen atoms in the ground state, which is designated from here on as (O) .

Method for calculation of the chemical lifetime for families of atmospheric constituents A_X

In this section we consider the method for calculation of τ_{A_X} at different altitudes in the atmosphere using, as an example, the chemical lifetime of the odd oxygen family τ_{O_X} . It should be emphasized that the proposed method is not a particular case, but the general method suitable for calculation of τ_{A_X} for any family of atmospheric constituents. According to the information available, there was no correct method for calculation of τ_{A_X} yet (see the literature cited).

To find τ_{O_X} , let us differentiate Eq. (1) with respect to t :

$$\frac{d(O_X)}{dt} = \frac{d(O_3)}{dt} + \frac{d(O_D')}{dt} + \frac{d(O)}{dt}. \quad (2)$$

Since, by the definition, all the known reactions with participation of ozone published, in particular, in Refs. 1–4 are taken into account in this case, the derivative $\frac{d(O_3)}{dt}$ expressing the rate of variation of the ozone concentration has the following form (our own numeration of the reaction rate constants K_i is used):

$$\begin{aligned} \frac{d(O_3)}{dt} = & [K_1(O)(O_2)(M) + K_{117}(BrO)(HO_2) + \\ & + K_{94}(ClO)(HO_2)] - [(J_{O_3} + J_{O_3}^*)(O_3) + \\ & + K_3(NO)(O_3) + K_{19}(Br)(O_3) + K_4(Cl)(O_3) + \\ & + K_{14}(OH)(O_3) + K_{24}(BrO)(O_3) + K_{16}(HO_2)(O_3) + \\ & + K_{10}(NO_2)(O_3) + K_2(O)(O_3) + K_{55}(O_D')(O_3) + \\ & + K_6(ClO)(O_3) + K_{68}(OClO)(O_3) + \\ & + K_{25}(SO_2)(O_3)], \quad (3) \end{aligned}$$

where the constituent concentrations are given in parentheses; $(M) = (N_2) + (O_2)$ is the third partner concentration; J_{O_3} is the coefficient of photodissociation of the ozone molecule, $J_{O_3}^*$ is the coefficient of photodissociation of the excited ozone molecule.

To estimate the terms in Eq. (3) and calculate τ_{O_X} , we used the values of K_i , J_i , and the concentrations of atmospheric constituents from Refs. 1–5. Estimates of the terms in Eq. (3) at the altitude of 20 km close to the altitude of the maximum ozone concentration is given in Table 1.

Table 1. Estimates of terms in Eq. (3) for the altitude of 20 km, $T = 217$ K

Term	Value, mol \times \times cm ⁻³ ·s ⁻¹	Term	Value, mol \times \times cm ⁻³ ·s ⁻¹
<i>Positive sign</i>			
$K_1(O)(O_2)(M)$	$2.5 \cdot 10^{11}$	$K_{14}(HO)(O_3)$	$4.9 \cdot 10^4$
$K_{117}(BrO)(HO_2)$	$9.0 \cdot 10^{-1}$	$K_{16}(HO_2)(O_3)$	$2.4 \cdot 10^4$
$K_{94}(ClO)(HO_2)$	$3.2 \cdot 10^{-1}$	$K_{19}(Br)(O_3)$	$2.5 \cdot 10^5$
<i>Negative sign</i>			
$J_{O_3}(O_3)$	$1.4 \cdot 10^9$	$K_{24}(BrO)(O_3)$	$2.7 \cdot 10^4$
$K_3(NO)(O_3)$	$1.3 \cdot 10^7$	$K_{10}(NO_2)(O_3)$	$7.3 \cdot 10^3$
$2K_2(O)(O_3)$	$1.0 \cdot 10^6$	$K_{55}(O_D')(O_3)$	$3.1 \cdot 10^2$
$K_4(Cl)(O_3)$	$9.0 \cdot 10^4$	$K_6(ClO)(O_3)$	$1.4 \cdot 10^{-1}$
		$K_{68}(OClO)(O_3)$	$4.3 \cdot 10^{-4}$
		$K_{25}(SO_2)(O_3)$	$3.2 \cdot 10^{-7}$

Keeping only the dominant terms in Eq. (3), without a prejudice to the result of τ_{O_X} calculation, we obtain

$$\begin{aligned} \frac{d(O_3)}{dt} = & K_1(O)(O_2)(M) - [(J_{O_3} + J_{O_3}^*)(O_3) + \\ & + K_3(NO)(O_3) + K_4(Cl)(O_3) + \\ & + K_{16}(HO_2)(O_3) + K_{14}(OH)(O_3) + K_2(O)(O_3)]. \quad (4) \end{aligned}$$

Similarly, we can obtain the derivatives $\frac{d(O_D')}{dt}$ and $\frac{d(O)}{dt}$:

$$\begin{aligned} \frac{d(O_D')}{dt} = & J_{O_3}^*(O_3) + J_{NO_2}^*(NO_2) + J_{O_2}^*(O_2) - \\ & - [K_{105}(O_D')(O_2) + K_{106}(O_D')(N_2) + \\ & + K_{55}(O_D')(O_3)], \quad (5) \end{aligned}$$

$$\begin{aligned} \frac{d(O)}{dt} = & J_{O_3}(O_3) + J_{NO_2}(NO_2) + 2J_{O_2}(O_2) + J_{O_2}^*(O_2) + \\ & + K_{105}(O_D')(O_2) + K_{106}(O_D')(N_2) + 2K_{55}(O_D')(O_3) - \\ & - [K_1(O)(O_2)(M) + K_8(O)(NO_2) + K_2(O)(O_3)]. \quad (6) \end{aligned}$$

Summing up Eqs. (4), (5), and (6), keeping only the dominant terms, taking into account that at the altitudes of 10–50 km $J_{NO_2}^* \ll J_{NO_2}$ and $J_{O_2}^* \ll J_{O_2}$, and using Eq. (2), we obtain

$$\begin{aligned} \frac{d(O_X)}{dt} = & J_{NO_2}(NO_2) + 2J_{O_2}(O_2) - \\ & - [K_3(NO)(O_3) + K_4(Cl)(O_3) + K_{16}(HO_2)(O_3) + \\ & + K_{14}(OH)(O_3) + K_8(O)(NO_2) + 2K_2(O)(O_3)]. \quad (7) \end{aligned}$$

Differential equation (7) allows the value of τ_{O_X} to be estimated.

Designating the third term in the square brackets in the right-hand side of Eq. (7) at the altitude h in the atmosphere as L_h [see Eq. (10)], we obtain that the rate of decrease in the concentration of the odd oxygen family is

$$\frac{d(O_X)}{dt} = -L_h. \quad (8)$$

Integrating Eq. (8) from $(O_X)_0$ to $(O_X)_t$ and from 0 to t , we obtain

$$\int_{(O_X)_0}^{(O_X)_t} d(O_X) = - \int_0^t L_h dt. \quad (9)$$

Let us estimate the value

$$L_h = K_3(NO)(O_3) + K_{14}(OH)(O_3) + K_{16}(HO_2)(O_3) + K_4(Cl)(O_3) + K_8(O)(NO_2) + 2K_2(O)(O_3) \quad (10)$$

at different altitudes in the atmospheric layer of 10–50 km. (Here the values of $K_{19}(Br)(O_3)$ and $K_{24}(BrO)(O_3)$ at different altitudes are not used, since they almost do not affect the value of L_h in Table 4.) The initial data for calculations and their sources are given in Tables 2, 3, 7 [fourth column with the refined data on (O)], and 8 (second column).

The allowance made for the terms neglected when keeping only the dominant terms in square brackets in Eq. (7) can only increase the value of L_h at the altitudes of 10–50 km in Table 4 and, according to Eq. (13a), decrease the value of τ_{O_X} at these altitudes, which confirms the developed concept of photochemical stability of the ozone layer.

It should be noted that the concentrations of (O), (O'_D) , (Cl), (OH), (HO_2) given in Refs. 2 and 5 and in Table 3 are determined quite roughly, therefore it is needed to further improve the technique for measuring the concentrations of these constituents. The values of terms in Eq. (10) and L_h at different altitudes are given in Table 4.

Table 2. Chemical reactions, reaction rate constants K_i (at $T = 217$ K), and photodissociation coefficients J_A at the altitude of 20 km (Refs. 2, 4, and 5)

#	Reaction	$K_i, \text{mol}^{-1} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$ for two-body reactions and $\text{mol}^{-2} \cdot \text{cm}^6 \cdot \text{s}^{-1}$ for three- body reactions; J_A, s^{-1}
1	$O + O_2 + M \rightarrow O_3 + M$	$K_1 = 1.3 \cdot 10^{-33}$
2	$O + O_3 \rightarrow O_2 + O_2$	$K_2 = 6.0 \cdot 10^{-16}$
3	$O_3 + NO \rightarrow NO_2 + O_2$	$K_3 = 3.2 \cdot 10^{-15}$
4	$O_3 + Cl \rightarrow ClO + O_2$	$K_4 = 8.7 \cdot 10^{-12}$
5	$O + NO_2 \rightarrow NO + O_2$	$K_8 = 1.1 \cdot 10^{-11}$
6	$O_3 + OH \rightarrow HO_2 + O_2$	$K_{14} = 2.1 \cdot 10^{-11}$
7	$O_3 + HO_2 \rightarrow OH + 2O_2$	$K_{16} = 1.4 \cdot 10^{-15}$
8	$(O'_D) + O_3 \rightarrow O_2 + O + O$	$K_{55} = 1.2 \cdot 10^{-10}$
9	$(O'_D) + O_2 \rightarrow O + O_2$	$K_{105} = 4.4 \cdot 10^{-11}$
10	$(O'_D) + N_2 \rightarrow O + N_2$	$K_{106} = 3.0 \cdot 10^{-11}$
11	$O_2 + h\nu \rightarrow O + O$	$J_{O_2} = 5.0 \cdot 10^{-14}$
12	$O_3 + h\nu \rightarrow O_2 + O$	$J_{O_3} = 5.0 \cdot 10^{-4}$
13	$O_3 + h\nu \rightarrow O_2 + (O'_D)$	$J_{O_3}^* = 1.5 \cdot 10^{-5}$
14	$NO_2 + h\nu \rightarrow NO + O$	$J_{NO_2} = 1.1 \cdot 10^{-2}$

It follows from Table 4 that the value of L_h , e.g., at the altitude of 30 km is mostly determined by the term

$K_3(NO)(O_3)$. Therefore, at this altitude Eq. (9) takes the form

$$\int_{(O_X)_0}^{(O_X)_t} d(O_X) = - \int_0^t K_3(NO)(O_3) dt. \quad (11)$$

Taking into account that K_3 in Eq. (11) is almost constant for several days, it can be factored out of the definite integral sign. Using the theorem of the mean value of a definite integral for a product of two functions and for a single function, from Eq. (11) we have

$$(O_X)_t - (O_X)_0 = -K_3(O_3)_{\xi_1} (NO)_{\xi_2} t, \quad (12)$$

where $(O_3)_{\xi_1}$ and $(NO)_{\xi_2}$ are the intermediate values of (O_3) and (NO) inside the interval $0 < \xi < t$. Assuming, according to the definition of τ_{O_X} , that

$$(O_X)_t = \frac{1}{e} (O_X)_0,$$

where

$$1/e = 0.368,$$

and, consequently,

$$(O_X)_t - (O_X)_0 = -0.632(O_X)_0,$$

and taking into account that in this case $t = \tau_{O_X}$, from Eq. (12) for the altitude of 30 km we obtain

$$\tau_{O_X} = 0.632(O_X)_0 / [K_3(O_3)_{\xi_1} (NO)_{\xi_2}]. \quad (13)$$

The values of $(O_3)_{\xi_1}$ and $(NO)_{\xi_2}$ in Eq. (13) from the geometrical meaning of the definite integral [from comparison of areas separated by the integrand functions (O_3) and (NO) in Eq. (11) in the interval from 0 to t with the rectangular areas of the same length having the ordinates $(O_3)_{\xi_1}$ and $(NO)_{\xi_2}$] can be taken equal to $(O_3)_{\text{mean}}$ and $(NO)_{\text{mean}}$ from the experimental data summarized in Tables 3 and 8. It was taken into account that the functions (O_3) and (NO) depending on t are always positive. In the general form for calculation at the altitudes of 30–50 km, the equation similar to Eq. (10) is used in the denominator of Eq. (13):

$$L'_h = K_3(NO)_{\xi_2} (O_3)_{\xi_1} + K_{14}(OH)_{\xi_3} (O_3)_{\xi_1} + K_{16}(HO_2)_{\xi_4} (O_3)_{\xi_1} + K_4(O_3)_{\xi_1} (Cl)_{\xi_5} + K_8(NO_2)_{\xi_6} (O)_{\xi_7} + 2K_2(O_3)_{\xi_1} (O)_{\xi_7}.$$

In this equation, the values of $(O_3)_{\xi_1}$, $(NO)_{\xi_2}$, $(OH)_{\xi_3}$, $(HO_2)_{\xi_4}$, $(Cl)_{\xi_5}$, $(NO_2)_{\xi_6}$, $(O)_{\xi_7}$ are close to their mean values at the considered altitude (Tables 3, 7 (fourth column) and 8 (second column)), and the value of L'_h is close to L_h .

Based on the above-said, in the layer of 10–50 km

$$\tau_{O_X} = [0.632(O_X)_0] / L_h. \quad (13a)$$

Table 3. Daytime concentration of atmospheric constituents (atom · cm⁻³ or mol · cm⁻³), photodissociation coefficients J_A (s⁻¹), and mean temperature T (K) at different altitudes in the atmosphere^{2,5}

h , km	(O_D)	(O_2)	(NO)*	(NO ₂)*	(HO ₂)	(OH)	(Cl)	J_{O_2}	J_{O_3}	T
10	–	$1.7 \cdot 10^{18}$	$8.6 \cdot 10^8$	$1.0 \cdot 10^9$	$3.0 \cdot 10^7$	$3.5 \cdot 10^5$	$(4 \cdot 10^1)$	$(2 \cdot 10^{-16})$	$(5 \cdot 10^{-4})$	223
15	–	$8.1 \cdot 10^{17}$	$1.6 \cdot 10^9$	$2.0 \cdot 10^9$	$3.0 \cdot 10^6$	$4.0 \cdot 10^5$	$(2 \cdot 10^2)$	$3.0 \cdot 10^{-15}$	$5.0 \cdot 10^{-4}$	217
20	0.9	$3.6 \cdot 10^{17}$	$1.4 \cdot 10^9$	$1.8 \cdot 10^9$	$6.0 \cdot 10^6$	$8.0 \cdot 10^5$	$3.6 \cdot 10^3$	$5.0 \cdot 10^{-14}$	$5.0 \cdot 10^{-4}$	217
25	5	$1.6 \cdot 10^{17}$	$1.7 \cdot 10^9$	$2.5 \cdot 10^9$	$2.0 \cdot 10^7$	$4.0 \cdot 10^6$	$8.3 \cdot 10^3$	$1.0 \cdot 10^{-12}$	$5.0 \cdot 10^{-4}$	222
30	25	$8.8 \cdot 10^{16}$	$2.3 \cdot 10^9$	$2.3 \cdot 10^9$	$2.5 \cdot 10^7$	$9.0 \cdot 10^6$	$1.2 \cdot 10^4$	$2.0 \cdot 10^{-11}$	$8.0 \cdot 10^{-4}$	227
35	$1.0 \cdot 10^2$	$3.5 \cdot 10^{16}$	$1.4 \cdot 10^9$	$1.0 \cdot 10^9$	$2.0 \cdot 10^7$	$2.5 \cdot 10^7$	$5.5 \cdot 10^4$	$2.0 \cdot 10^{-10}$	$1.5 \cdot 10^{-3}$	237
40	$3.3 \cdot 10^2$	$1.7 \cdot 10^{16}$	$1.3 \cdot 10^9$	$2.7 \cdot 10^8$	$1.3 \cdot 10^7$	$2.0 \cdot 10^7$	$1.7 \cdot 10^5$	$5.0 \cdot 10^{-10}$	$3.0 \cdot 10^{-3}$	250
45	$6.0 \cdot 10^2$	$8.9 \cdot 10^{15}$	$6.2 \cdot 10^8$	$8.2 \cdot 10^7$	$1.0 \cdot 10^7$	$1.5 \cdot 10^7$	$4.1 \cdot 10^5$	$1.0 \cdot 10^{-9}$	$5.0 \cdot 10^{-3}$	264
50	$6.1 \cdot 10^2$	$4.8 \cdot 10^{15}$	$4.2 \cdot 10^8$	$2.1 \cdot 10^7$	$8.5 \cdot 10^6$	$1.2 \cdot 10^7$	$4.2 \cdot 10^5$	$1.5 \cdot 10^{-9}$	$8.0 \cdot 10^{-3}$	271

* The values of (NO) and (NO₂) are obtained from the mean experimental data published in Ref. 2.

Table 4. Value of the terms and L_h (mol · cm⁻³ · s⁻¹) in Eq. (10) at different altitudes in the atmosphere

h , km	$K_3(\text{NO})(\text{O}_3)$	$K_{14}(\text{OH})(\text{O}_3)$	$K_{16}(\text{HO}_2)(\text{O}_3)$	$K_4(\text{Cl})(\text{O}_3)$	$K_8(\text{O})(\text{NO}_2)$	$2K_2(\text{O})(\text{O}_3)$	L_h
10	$3.3 \cdot 10^6$	$8.3 \cdot 10^3$	$4.5 \cdot 10^4$	$3.6 \cdot 10^2$	$7.0 \cdot 10^6$	$1.0 \cdot 10^6$	$1.1 \cdot 10^7$
15	$5.6 \cdot 10^6$	$9.2 \cdot 10^3$	$4.6 \cdot 10^3$	$1.9 \cdot 10^3$	$1.6 \cdot 10^7$	$9.4 \cdot 10^5$	$2.3 \cdot 10^7$
20	$1.3 \cdot 10^7$	$4.9 \cdot 10^4$	$2.4 \cdot 10^4$	$9.0 \cdot 10^4$	$5.9 \cdot 10^6$	$1.0 \cdot 10^6$	$2.0 \cdot 10^7$
25	$2.0 \cdot 10^7$	$3.0 \cdot 10^5$	$9.4 \cdot 10^4$	$2.4 \cdot 10^5$	$8.5 \cdot 10^6$	$1.5 \cdot 10^6$	$3.0 \cdot 10^7$
30	$2.5 \cdot 10^7$	$6.0 \cdot 10^5$	$1.0 \cdot 10^5$	$2.9 \cdot 10^5$	$2.8 \cdot 10^6$	$5.3 \cdot 10^5$	$2.8 \cdot 10^7$
35	$1.5 \cdot 10^7$	$1.5 \cdot 10^6$	$6.8 \cdot 10^4$	$1.1 \cdot 10^6$	$4.6 \cdot 10^6$	$2.4 \cdot 10^6$	$2.3 \cdot 10^7$
40	$1.5 \cdot 10^7$	$7.4 \cdot 10^5$	$2.5 \cdot 10^4$	$1.7 \cdot 10^5$	$5.1 \cdot 10^6$	$7.6 \cdot 10^6$	$2.8 \cdot 10^7$
45	$2.0 \cdot 10^6$	$2.2 \cdot 10^5$	$6.7 \cdot 10^3$	$1.4 \cdot 10^6$	$4.6 \cdot 10^6$	$1.1 \cdot 10^7$	$1.9 \cdot 10^7$
50	$4.6 \cdot 10^5$	$6.0 \cdot 10^4$	$1.9 \cdot 10^3$	$4.6 \cdot 10^5$	$1.9 \cdot 10^6$	$7.0 \cdot 10^6$	$9.9 \cdot 10^6$

Calculated chemical lifetime of the odd oxygen family τ_{O_X} and comparison with other results

The results of τ_{O_X} calculation by Eq. (13a) are given in Table 5 (second column). As $(\text{O}_X)_0$ entering into Eq. (13a), we used the values of (O_3) given in Table 8 based on the data of Ref. 2, and as L'_h we used the values of L_h given in Table 4.

Table 5. Chemical lifetime of the odd oxygen family in daytime τ_{O_X} (h) in the atmospheric layer of 10–50 km based on different data

h , km	τ_{O_X} by Eq. (13a)	τ_{O_X} from Ref. 2	τ_{O_X} , Refs. 1, 6, winter, 45°N
10	16	–	–
15	7.2	$2.5 \cdot 10^4$	$2.8 \cdot 10^5$
20	25	$1.4 \cdot 10^4$	$2.8 \cdot 10^4$
25	19	$1.7 \cdot 10^3$	$9.7 \cdot 10^3$
30	16	$2.8 \cdot 10^2$	$2.5 \cdot 10^3$
35	15	55	$2.8 \cdot 10^2$
40	6.3	19	$1.7 \cdot 10^2$
45	2.9	5.5	42
50	1.8	2.2	22

For a comparison, Table 5 presents the widely used data on τ_{O_X} published in Refs. 1, 2, and 6. As is seen from Table 5, our values of τ_{O_X} differ strongly from the values accepted in Refs. 1, 2, and 6 for the altitudes below

35 km. The values of τ_{O_X} obtained in this work for the altitudes of 15–35 km are 18–39000 times smaller than those published in Refs. 1, 2, and 6. Hence, taking into account the above criteria of photochemical equilibrium, as well as the calculated results on τ_{O_X} , it can be concluded that, contrary to the existing ideas, the odd oxygen family is in the state of photochemical equilibrium in daytime in the entire atmospheric layer from 10 to 50 km, including the layer of 10–30 km. Above 40 km, the values of τ_{O_X} obtained here and in other works are relatively close.

The data on τ_{O_X} from Refs. 1 and 6 used for comparison (see Table 5, fourth column) were obtained, as was mentioned in Ref. 1, based on the rate of ozone generation in the case of photochemical equilibrium, rather than the rate of ozone destruction, as follows from the definition of τ_{O_X} . The rate of ozone formation in that case was calculated only from the value of $2J_{\text{O}_2}(\text{O}_2)$, that is, only the reaction of photodissociation 11 (see Table 2) was taken into account, this reaction produces two oxygen atoms, which recombine quickly with the oxygen molecules by the reaction 1 (see Table 2) and form ozone. However, in the atmosphere, as seen from the reaction 14 (see Table 2), atomic oxygen also occurs under the effect of NO₂ photodissociation with the following formation of ozone by reaction 1 (see Table 2). The rate of formation of atomic oxygen by the reactions 11 and 14 (see Table 2) equal to $2J_{\text{O}_2}(\text{O}_2)$ and $J_{\text{NO}_2}(\text{NO}_2)$, respectively, and their values at different altitudes in the atmosphere are given in Table 6.

Table 6. Rate of formation of atomic oxygen by reactions 11 and 14 (Table 2) at different altitudes in the atmosphere

h , km	By reaction 11 $2J_{O_2}(O_2)$, atom · cm ⁻³ · s ⁻¹	By reaction 14 $J_{NO_2}(NO_2)$, atom · cm ⁻³ · s ⁻¹
10	$6.8 \cdot 10^2$	$1.1 \cdot 10^7$
15	$4.9 \cdot 10^3$	$2.2 \cdot 10^7$
20	$3.6 \cdot 10^4$	$2.0 \cdot 10^7$
25	$3.2 \cdot 10^5$	$2.8 \cdot 10^7$
30	$3.5 \cdot 10^6$	$2.5 \cdot 10^7$
35	$1.4 \cdot 10^7$	$1.1 \cdot 10^7$
40	$1.7 \cdot 10^7$	$3.0 \cdot 10^6$
45	$1.8 \cdot 10^7$	$9.0 \cdot 10^5$
50	$1.4 \cdot 10^7$	$2.5 \cdot 10^5$

It follows from Table 6 that at the altitudes of 10–30 km the rate of formation of atomic oxygen by the reaction 11 (see Table 2) is much lower than the rate of the reaction 14 (see Table 2) and only above 40 km the rate of the reaction 11 exceeds that of the reaction 14. Consequently, Ref. 6 ignored the effect of nitrogen dioxide on ozone, and this has led to the overestimated values of τ_{O_X} at the altitudes of 10–30 km that were reported in Refs. 1 and 6.

In Ref. 2, the value of τ_{O_X} was calculated by the equation, whose derivation is unknown and not given and which finally ignored nitrogen oxides:

$$\tau_{O_X} = \frac{(O_X)}{2K_{34}(O)^2(M) + 2K_2(O)(O_3) + D}, \quad (14)$$

where

$$D = K_{76}(H)(O_3) + K_{11}(O)(OH) + K_{12}(O)(HO_2) + K_{14}(OH)(O_3) + K_{16}(HO_2)(O_3) + K_8(O)(NO_2) + K_3(NO)(O_3) + K_5(O)(ClO) + K_4(Cl)(O_3). \quad (15)$$

The denominator of Eq. (14) includes all terms with negative signs (including D), that is, the terms responsible for destruction of the odd oxygen family.

From the physical meaning of Eq. (14) it follows that τ_{O_X} here is understood as the period, during which all (O_X) molecules in a unit volume are destroyed (since the number of molecules in 1 cm³ is divided by the rate of destruction of these molecules in 1 cm³), rather than the period, during which the concentration decreases 2.72 times, as follows from the definition.

Taking into account the above comments, it should be noted that Refs. 2 and 6 report the chemical lifetime of the odd oxygen family (O_X) obtained as a result of fuzzy formulation of the problem and neglect of a number of factors related to calculation of the chemical lifetime of families of atmospheric constituents.

On the concentration of atomic oxygen at different altitudes in the atmosphere

The concentration of atomic oxygen (O) in the atmosphere is still a hard-to-determine parameter, while atomic oxygen is one of the most important atmospheric constituents. There exist significant discrepancies

between the mean values of the atomic oxygen concentration in different publications. Thus, at the altitude of 20 km, according to the data of Ref. 7, the concentration of (O) is equal to $1.85 \cdot 10^7$, while according to the data from Ref. 16, it is $2.4 \cdot 10^6$ and, according to Ref. 2, $9.4 \cdot 10^5$. There are two methods to calculate theoretically the concentration of atomic oxygen in the atmosphere: the old one and the new one proposed here. In the old, well-known method^{2,10,13} calculating of (O), imposes the limitation of stationary conditions (or conditions of photochemical equilibrium) only on one component, – the concentration of atomic oxygen, that is,

$$\frac{d(O)}{dt} = 0. \quad (16)$$

In this case from Eq. (6) in the atmospheric layer of 10–50 km with only the dominant terms taken into account, we have

$$\frac{d(O)}{dt} = J_{O_3}(O_3) - K_1(O)(O_2)(M), \quad (17)$$

hence based on Eq. (16) we obtain the well-known equation^{2,10,13}:

$$(O) = J_{O_3}(O_3) / [K_1(O_2)(M)]. \quad (18)$$

The results of (O) calculation by Eq. (18) with the use of the initial data from Refs. 2 and 4 are given in Table 7 (third column).

Table 7. Concentration of atomic oxygen (O) at different altitudes in the atmosphere according to the data from Ref. 2 and calculations by Eqs. (18) and (20)

h , km	Concentration of atomic oxygen (O), 1 · cm ⁻³		
	According to Ref. 2	By Eq. (18)	By Eq. (20)
10	$1.5 \cdot 10^4$	$2.8 \cdot 10^4$	$6.4 \cdot 10^8$
15	$5.5 \cdot 10^4$	$1.3 \cdot 10^5$	$7.1 \cdot 10^8$
20	$9.4 \cdot 10^5$	$1.7 \cdot 10^6$	$3.0 \cdot 10^8$
25	$6.7 \cdot 10^6$	$1.0 \cdot 10^7$	$3.1 \cdot 10^8$
30	$4.0 \cdot 10^7$	$5.6 \cdot 10^7$	$1.1 \cdot 10^8$
35	$2.4 \cdot 10^8$	$5.0 \cdot 10^8$	$4.2 \cdot 10^8$
40	$1.2 \cdot 10^9$	$2.9 \cdot 10^9$	$1.8 \cdot 10^9$
45	$3.7 \cdot 10^9$	$5.4 \cdot 10^9$	$5.3 \cdot 10^9$
50	$6.5 \cdot 10^9$	$1.0 \cdot 10^{10}$	$8.7 \cdot 10^9$

In the new method of (O) calculation, the stationary conditions are imposed on the concentration of the odd oxygen family (1), that is,

$$\frac{d(O_X)}{dt} = 0. \quad (19)$$

Then from Eqs. (7) and (19) we obtain

$$\begin{aligned}
 (\text{O}) = & [J_{\text{NO}_2}(\text{NO}_2) + 2J_{\text{O}_2}(\text{O}_2) - K_3(\text{NO})(\text{O}_3) - \\
 & - K_4(\text{Cl})(\text{O}_3) - K_{14}(\text{OH})(\text{O}_3) - \\
 & - K_{16}(\text{HO}_2)(\text{O}_3)] / [K_8(\text{NO}_2) + 2K_2(\text{O}_3)]. \quad (20)
 \end{aligned}$$

The results on the (O) concentration calculated by Eq. (20) with the use of Tables 3, 4, and 8 (second column) are given in Table 7 (fourth column). The main contribution to the (O) concentration in Eq. (20) at the altitudes of 10–30 km is due to the (O₃), (NO₂), and (NO) concentrations. To calculate the (O) concentration by Eq. (20), we used the mean experimental data on these concentrations borrowed from Ref. 2 (Tables 3 and 8). Note that in Eq. (20), unlike Eq. (18), the (O) concentration decreases with the increase of the (O₃) concentration.

From consideration of the calculated results presented in Table 7, it follows that, first, the data on the (O) concentration in Ref. 2 are close to the data calculated by the old method by Eq. (18). Comparatively minor discrepancies in the obtained (O) values (second and third columns of Table 7) can be explained by different initial data on the values of J_{O_3} and K_1 used for (O) calculation. Second, the (O) concentrations obtained by the new method by Eq. (20) (fourth column of Table 7) differ very widely at the altitudes of 10–30 km from the (O) concentrations obtained by the old method (second and third columns of Table 7).

The concentrations of atomic oxygen obtained by the new method are 30 times higher at the altitude of 25 km and 23000 times higher at the altitude of 10 km than those calculated by the old method. At the altitude of 35–50 km the (O) concentrations obtained by the old and new methods are close. The correctness of the new method for (O) calculation can be confirmed, obviously, by direct measurements of (O) in the atmosphere. It should be added that, unlike the old method of (O) calculation, the new method accounts for the concentrations of nitrogen oxides (NO₂) and (NO) [Eq. (20)], and this significantly increases the calculated (O) concentration at the altitudes of 10–30 km.

On the effect of nitrogen oxides on atmospheric ozone

The first works devoted to investigation of the effect of nitrogen oxides NO and NO₂ on the ozone distribution in the atmosphere arose, as was noted in the monograph by Perov and Khrgian,⁷ in 1968. (Reference 7 mentions the hypothesis by Konashenok¹⁵ on the possibility of the ozone concentration in the atmosphere to decrease because of the decreasing concentration of atomic oxygen due to its reactions with atmospheric constituents, including nitrogen oxides. However, according to Eq. (22), the decrease in the concentration of atomic oxygen in the atmosphere leads to an increase in the photochemically equilibrium ozone concentration.)

In 1968 based on calculations and analysis of their results using chemical and photochemical reactions,⁸ I have shown that *the presence of nitrogen oxides in the lower stratosphere causes decrease of the ozone equilibrium concentration and chemical lifetime in comparison with the purely oxygen atmosphere*. These results were thoroughly considered in my abstract of the doctor's thesis⁹ sent to all Russian research institutions dealing with atmospheric research and central libraries. In Refs. 8 and 9 in 1968 and then again in Ref. 10 in 1972, I have derived the equation for calculation of τ_{O_X} under the following conditions

$$\frac{d(\text{O})}{dt} = 0, \quad \frac{d(\text{O}_3)}{dt} = 0,$$

that correspond to the O_X' family consisting of the components O and O₃. In this case, τ_{O_3} was understood as the period, during which the (O₃) concentration with the allowance for the family mentioned was halved. It was found that^{8,9}:

$$\tau_{\text{O}_X} = 0.7 / K_3(\text{NO}). \quad (21)$$

This result is very close to Eq. (13), when $(\text{O}_X)_0 = (\text{O}_3)_{\xi_1}$, despite these equations were derived in different time by different methods.

Later and independently, Crutzen in 1970 in a short paper¹¹ suggested that the ozone balance in the stratosphere very strongly depends on nitrogen oxides produced due to oxidation of nitrous oxide N₂O released on the Earth's surface. (P. Crutzen is a Nobel Prize Laureate in Chemistry in 1995 together with his colleagues F. Sherwood Rowland and Mario Molina for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone. He is known as a pioneer in the problem on the effect of nitrogen oxides on atmospheric ozone, and his priority is based on Ref. 11. Rowland and Molina won the Nobel Prize for investigations of the effect of chlorine-containing compounds on atmospheric ozone.) Having used 19 chemical and photochemical reactions with the participation of odd oxygen, nitrogen oxides, and hydrogen radicals, Crutzen¹¹ showed that the rates of ozone-destroying reactions are higher than the rates of ozone-forming reactions at the altitudes above 25 km. This means that the ozone concentration at these altitudes under the dominant effect of nitrogen oxides in the equilibrium state should be lower than in the purely oxygen atmosphere. However, Crutzen in Ref. 11, unlike me in Refs. 8 and 9, presented neither particular results of calculation of the equilibrium ozone concentrations nor the chemical lifetime for ozone and the odd oxygen family. According to the latest estimates (Table 8, third and fourth columns), the decrease of the equilibrium ozone concentration under the effect of nitrogen oxides occurs also at the altitudes below 25 km, covering the altitude range from 10 to 35 km [see also Ref. 12].

Table 8. Ozone (O₃) concentration at different altitudes in the atmosphere according to the mean experimental data and calculations by equations under daytime conditions

h, km	Ozone (O ₃) concentration, mol · cm ⁻³			
	According to mean exp. data ²	By Eq. (22) for atmosphere containing nitrogen oxides and (O) from Ref. 2, Table 7	By Eq. (23) for purely oxygen atmosphere	By Eq. (22) for atmosphere containing nitrogen oxides and (O) from Table 7 calculated by Eq. (20)
10	1.0 · 10 ¹²	2.7 · 10 ¹²	4.8 · 10 ¹²	1.0 · 10 ¹²
15	1.1 · 10 ¹²	4.2 · 10 ¹²	5.8 · 10 ¹²	1.1 · 10 ¹²
20	2.9 · 10 ¹²	4.3 · 10 ¹²	7.1 · 10 ¹²	2.9 · 10 ¹²
25	3.2 · 10 ¹²	4.4 · 10 ¹²	1.2 · 10 ¹³	3.2 · 10 ¹²
30	2.6 · 10 ¹²	2.8 · 10 ¹²	9.4 · 10 ¹²	2.6 · 10 ¹²
35	2.0 · 10 ¹²	1.6 · 10 ¹²	4.4 · 10 ¹²	2.0 · 10 ¹²
40	1.0 · 10 ¹²	1.0 · 10 ¹²	1.2 · 10 ¹²	1.0 · 10 ¹²
45	3.2 · 10 ¹¹	4.6 · 10 ¹¹	4.0 · 10 ¹¹	3.2 · 10 ¹¹
50	1.0 · 10 ¹¹	1.4 · 10 ¹¹	1.8 · 10 ¹¹	1.0 · 10 ¹¹

From the viewpoint of this work, the problem of the effect of nitrogen oxides on atmospheric ozone can be reduced to the following. Taking into account the above-said and assuming that odd oxygen in the atmosphere is in the photochemical equilibrium, from Eq. (7) at $\frac{d(O_X)}{dt} = 0$ we obtain the photochemically equilibrium value of (O₃):

$$(O_3) = [J_{NO_2}(NO_2) + 2J_{O_2}(O_2) - K_8(O)(NO_2)] / \{ [K_3(NO) + K_4(Cl) + K_{14}(OH) + K_{16}(HO_2) + 2K_2(O)] \}. \quad (22)$$

For the purely oxygen atmosphere [more precisely, the atmosphere containing only the odd oxygen family and, for example, argon in place of nitrogen in the same concentration, which is needed to keep the concentration (M)], the equation for the ozone concentration at different altitudes in the atmosphere is well-known^{2,10,13,14}

$$(O_3) = (O_2) \sqrt{\frac{J_{O_2} K_1(M)}{J_{O_3} K_2}}. \quad (23)$$

Table 8 presents the data for a comparison of the ozone concentrations in the 10–50 km layer calculated assuming the mean conditions by Eqs. (22) and (23) with each other and with the mean experimental data. The data for calculation of the results summarized in Table 8 were taken from Tables 2–4 and 7. It follows from Table 8 that the data on the equilibrium (O₃) concentrations obtained by Eq. (22) are close to the mean data of (O₃) observations² at the altitudes of 30 to 50 km and exceed them in the 10 to 30 km layer. If in Eq. (22) we use the (O) concentrations obtained by the new method (see Table 7, fourth column), then the calculated (O₃) values are close to the mean experimental

data in the entire atmospheric layer of 10 to 50 km that are given in the fifth column of Table 8. (This circumstance follows from the fact that Eqs. (20) and (22) are derived from the same equation (7) at $\frac{d(O_X)}{dt} = 0$.) The data obtained by Eq. (23) for the purely oxygen atmosphere at the altitudes below 35 km are markedly overestimated, and, in comparison with them, the data obtained by Eq. (22) are 1.5 to 3 times lower and, with the allowance made for the new (O) values, 2.5–5 times lower.

The (O₃) values presented in Table 8 suggest that the presence of nitrogen oxides in the atmosphere causes the decrease of the ozone concentration in the considered case at the altitudes of 10–35 km (see the third and fourth columns of Table 8) as compared with that in the purely oxygen atmosphere.

Conclusions

By applying the developed technique to calculation of the chemical lifetime for families of atmospheric constituents, it has been shown that the odd oxygen family and, in particular, ozone, in contrast to the existing ideas, are in photochemical equilibrium in daytime all over the stratospheric depth, including the altitudes of 10 to 30 km. This result should lead to revision of the current concepts about atmospheric ozone, including those concerning its photochemical stability in the lower stratosphere. In modeling photochemical processes affecting ozone using the chemical lifetime of the odd oxygen family τ_{O_X} , one should take into account the significantly refined value of this characteristic at the altitudes of 10–30 km that was obtained in this work.

Application of the new developed method for theoretical calculation of the concentration of atomic oxygen with allowance for photochemical equilibrium of the odd oxygen family and the presence of nitrogen oxides in the atmosphere has yielded the calculated concentrations of atomic oxygen at different altitudes in the stratosphere. At the altitudes of 10–30 km, the new values turned out to be 30–23000 times higher than those accepted earlier. The equation has been derived for calculation of the vertical ozone distribution in the atmosphere with allowance for photochemical equilibrium of the odd oxygen family.

References

1. E.L. Aleksandrov, Yu.A. Izrael, I.L. Karol, and A.Kh. Khrgian, *Ozone Shield of the Earth and Its Variations* (Gidrometeoizdat, St. Petersburg, 1992), 288 pp.
2. G. Brasseur and S. Solomon, *Aeronomy of the Middle Atmosphere* (D. Reidel Publishing Company, Dordrecht, Holland, 1984).
3. E.L. Aleksandrov, I.L. Karol', L.R. Rakipova, Yu.S. Sedunov, and A.Kh. Khrgian, *Atmospheric Ozone and Global Climate Change* (Gidrometeoizdat, Leningrad, 1982), 167 pp.
4. W.B. De More, S.P. Sander, D.M. Golden, et al., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modelling* (NASA, California, 1990), 217 pp.

5. M. Nicolet, *Etude des Reactions Chimiques de l'Ozone dans la Stratosphere* (Institut Roy. Met. de Belgique, 1978), 536 pp.
6. *Atmospheric Ozone 1985. Assessment of Our Understanding of the Processes Controlling the Present Distribution and Changes* (WMO, Geneva, 1986), Vols. I–III, Report No. 16.
7. S.P. Perov and A.Kh. Khrgian, *Modern Problems of Atmospheric Ozone* (Gidrometeoizdat, Leningrad, 1980), 288 pp.
8. G.P. Gushchin, "Investigations of Ozone in the Earth's Atmosphere," Doct. Phys.-Math. Sci. Dissert., Leningrad (1968), 436 pp.
9. G.P. Gushchin, "Investigations of Ozone in the Earth's Atmosphere," Author's Abstract of Doct. Phys.-Math. Sci. Dissert., Leningrad (1969), 64 pp.
10. G.P. Gushchin, Trudy Gl. Geofiz. Obs., Issue 279, 94–127 (1972).
11. P.J. Crutzen, Quart. J. Roy. Meteorol. Soc. **96**, No. 408, 320–325 (1970).
12. H.S. Johnston, Science **173**, No. 3996, 517–522 (1971).
13. H.U. Dütsh, *Photochemische Theorie des Aatmosphärischen Ozons unter Berücksichtigung von Nichtgleichgewicht. Zuständen*. Diss. (Zürich, 1946), 113 S.
14. G.P. Gushchin, *Ozone and Areosynoptic Conditions in the Atmosphere* (Gidrometeoizdat, Leningrad, 1964), 341 pp.
15. V.N. Konashenok, Izv. Akad. Nauk SSSR, Ser. Fiz. Atmos. Okeana **4**, No. 7, 797–799 (1968).
16. A.Kh. Khrgian, *Physics of Atmospheric Ozone* (Gidrometeoizdat, Leningrad, 1973), 292 pp.