

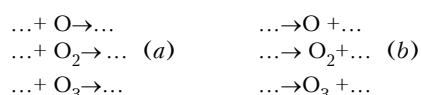
## EFFECT OF PRODUCTION AND LOSS OF THE OXYGEN CONSTITUENTS ON THE OZONE CYCLE STABILITY

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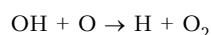
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*The incorporation of reactions with foreign species into the ozone cycle under assumption of their concentrations held constant is considered. An analog of the conservation law is obtained for the change of number of oxygen atoms occurring due to this incorporation which can be considered as additional condition imposed on the concentrations of oxygen constituents in the steady state. The state is unstable when this condition does not hold.*

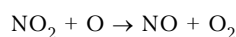
1. In studies of chemical evolution of the ozone layer it is necessary to take into account the tens of reactions of the oxygen constituents ( $O$ ,  $O_2$ ,  $O_3$ ) with different species that brings into existence the vast systems of equations of chemical kinetics. The technique of the qualitative analysis of systems of nonlinear differential equations seems to be most suitable to analyze the potential changes of concentrations. However, it is developed in detail only for small systems (2–3 equations), see, for example, Refs. 1 and 2, so that to use it in examinations of the ozone evolution some approximations should be made. First of all, the qualitative analysis of the elementary ozone cycle including only the oxygen constituents should be performed. In this case, the approximation consists in omitting the reaction between the oxygen constituents and foreign species. In this approximation, the different ways for writing the elementary cycle are possible, including one or other particular reactions. Some papers were devoted to their qualitative analysis.<sup>3–8</sup> The peculiarities in the steady state behavior come to be clear, and the occurrence of the exhaustive qualitative analysis in this approximation is, probably, a short way in the future.



The dots in system (2) denote some reactants which may contain the oxygen atoms among others as well. Thus, for example, the reactions including the hydrogen-containing compounds



or nitrogen oxides

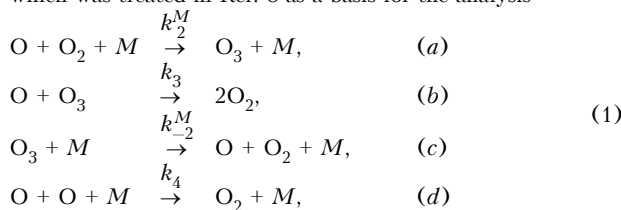


belong to the type shown in the first line of the group (2c). Separately, the photochemical reactions of the  $O_2$  and  $O_3$  destruction are presented in the group (2d).

Table I lists the contributions from reactions of different types into the equations for the  $O_2$ ,  $O$ , and  $O_3$  concentrations (denoted as  $x$ ,  $y$ , and  $z$ , respectively). In

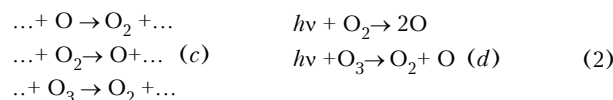
The present paper concerns the system of equations for oxygen constituents including the foreign species as the terms described production and loss of the oxygen constituents. The approximation in this case consists in that the concentrations of the foreign species are held constant.

Let us consider a set of reactions of the ozone cycle in the absence of radiation (it can be related to the night time) which was treated in Ref. 8 as a basis for the analysis



where  $M$  is an arbitrary third particle which is none of  $O$ ,  $O_2$ , or  $O_3$ , and  $k_i$  are the rate constants of corresponding reactions. Let us examine the changes in qualitative behavior of the system initiated by the reactions with foreign species.

2. Reactions of the oxygen constituents with foreign species can be schematically divided into the following groups:



the lower row of the table the coefficients are given, by which the values in a given column should be multiplied. The first four columns of the table refer to the reactions (1), the rest of ones – to different types of reactions (2).

3. The conservation law for the number of atoms in the case of system of reactions (1) takes the form

$$2x + y + 3z = A_1. \quad (3)$$

Since the reactions of the types (2a, b, and c) initiate the production or the loss of species including the oxygen atoms, and the equations for their concentrations are not included into the system under consideration, the conservation law for this system does not hold in general case. However, some analog of the conservation law can be derived in this case as well. Let us write the system of reactions including foreign species in the following form:

$$\begin{aligned}\dot{x} &= -a_1 x y + 2 a_5 y z + a_6 z + a_{10} y^2 + A, \\ \dot{y} &= -a_1 x y - a_5 y z + a_6 z - 2 a_{10} y^2 + B, \\ \dot{z} &= a_1 x y - a_5 y z - a_6 z + C.\end{aligned}\quad (4)$$

The notations  $A$ ,  $B$ , and  $C$  are obvious from the table. From Eqs. (4) for the steady states

$$\dot{x} = 0, \dot{y} = 0, \dot{z} = 0$$

the relation

$$2x + y + 3z = 2A + B + 3C = 0 \quad (5)$$

follows, which, in essence, implies that if the steady-state points occur then the change of the number of atoms due to foreign species must vanish in these points. Being written in the explicit form, Eq. (5) reduces to

$$\begin{aligned}-(2a_{15} + a_{21})x_0 + (a_{20} - a_{14})y_0 - (3a_{16} + a_{22})z_0 + \\ + (2a_{18} + a_{17} + 3a_{19}) = 0.\end{aligned}\quad (6)$$

In the absence of reactions with foreign species ( $A = B = C = 0$ ) the conservation law (3) follows from Eq. (5). In the presence of such reactions the relation (6) has as a consequence rather stringent limitations on the occurrence of steady states, because, taking into account the variability of concentrations of the species which can be involved in the reactions of the type (2), the relation (5) is probably never hold. This is also supported by the estimates, although, very rough ones, of the quantities entering into Eq. (6), that show that the term  $x(2a_{15} + a_{21})$  exceeds the other terms by some orders of magnitude for the concentrations peculiar to the atmospheric conditions.

Let us now consider what changes are produced within the characteristic times of the processes due to the reactions with foreign species. Remind, that the stable node

$$x = A_1/2, y = 0, z = 0 \quad (7)$$

for system (1), which corresponds to the total absence of O and O<sub>3</sub>, is practically unattainable from the state with concentrations observed in the atmosphere. According to the formal estimates, the characteristic times of the attainment of steady states in the system (1) can be written as follows:

$$\begin{aligned}\tau_{O_2} &\cong (a_1 y)^{-1} \sim 3 \cdot 10^{22} \text{ s}, \\ \tau_O &\cong (a_1 x + a_5 z + 2 a_{10} y)^{-1} \sim 7 \cdot 10^{-2} \text{ s}, \\ \tau_{O_3} &\cong (a_5 y + a_6)^{-1} \sim 6 \cdot 10^{13} \text{ s}.\end{aligned}\quad (8)$$

The reactions resulting in the loss of O<sub>2</sub>( $a_{15}$ ,  $a_{21}$ ) initiate changes of  $\tau_{O_2}$

$$\tau_{O_2} \cong (a_1 y + a_{15} + a_{21})^{-1},$$

moreover this change can be essential. Thus, for

$$k_2^M = 6.6 \cdot 10^{-34} \text{ cm}^6/\text{s}, C_M = C_{N_2} = 3 \cdot 10^{17} \text{ cm}^{-3},$$

$$k_{15}(\text{O}_2 + 2 \text{NO} \rightarrow 2 \text{NO}_2) = 3.5 \cdot 10^{-38} \text{ cm}^3/\text{s},$$

$$C_{\text{NO}} = 10^9 \text{ cm}^{-3}, k_{21}(\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}) = 6 \cdot 10^{-12} \text{ cm}^3/\text{s},$$

$$C_{\text{N}} = 10^7 \text{ cm}^{-3}, C_{\text{O}} = 2 \cdot 10^{-7} \text{ cm}^{-3}$$

the value  $\tau_{O_2}$  is  $2 \cdot 10^4$  s. To make concrete conclusions based on these estimates would be premature, however, the sophisticated treatment of the problem seems to be required.

4. We use in this paper the approximation of constant concentrations of foreign species. It can be considered as reasonable, at least, in the cases when the species in question are the products either of the constant anthropogenic ejections (for example, nitrogen oxides) or of the natural sources (for example, the production of O<sub>2</sub> due to photosynthesis). To obtain the exhaustive answer on the question how can the phase portrait of the system change as a result of such an approximation, is likely to be impossible. However, some examples already considered have not show considerable changes in the physically allowed region of the phase space.

Let us consider the system of equations describing the reactions (1a) and (1b) (see Ref. 7). The constant concentration of O<sub>2</sub> is frequently used approximation in studies of the ozone cycle. The total and approximate systems of equations look as follows (the oxygen molecule is taken as the third particle  $M$ ):

$$\begin{aligned}\dot{x} &= -a_2 x^2 y + 2 a_5 y z, \quad \dot{y} = -a_2 x^2 y - a_5 y z, \\ \dot{z} &= a_2 x^2 y - a_5 y z;\end{aligned}\quad (9)$$

$$\dot{y} = -y(a + z), \quad \dot{z} = y(a - z). \quad (10)$$

The fragments of the phase portraits of these systems are shown in Fig. 2. The trajectories behavior differs considerably, if the whole of phase space up to infinity is considered. However, within the reaction triangle the difference in the trajectories behavior is unessential. Note, that each particular case should still be examined separately.

5. Thus, the incorporation into the ozone cycle reactions with foreign species under the assumption that their concentrations are held constant, can lead to disappearance of the steady state. In this connection the question about the correspondence between the used model and the real situation in the atmosphere arises inevitably. Remind, however, that from the standpoint of the system (1) the state, taking place in the atmosphere, is not steady, and the matter is saved, as it was already mentioned above, due to the very long time of the steady state attainment. The very existence of the present atmospheric state is, probably, conditioned by the presence of the variable process of alternation of night and day (see, for example, Ref. 9). So to make confident conclusion concerning O<sub>2</sub>, the analysis of the consequences of incorporating the reactions with foreign species in such more extended model is needed.

TABLE I. Types of reactions and the corresponding terms in the equations of chemical kinetics.

	(1, a)	(1, b)	(1, c)	(1, d)	O →	O <sub>2</sub> →	O <sub>3</sub> →	→O	→O <sub>2</sub>	→O <sub>3</sub>	O→O <sub>2</sub>	O <sub>2</sub> →O	O <sub>3</sub> →O <sub>2</sub>	O <sub>2</sub> +hν→2O	O <sub>3</sub> +hν→O <sub>2</sub> +O
$\dot{x}$	-x y	+2 y z	+ z	+ y <sup>2</sup>		-x			+ 1		+ y	- x	+ z	- x	+ z
$\dot{y}$	-x y	-y z	+ z	- 2 y <sup>2</sup>	- y			+ 1			- y	+ x		+ 2 x	+ z
$\dot{z}$	x y	-y z	- z				-z			+ 1			- z		- z
	$a_1=k_2^M C_M$	$a_5=k_3$	$a_6=k_{-2}^M C_M$	$a_{10}=k_4^M C_M$	$a_{14}=k_{14} C'$	$a_{15}=k_{15} C'$	$a_{16}=k_{16} C'$	$a_{17}=k_{17} C'$	$a_{18}=k_{18} C'$	$a_{19}=k_{19} C'$	$a_{20}=k_{20} C'$	$a_{21}=k_{21} C'$	$a_{22}=k_{22} C'$	$a_{23}=J_2^*$	$a_{24}=J_3$

Notes: \* J<sub>2</sub> and J<sub>3</sub> are the rate constants of the corresponding processes integrated over the solar spectrum. C' is the product of corresponding concentrations.

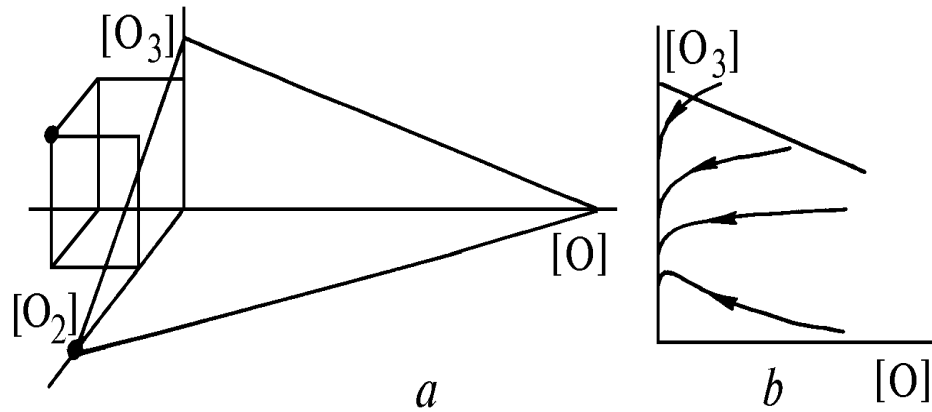


FIG. 1. Phase portrait of the system (1): three-dimensional picture (a) and projection on the plane O, O<sub>3</sub> (b).

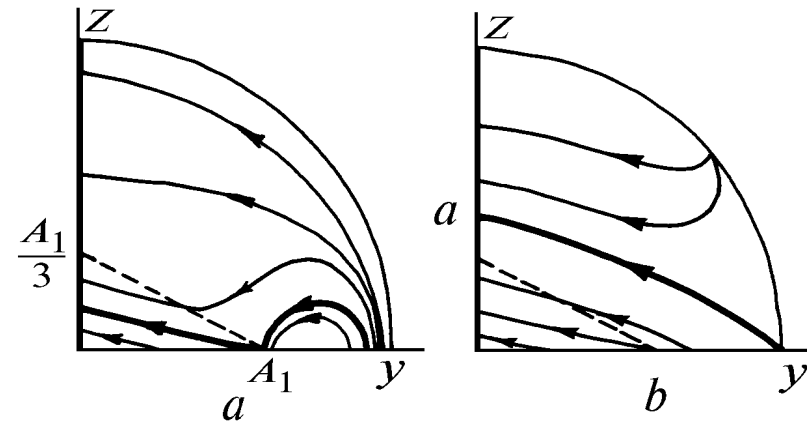


FIG. 2. Fragments of phase portraits for the system (9) (a) and for the system (10) (b).

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**REFERENCES**

1. A.A. Andronov, E.A. Leontovich, I.I. Gordon, and A.G. Mayer, *Qualitative Theory of the Second-Order Dynamic Systems* (Nauka, Moscow, 1966), 568 pp.
2. N.N. Bautin and E.A. Leontovich, *Methods and Techniques of Qualitative Investigations of Dynamic Systems on a Plane* (Nauka, Moscow, 1976), 494 pp.
3. I.L. Karol, *Pure and Appl. Geophys.* **118**, No. 3, 695–705 (1980).
4. M.V. Shabalova, *Tr. Gl. Geofiz. Obs.*, No. 494, 77–82 (1985).
5. J.J. Kozak, G. Nicolis, J.W. Kress, and M. Sanglier, *J. Non-Equilibrium Thermodyn.* **4**, No. 62, 67–74 (1979).
6. E.P. Gordov, O.B. Rodimova, and Yu.E. Smirnov, *Atm. Opt.* **1**, No. 7, 56–63 (1988).
7. V.G. Monoshkina and O.B. Rodimova, *Atmos. Oceanic Opt.* **5**, No. 2, 93–98 (1992).
8. E.P. Gordov, O.B. Rodimova, and V.A. Sennikov, *Atmos. Oceanic Opt.* **6**, No. 4, 274–276 (1993).
9. B. Fichtelmann and G. Sonnenmann, *Ann. Geophys.* **10**, No. 10, 719–728 (1992).