

## ON THE EFFECT OF DIFFERENT REACTIONS OF THE OZONE CYCLE ON ITS STABILITY IN THE ABSENCE OF RADIATION

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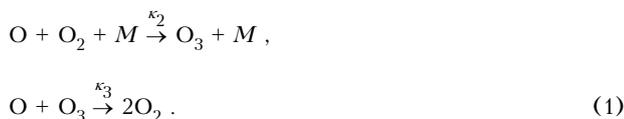
*Several variants of reaction sets forming the ozone cycle in the absence of radiation are treated. Their phase portraits in the reaction triangle are drawn. The variations in the simplest phase portrait due to incorporating the additional reactions are described. It is shown that the system including all the considered reactions has a steady state with the zero ozone concentration. However, this steady state is not really reached because of the extremely large characteristic time of the process.*

1. Recently arisen question on the nature of physical processes responsible for specific seasonal decreases of concentrations of the stratospheric ozone above some regions of the Earth's surface appears to be a subject of not only scientific discussions. Up to now it is impossible to argue either natural or anthropogenic factors play a primary role in this decrease.

We would like to answer the question whether the variations in the atmospheric photochemical processes caused by additional reactants and reactions could lead to the qualitative changes in the behavior of the oxygen species. We use the qualitative analysis of systems of nonlinear differential equations<sup>1,2</sup> as a mathematical instrument which is the best suited for searching for an answer to the question in hand. Note that earlier there were attempts to use this mathematical instrument for investigating the ozone cycle. The stability of the system was analyzed in the vicinity of steady states of the Chapman cycle.<sup>3-6</sup>

This paper is concerned with the simplest ozone cycle in the absence of radiation and variations in its phase portrait resulting from two additional reactions.

2. The simplest possible system of reactions of the ozone cycle includes the ozone formation during three-particle collision and its decomposition in the collision with the oxygen atom.



Here M is an arbitrary particle. The qualitative analysis of the set of reactions (1) with  $M = \text{O}_2$  was performed in Ref. 7 where on its basis the difference in the behavior of this system and the similar system with the constant  $\text{O}_2$  concentration was discussed.

If the process (1) is treated as taking place in the homogeneous closed isothermic reactor of ideal mixing it is described by the following system of differential equations for concentrations ( $[\text{O}_2] = \tilde{x}$ ,  $[\text{O}] = \tilde{y}$ ,  $[\text{O}_3] = \tilde{z}$ ,  $[\text{M}] = \tilde{M}$ )

$$\begin{aligned} \dot{\tilde{x}} &= -\kappa_2 \tilde{M} \tilde{x} \tilde{y} + 2\kappa_3 \tilde{y} \tilde{z}, \\ \dot{\tilde{y}} &= -\kappa_2 \tilde{M} \tilde{x} \tilde{y} - \kappa_3 \tilde{y} \tilde{z}, \\ \dot{\tilde{z}} &= \kappa_2 \tilde{M} \tilde{x} \tilde{y} - \kappa_3 \tilde{y} \tilde{z}. \end{aligned} \quad (2)$$

It is assumed hereafter that M is neither the  $\text{O}_2$ ,  $\text{O}_3$  molecules, nor the O atom. This situation, in principle, could be related to the species O,  $\text{O}_2$ , and  $\text{O}_3$  placed into the "bath" with chemically inert species ( $\text{N}_2$ , He, etc.). We consider this model situation to obtain the simplest system of equations for analysis.

For the sake of further convenience let us introduce the new dimensionless variables in Eq. (2)

$$t = \alpha \tilde{t}, \quad x = \beta \tilde{x}, \quad y = \gamma \tilde{y}, \quad z = \delta \tilde{z}, \quad M = \mu \tilde{M}, \quad (3)$$

where

$$\beta = \gamma = \delta, \quad \alpha = \kappa_3 / \gamma, \quad \mu = \kappa_2 / k_3, \quad (4)$$

and the absolute value of  $\gamma$  is immaterial (it can be chosen to be equal to unity, for example). Then we obtain the system of equations

$$\begin{aligned} \dot{x} &= -M x y + 2 y z, \\ \dot{y} &= -M x y - y z, \\ \dot{z} &= M x y - y z. \end{aligned} \quad (5)$$

As is well known, when solving this system, the conservation law of the number of atoms participating in the reaction should be taken into account, namely

$$\begin{aligned} 2\tilde{x} + \tilde{y} + 3\tilde{z} &= \tilde{A} \\ \text{or} \\ 2x + y + 3z &= \gamma \tilde{A} = A \end{aligned} \quad (6)$$

in terms of variables (3). Using the conservation law in Eq. (6) system (5) can be reduced to the system of two equations for any chosen pair of variables. Thus, for example, for the variables  $y$  and  $z$  it takes the form

$$\begin{aligned} \dot{y} &= -(AM/2)y + (3M/2 - 1)yz + (M/2)y^2, \\ \dot{z} &= -(AM/2)y + (-3M/2 - 1)yz + (M/2)y^2. \end{aligned} \quad (7)$$

In the finite part of the plane the system of Eqs. (7) has one singular point which is a saddle ( $y = A$ ,  $z = 0$ ) and one singular line (the straight line consisting of the singular points) described by the equation  $y = 0$ . The physically allowable region for  $y$  and  $z$  is the first quadrant (since the concentrations cannot be negative) in which the conservation law Eq. (6) separates out the finite region,

the so-called reaction triangle, so that the concentrations cannot exceed certain values. The reaction triangle in the three-dimensional space ( $x, y, z$ ) and as projected onto three planes is presented schematically in Fig. 1 together with trajectories and saddle separatrixes. The trajectories starting from any point of the triangle terminate at the singular line with the zero concentration and with some finite values of concentrations of  $O_3$  and  $O_2$ . The regions of the triangle divided by the saddle separatrix cannot be connected with any trajectory.

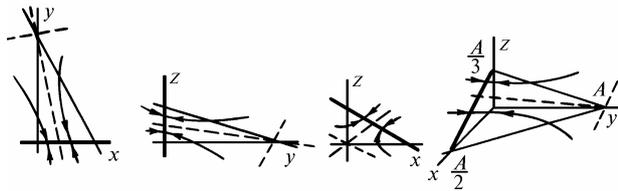


FIG. 1. Three-dimensional phase portrait and its projections for system (4).

3. Let us consider the set of reactions (1) supplemented by the reaction reverse to the reaction of ozone formation (1) and by the reaction of recombination of oxygen atoms

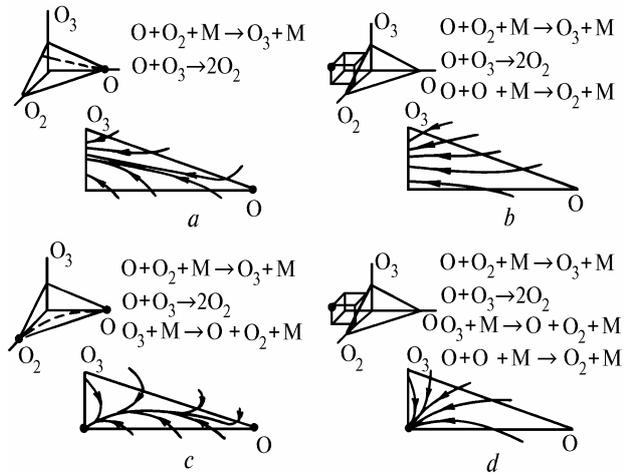
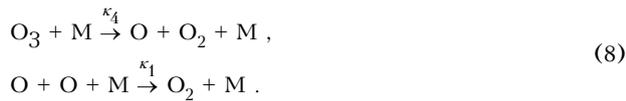


FIG. 2. Three-dimensional phase portraits and their projections on the plane ( $y, z$ ) for four sets of reactions. Trajectories on the plane correspond to  $M = 1$  and  $A = 1$ .

The three-dimensional phase portraits and their projections on the plane ( $y, z$ ) in the case of successive inclusion of reactions (8) are depicted in Fig. 2. For visualization the axes are denoted by the symbols of the oxygen species. It can be seen that the inclusion of additional reactions changes the phase portrait of the system significantly. For example, the incorporation of the reverse reaction, i.e., the additional channel of ozone decomposition "reduces" the singular line into the complex singular point at the origin of coordinates retaining the saddle unchanged while the recombination reaction retains the singular line unchanged but displaces

the singular point toward the nonphysical region of negative concentrations and changes its character. At the values of parameters compatible with the atmospheric concentrations and corresponding reaction rates (see below) this point has the coordinates  $x > 0, y < 0, z > 0$  and is the node. In the reaction triangle the concurrent inclusion of both reactions (8) leaves only one singular point at the origin of coordinates which is the complex singular point with the nodal sector within the reaction triangle. Thus, the changes are essential. Especially dramatic change is that caused by the inverse reaction, namely, the steady state of the system appears to be the state with zero concentrations of both atomic oxygen and ozone (see Figs. 2 c and 2 d). Since reactions (1) and (8) are the reactions naturally taking place in the atmosphere and disappearance of ozone was not observed even during the polar night, the question arises of whether the model under study is adequate to the real state of the ozonosphere. The answer can be obtained by means of numerical simulations.

4. The system of equations for concentrations of  $O$  and  $O_3$  in the case presented in Fig. 2 d [analogous to system (7)] has the form

$$\dot{y} = -(AM/2)y + Mz + (3M/2 - 1)yz + (M/2 - 2cM)y^2, \tag{9}$$

$$\dot{z} = -(AM/2)y - Mz + (-3M/2 - 1)yz - (M/2)y^2,$$

where, in addition to relations (3) and (4) we have

$$\gamma = \kappa_2/\kappa_4, \quad c = \kappa_1/\kappa_2. \tag{10}$$

The concentration behavior depicted in Fig. 2 d corresponds to system (9) with  $A = 1$  and  $M = 1$ , i.e., to the case when all the terms in the right-hand sides of equations are comparable in their values, that best demonstrates the qualitative peculiarities of the system. Under conditions of the real atmosphere the concentrations of the oxygen species differ radically in their values. For estimates let us take the values of concentrations given in Ref. 8 for a height of 30 km [ $O_2$ ]= $2.93 \cdot 10^{17} \text{ cm}^{-3}$ ,  $[O]$ = $6.75 \cdot 10^7 \text{ cm}^{-3}$ ,  $[O_3]$ = $3.96 \cdot 10^{12} \text{ cm}^{-3}$ , and  $[M] = [N_2] = 2.93 \cdot 10^{17} \text{ cm}^{-3}$ , and the values of reaction rate constants from Ref. 9 at  $T = 224.6 \text{ K}$  are  $\kappa_3 = 6.782 \cdot 10^{-16} \text{ cm}^3/\text{s}$ ,  $\kappa_1 = 7.937 \cdot 10^{-33} \text{ cm}^6/\text{s}$ ,  $\kappa_2 = 1.023 \cdot 10^{-33} \text{ cm}^6/\text{s}$ , and  $\kappa_4 = 5.822 \cdot 10^{-32} \text{ cm}^3/\text{s}$ . For the above-enumerated values of rate constants and concentrations the trajectory behavior in the coordinates  $\tilde{y}$  and  $\tilde{z}$  has the form shown in Fig. 3 a. At first sight the trajectory behavior is completely analogous to that shown in Fig. 2 b, i.e., the concentration of the oxygen atoms drops almost to zero over the periods of time of some seconds and, within the figure scale, the process terminates at a certain finite ozone concentration. However, closer investigation shows that at the times long enough a very slow decrease of the ozone concentration starts, even at those trajectories where initially its radical increase takes place, see Table I. In the table, for the more convenient illustration, the example shown in Fig. 3 a with the initial conditions at the point A is chosen. Whereby, during a fraction of second, the ozone concentration increases up to its maximum value and its subsequent decrease at the considered times is observed only at the 11th significant figure. Schematically, this situation is shown in arbitrary scale in Fig. 3 b.

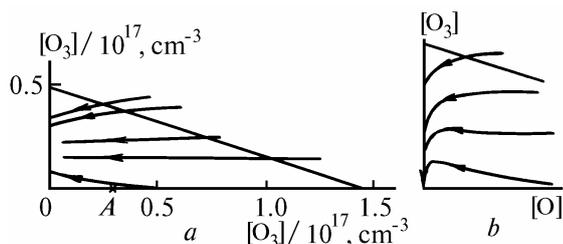


FIG. 3. The O and O<sub>3</sub> concentration behavior: (a) calculated under atmospheric conditions and (b) schematically depicted in the vicinity of the O<sub>3</sub> axis.

TABLE I.

<i>t</i> , s	[O], cm <sup>-3</sup>	[O <sub>3</sub> ], cm <sup>-3</sup>
0.0000	2.845 759 + 16	0.0
0.0259	4.502 485 + 15	4.772 248 400 802 + 15
0.1036	4.253 760 + 14	6.615 853 858 618 + 15
2.5907	4.981 498 + 00	6.864 939 646 371 + 15
32.7370	4.981 498 + 00	6.864 939 646 370 + 15
110.8400	4.981 498 + 00	6.864 939 646 366 + 15
207.2500	4.981 498 + 00	6.864 939 646 362 + 15

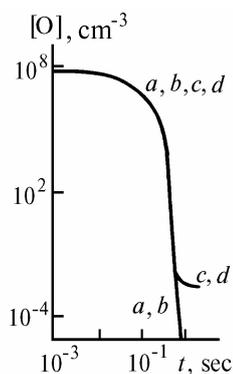


FIG. 4. Temporal behavior of the atomic oxygen concentration for the sets of reactions shown in Fig. 2.

Finally, within the framework of the model the ozone concentration actually diminishes, however, this decrease is so slow (the formal estimate gives the time of reaching the steady state of the order of about 10<sup>7</sup> years), that could not be fixed experimentally during daily and monthly variations in ozone concentrations. The variations in temperatures and rate constants do not affect practically the characteristic time.

It should be noted that the sharp decrease of the atomic oxygen concentration virtually stops at some small value due to the inverse reaction, see Fig. 4, that also prevents, to some extent, the total disappearance of ozone.

To this end, within the framework of the above-discussed models of the ozone cycle under atmospheric conditions there are no chemical reactions which could result in a noticeable decrease of the ozone concentration. Nevertheless, the existence of the steady state with zero concentrations makes one pay a special attention to other reactions and accelerate the attainment of a steady state. Study of such potentialities will be a subject of further investigations.

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