Multiple steady states in atmospheric photochemistry

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Received August 22, 2001

The papers devoted to the search for peculiarities conditioned by the nonlinearity of equations of atmospheric photochemistry are reviewed. A tendency to construction of low-order models of photochemical processes accounting for their main qualitative features is emphasized. Two approaches to obtaining the low-order models are described, one of which starts from exhaustive systems of kinetic equations for the reactions in the atmosphere and another is based on the analysis of equations of elementary reaction sets.

Introduction

Solving problems of atmospheric chemistry is traditionally oriented on making use of numerical simulations based on detailed photochemical models with the exhaustive number of reagents and reactions (see, for example, Refs. 1 and 2). In particular, numerous papers published in recent years are devoted to the study of chemical evolution of ozone in the Earth's atmosphere. The roles of various reactions and compounds in possible changes of the total content of ozone or other substances interesting from the viewpoint of atmospheric chemistry are being revealed, as a rule, by means of numerical solution of systems of differential equations of chemical kinetics.

The use of even this approach enabled revealing that rather complex photochemical systems show, under certain conditions, a tendency to sharply change one state for another, and the concentrations of reagents in these states can differ by orders of magnitude.

The necessity of dealing with a large number of variables and parameters (because of the complexity of the process to be simulated) hampers both the understanding of the situation and the prediction of its long-term behavior. At the same time, behavior of only a small number of variables is of interest in some problems. Thus, in the problem of the ozone layer, we, in fact, would like to know sufficiently long-term behavior of only one variable, *viz.*, mean ozone concentration. The complexity and nonlinearity of the problem call for applying the methods of nonlinear dynamics to description of the evolution of the system.

Application of the methods of nonlinear dynamics to the study of the behavior of complex systems involves seeking steady states of the full system of equations and determination of the type of these states. For systems with a large number of variables, it is a very laborious problem. Therefore, it is preferable to separate out a small group of variables determining qualitative peculiarities of the behavior of the system as a whole. Nonlinear equations for these functions give a mathematical model describing the behavior of the initial system in a low-dimensional phase space. A tendency to construct low-order models for some phenomena of atmospheric photochemistry has recently appeared in the literature and continues to develop by now.

Brief analysis of the state of the art in the use of nonlinear dynamics methods as applied to problems of chemical kinetics of atmospheric gases is presented in Section 1. This section discusses various versions of construction of low-order models based on equations of chemical kinetics written for the case of a large number of reagents.

Obviously, the appearance of one or another nonlinear phenomenon cannot be understood clearly if we analyze only elementary sets of reactions. For this reason, it is logical to start the systematic search for the corresponding low-order model of stratospheric conditions from the system of equations proposed by Chapman for the oxygen atmosphere. However, it turned out that the simplest ozone cycle is not still studied thoroughly from the viewpoint of nonlinear analysis, i.e., the full number of steady states of the system, their character, and variation of the general pattern in response to variations of particular parameters are not determined. Therefore, it is unclear whether the features of nonlinear absorption are inherent in the ozone cycle, i.e., the well known set of reactions in the purely oxygen atmosphere, or they are introduced into the problem by additional chemical compounds or other circumstances, for example, heterogeneous reactions or diurnal periodicity.

Full qualitative analysis of the Chapman set of equations for the oxygen atmosphere is given in Section 2. It is of interest for us the presence of qualitative peculiarities in the phase portrait of the system, as well as the degree, to which the set of reactions in the oxygen atmosphere can serve a basic photochemical model. This set could be the basis for construction of the low-order model of chemical dynamics for more general atmospheric systems.[3,4]

The object of the study in Section 2 is the system of kinetic equations for three oxygen components. Any enlargement of the list of reagents leads to a significant growth of the number of equations and, correspondingly, to analysis of multidimensional phase portraits. To keep the geometric clearness and the possibility of interpreting the obtained results, it is important to find a compromise version, which would allow us to take various substances reacting with oxygen components into consideration and, at the same time, to keep the advantages of qualitative analysis. One of the possible ways is simulation of additional substances and reactions by introducing sources and sinks into the equations for oxygen components. Another way is separation of significant variables according to the values of the relaxation time.[5–7] And, finally, in one possible version more, the equations of a simple model follow (or their guesses constructed) from prior estimates or for some extra reasons.

In Section 3, we consider the latter approach, illustrating its efficiency by applying it to the chemistry of the mesosphere, as it contributed to separation of two modes in the behavior of the oxygen components.

Thus, it is shown in this paper how different approaches based on the full set and elementary sets of reactions and aimed at constructing low-order models of the atmospheric chemistry contribute to a more comprehensive understanding of nonlinear phenomena occurring in it.

1. Study of nonlinear phenomena in atmospheric chemistry

1.1. Modes with high and low NO_x content in tropospheric photochemical systems

Reference 8 was likely the first paper devoted to multiple steady states in the atmospheric chemical systems. This paper considered equations describing the behavior of the concentrations of atmospheric constituents Cl_x (HCl, Cl, ClO, $ClNO_3$), NO_y (NO, NO_2, NO_3, N_2O_5, HNO_2, $ClNO_3$, HNO_3), and HO_x (OH, HO_2) under conditions of winter stratosphere in high latitudes. It was initiated by observations of sharp variations in the spatial and temporal behavior of NO_2 in the latitude regions higher than 50°N (Ref. 9). Prather et al.[8] showed that these variations could be explained, at least partly, by the presence of multiple solutions for the chemical system considered. This problem, interesting because of the roles of nitrogen and chlorine cycles in ozone depletion, was analyzed in a more detail in Ref. 10. The photochemical model containing 30 reactions was reduced to 10 reactants under conditions of diurnally mean insolation, and stability of solutions was studied.

The curves describing the concentrations of the ClO, NO_2, and OH as functions of the total concentration of chlorine compounds Cl_x have the characteristic *S*-type shape. Their intersection by a straight line corresponding to a certain value of the Cl_x concentration gives steady-state solutions. Two of three solutions occurring in a certain range of the concentrations prove to be stable. The solution with high content of ClO and the low content of NO_2 is more stable under most conditions. The solution with the low content of ClO and high content of NO_2 exists only in a narrow range of the NO_y concentrations near the Cl_x concentration. Sharp drop of the stratospheric NO_2 between 40 and 50°N, which was observed in Ref. 9, likely indicates just the presence of the solution with high content of ClO and low content of NO_2. The refinement of the photochemical model from Ref. 7 by adding current data on the chemical processes to it did not affect qualitatively the results described above. The introduction of the diurnal variations of insolation also did not lead to disappearance of multiple states.

Similar modes with the high and low content of NO_x were found in photochemical systems describing the troposphere and including O_x, HO_x, NO_x, CH_4 (Refs. 11–20). They also arise because of the nonlinearity of the equations of tropospheric chemistry. In Ref. 11, White and Dietz used a zero-dimensional box model with 22 reactions ignoring transport with the NO_x source rate as a parameter to emphasize the chemical nature of the phenomenon. At the same emission rate, the steady states with different NO_x concentrations can occur, i.e., the existence of multiple solutions was implicitly established. In the most part of the troposphere, the mode with low content of NO_x takes place.

In Ref. 13, Stewart considered some hierarchy of photochemical models with the increasing chemical complexity, including models less and more detailed than the model from Ref. 11, and each model was studied for the presence of multiple steady states (MSS). One model included 13 reactions for 5 hydrogen-containing variables, the other was for 12 variables, including the nitrogen-containing variables, and the third one included additionally the CH_4 chemistry. The calculations were conducted within a box model using two methods of determining the MSS. In the first method, different initial conditions were taken to find whether or not they lead to different solutions. The second method included a set of approaches known as the method of homotopies, which, in principle, guarantees that all solutions are found. For the first two models only one state was found. The WD model and the third model included the transition from low to high NO_x content. For some substances, this jump is several orders of magnitude. The presence of methane among reactants is necessary for the MSS to occur.

In principle, such MSS can appear in 3D models as well, because this generalization still keeps significant nonlinearity in the equations of chemical kinetics. MSS are likely possible in other models with other hydrocarbons without the methane. Although several models of different chemical complexity were considered in Ref. 13, it was unclear which particular nonlinearity in kinetic equations causes the appearance of MSS.

In Ref. 15, Krol refined significantly the qualitative pattern of the nonlinear behavior of tropospheric chemical systems, which was drawn in Ref. 13. It was shown[15] that in the absence of hysteresis the transition between the modes with the high and low NO_x content is characterized by the presence of oscillating solutions and the qualitative behavior of the system was presented as a function of the CH_4 and NO emission flows. In the system of reactions considered in Ref. 13, four situations are possible, namely, the modes with the high and low NO_x content, their coexistence, and periodic solutions (without steady states). The boundaries of these four modes are determined by the Hopf bifurcation points (HBP). In Ref. 15 periodic solutions were simulated numerically using the software package for chemical rate equations based on the Gir method for time integration. The existence of an oscillating solution was also reported in Ref. 20.

It is interesting to note that the WD model and the model 3 in Ref. 13 show the same qualitative behavior. A question arises[15] on the minimum number of reactions to be included in a model for it to reproduce the same qualitative behavior. Such a minimum system was studied recently in Ref. 21. It was based on physicochemical analysis of the processes occurring with nitrogen oxides and radicals and included the following five processes:

$$\begin{aligned}
&R + NO_x \xrightarrow{k_1} HNO_3\\
&R + R \xrightarrow{k_2} H_2O_2\\
&NO_x \xrightarrow{k_3} \qquad\qquad (1)\\
&H_2O_2 \xrightarrow{k_4}\\
&HNO_3 \xrightarrow{k_5}
\end{aligned}$$

The last three reactions correspond to leaving of the corresponding substances. For connection with the real atmospheric photochemistry, a feedback function $S(NO_x)$ was introduced. This function was constructed in such a manner that it was positive at low concentrations of NO_x, i.e., leading to the increased production of radicals at the increasing NO_x concentration, and negative at high concentrations of NO_x. In calculations, $S(NO_x)$ was taken in the following parametric form:

$$S(NO_x) = S_0 + \Delta S \sin [(NO_x/NO_x^*)\, \pi/2],$$
$$NO_x < NO_x^*,$$
$$S(NO_x) = (S_0 + \Delta S)\, [1 - (NO_x - NO_x^*)/(NO_x - NO_x^* + 2.45 \cdot 10^{10}\, \beta)],\quad NO_x \ge NO_x^*, \qquad (2)$$

where $NO_x^* = 1.5 \cdot 10^{10}$ mol · cm^{-3}; β is the fitting parameter characterizing the feedback.

The steady states of this system of reactions were found from the condition of zero time derivatives of the concentrations, which gives

$$S(NO_x) = k_1\, R\, NO_x + k_2\, R^2,$$
$$NO_x = E_{NO_x}/(k_1\, R + k_3), \qquad (3)$$

where E_{NO_x} is the generalized rate of NO_x emission. The surface of the NO_x concentration as a function of E_{NO_x} and β parameters is a surface characteristic of fold catastrophe. Construction of such a model has allowed a conclusion to be drawn that the reason for presence of two modes corresponding to the states with high and low NO_x content is fast reaction between NO_x and free radicals, in which any reagent may prove to be in excess depending on the particular conditions. The negative feedback, under which the production of radicals decreases at high concentrations of NO_x, is just a direct reason for the MSS appearance.

The aim of the study in Ref. 22 was investigating the response (contrary to the steady state) of the boundary layer air to a short-term (several days long) emission of pollutants. This problem is characterized by a less sharp transition between different modes, but those are, nevertheless, observed. If in Ref. 11 it was stated that the emissions capable of bringing the major part of the troposphere into the mode with high NO_x content are not impossible (whereas in Ref. 12 comets were considered as possible causes of the transition between the two states), then in Ref. 22 it is shown that such a transition is the prevailing feature of the boundary layer photochemistry in industrial regions.

Thus, the internal line of search for the MSS in nonlinear chemical models representative of the medium tropospheric situation and containing a large number of reactions has led to construction of a simplified low-order model. It is just the low-order model constructed thanks to the intuitive understanding of chemical processes occurring in the troposphere that has allowed the mechanism of MSS appearance to be revealed.

1.2. Oxygen–hydrogen photochemistry in the mesosphere

From the viewpoint of MSS existence, the oxygen–hydrogen photochemistry of the mesosphere was studied in Ref. 23. The system was presented by 14 reactions supplemented with the source of water vapor and sink of hydrogen, whose rates served the control parameters. To find the steady states, Yang and Brasseur[23] used the method of exclusion, which gradually reduces the system of equations to a high-order polynomial and, in principle, guarantees that all its steady states are found. The result of their analysis was the bifurcation diagram in the phase space determined by the source and sink rates. Yang and

Brasseur have separated the domains with three solutions, one solution, and no one solution. In different cross sections of the diagram corresponding to the fixed values of the hydrogen sink rate k_H, the behavior of the concentrations of chemical components was found as a function of the rate of the water vapor source f. These curves, in particular, the curve of ozone concentration, in some cases have the characteristic S-type shape, thus indicating the presence of three steady states at the same f and allowing a sharp transition between them. It is interesting that the amplitude of the transition is controlled by the parameter k_H. However, the values of the parameters corresponding to the presence of three states and transitions between them proved to be relatively far from the values characteristic of the current state of the mesosphere.

Let us note also several papers devoted to determining the dimensions of attractors of dynamic systems through analysis of time series representing the behavior of these dynamic systems.[24–26] In Ref. 26, analysis involved 15 time series for five latitudes that were obtained from the Nimbus-7 satellite on the global distribution of ozone. This analysis has shown that the correlation dimension of the ozone attractor estimating the minimum number of connected equations needed to describe the behavior of the system is relatively low – between 3 and 7, i.e., the actual ozone system has not so many degrees of freedom. It is interesting that the dimensions are distinct for middle and equatorial latitudes, so that the ozone dynamics is more complicated in the midlatitudes.

1.3. Simple model of stratospheric Antarctic photochemical system including heterogeneous reactions

In the papers mentioned above, analysis of qualitative behavior of a photochemical dynamic system used the set of reactions that is representative to as high degree as possible. In using such an approach, it is most often impossible to determine what chemical processes are responsible for qualitative characteristics inherent in the system. If we conduct the corresponding inquiry by simplifying the system gradually, then we can find at what stage the qualitative features disappear (or appear). A step in this direction was made in Ref. 21. It is clear that such a minimized system is useful for practical applications.

A successful attempt to construct a low-order model for the photochemical Antarctic system was undertaken in Ref. 27, which considered the gas-phase and heterogeneous reactions occurring in the Antarctic stratosphere. Feigin and Konovalov[27] used two methods for parameterization of heterogeneous processes connected with polar stratospheric particles, which are assumed consisting of HNO_3. The parameter of the model was the concentration of the saturating vapor $HNO_3^{sat}(g)$.

In Ref. 27, the low-order model was constructed based on analysis of variables for their characteristic time. Because this study was oriented largely on the ozone dynamics and based on the fact that the ozone lifetime in the period of formation of a ozone hole is $\sim 10^5$–10^6 s (Ref. 28), it was accepted that the variable is fast if its lifetime $\tau \ll 10^5$ s and slow if $\tau \cong 10^5 - 10^6$ s. Concentrations of the components with $\tau \gg 10^6$ s were the parameters of the model. The concentrations of HCl, HNO_3, and O_3 turned out to be slow variables. The differential equations for them have the following form:

$$\begin{aligned}
&dNO_x/dt = -d\,HNO_3/dt = (R34 + R30)\,HNO_3(g) - \\
&\quad - R27\,NO_2\,OH - R1\,Cl\,ONO_2, \\
&dCl_x/dt = -dHCl/dt = \\
&\quad = -\,(R44\,CH_4 + R39\,HO_2 + R40\,H_2)\,Cl + \\
&\quad + R1\,ClONO_2 + R2\,HOCl + R41\,OH\,HCl, \\
&dO_3/dt = -\,(2\,R7\,O\,O_3 + 2\,(R18\,O_3 + R14\,O)\,OH + \\
&\quad + R24\,O\,NO_2 + R16\,O_2\,H + R25\,NO\,O_3 + \\
&\quad + R37\,ClO\,O + R36\,Cl\,O_3) + R22\,OH\,OH + \\
&\quad + 2\,R9\,O_2 + R28\,NO_2\,O_3 + R17\,H\,O_3. \qquad (4)
\end{aligned}$$

The concentrations of fast components as functions of concentrations of the slow components were found from algebraic equations derived from the differential equations for the fast components in their equilibrium states. After their substitution into the equations for HCl, HNO_3, and O_3, these equations acquired high degree of nonlinearity. The model parameters, in addition to those mentioned above, are the concentrations of CH_4, H_2, H_2O, N_2, and O_2, as well as the temperature and the reaction rates. The results calculated by the obtained model for actual atmospheric conditions, for which the field observations of the ozone concentration were available, showed the adequacy of the model to these conditions.

Then the dynamic properties of the obtained model were analyzed in its autonomous (time-independent parameters) version with variation of the parameter $HNO_3^{sat}(g)$. Note that in Ref. 27 all parameters were taken corresponding to the conditions occurring in the area of the Antarctic ozone hole in 1987. The behavior of the calculated concentrations is indicative of the presence of a self-maintained oscillation process. The three-dimensional phase space of the system (HCl, HNO_3, O_3) includes two subspaces joined along the plane $HNO_3 = HNO_3^{sat}(g)$. The area $HNO_3 < HNO_3^{sat}(g)$ corresponds to the cloudless atmosphere described by only gas-phase photochemistry. The condition $HNO_3 > HNO_3^{sat}(g)$ means that stratospheric clouds are present and therefore, heterogeneous reactions should be taken into consideration. The structure of the gas-phase space is very simple – a point in it is either attracted to the sole steady state of the nodal type or goes away to the heterogeneous space. The latter takes place when the value of HNO_3 exceeds the boundary value of $HNO_3^{sat}(g)$. In this case, the sole attractor disappears from the gas-phase part of the phase space. In the heterogeneous area, there exists a stable limiting cycle, whose manifestations are the self-maintained oscillations of the concentrations. Appearance of self-maintained oscillations is the result of bifurcation of birth of the stable and unstable limiting cycles or, in other words, strict excitation of self-maintained oscillations. Then the system may lose its stability, what, generally speaking, seems dangerous, if we take into account that calculations were oriented on using real parameters. Modeling the behavior of the O_3 concentration in the Antarctic stratosphere in August–October 1987, Feigin and Konovalov concluded that in this period the photochemical system first was in the steady node-focus state, then it underwent a cycle of birth bifurcation and then bifurcation of disappearance of the steady state, and finally, with the disappearance of stratospheric clouds, transited into the gas-phase area with the only steady state.

In Ref. 29, Konovalov, Feigin, and Muchina proposed to consider a simple photochemical model of the Antarctic stratosphere by studying its behavior at variations of the concentrations of substances containing inorganic chlorine Cl_y. The behavior of the concentrations of other compounds as a function of Cl_y has a typical *S*-shape, thus indicating the presence of multiple steady states. The situation, when the equilibrium value of HNO_3 becomes close to $HNO_3^{sat}(g)$, is characterized by the presence of two steady states, but the domain of their existence extends significantly. Appearance of multiple steady states at variation of the Cl_y concentration precedes the birth of the limiting cycle. Note, however, that if the formal method[27,29] of construction of the low-order model is used, it is rather difficult to follow the mechanism of appearance of nonlinear phenomena. The situation that the low-order model is constructed based on physical reasons is likely preferable.[21]

Thus, construction of a low-order model of the Antarctic stratosphere[24,26] has allowed description of the behavior of the HCl, HNO_3, and O_3 concentrations in 1987 with the identification of the decisive nonlinear phenomena at every moment in time. As was noted by the authors, for reliable prediction of the future behavior, further investigations are needed, because new nonlinear features may manifest themselves in connection with the trends of other parameters of the Antarctic stratospheric photochemical system, such, for example, as temperature and CH_4.

1.4. Manifestations of nonlinearity in dynamics of the reagents

The effects typical of nonlinear systems, such as oscillations, period doubling, and chaotic solutions, were studied in detail by Sonnenmann, Fichtelmann, et al., in Refs. 30–37 using a simplified model of the upper mesosphere, taking into account the diurnal periodicity of the solar radiation.

As an explanation of the possible appearance of the oscillation process in a photochemical system, Ref. 35 presented a system of two equations relating to the ozone cycle:

$$\frac{\mathrm{dO}}{\mathrm{d}t} = 2\,J_{O_2}\,[O_2]_0 - k\,[O_2]_0^2\,O,$$
$$\frac{\mathrm{dO_3}}{\mathrm{d}t} = k\,[O_2]_0^2\,O - l\,[X]_0\,O_3. \tag{5}$$

Substituting one of these equations into another, we obtain

$$\frac{\mathrm{d}^2O_3}{\mathrm{d}t^2} + (k\,[O_2]_0^2 + l\,[X]_0)\,\frac{\mathrm{dO_3}}{\mathrm{d}t} +$$
$$+ (k\,[O_2]_0^2\,l\,[X]_0)\,O_3 = 2\,k\,O_3\,[O_2]_0^3\,J_{O_2}. \tag{6}$$

This equation has a structure of an oscillation equation usual in mechanic or electrical systems. There exists natural frequency ω_0 such that:

$$\omega_0^2 = (2\pi\nu_0)^2 = k\,[O_2]_0^2\,l\,[X]_0 = (\tau_O\,\tau_{O_3})^{-1}, \tag{7}$$

where $2\,k\,[O_2]_0^3\,J_{O_2}$ is the external exciting force; $\tau_O^{-1} + \tau_{O_3}^{-1}$ is the damping term. If the period of the exciting force is close to the resonance frequency, then the system most strongly reacts to the excitation. Similar effects were studied with the simplified model of the upper mesosphere. The concentrations of O_2, N_2, and H_2O were assumed constant. The variables were concentrations of five substances: O, O_3, H, OH, and HO_2. The evolution of the considered system was described by the equations

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = P_i - L_i\,n_i, \tag{8}$$

where n_i is the concentration of a substance ($i = 1, \ldots, 5$), P_i is the rate of this substance production, and L_i is the loss rate.

The diurnal behavior of insolation was modeled by rectangular pulses with the period T close to 24 hours. For the oscillation effects to manifest themselves in the system, an important parameter is the relation between the period of the external driving force and the relaxation period inherent in the system. Rough estimates of the latter have led Sonnenmann and Fichtelmann to the conclusion that the necessary condition can be satisfied in the mesosphere. Analysis of the chosen system was complicated because it contained five variables (or six – for an autonomous system). The photochemical systems with the phase space of such a dimensionality were not considered earlier, and Sonnenmann and Fichtelmann thought that the high dimensionality of the phase space is generally characteristic of chemical systems and they can hardly be reduced to low-order systems.

The concentration of water vapor and the period of the driving force were taken as control parameters. The bifurcation diagram in the coordinates of the water vapor density and ozone concentration shows that more than 75% of water vapor density interval, in which nonlinear effects manifest themselves, is occupied by oscillations with a doubled period. As the H_2O density decreases, the period quadrupling is observed and then chaos. A question appears: whether such phenomena are observed in calculations using more complex climate models and are there some real phenomena corresponding to these calculations, at least the oscillations with doubled period? The answer to the first question is still negative, because the 3D model of dynamics and chemistry[36] did not show oscillations with the doubled period. Indeed, these oscillations were not sought specially. As to real phenomena with such a period, the indirect signs of their existence are quasi-two-day variations of the dominant wind, which are regularly observed in summer in the mesopause and in the low troposphere. We still have no direct proofs of two-day variations of the ozone concentration in the mesosphere.

The low-order model for the system of reactions in the mesosphere, similar to the system studied in Refs. 35 and 37, was constructed in Ref. 7. As in Ref. 35, the model describes the behavior of five components: O, H, O_3, OH, HO_2. Their concentrations are denoted as x_1, x_2, x_3, x_4, x_5 and obey the following equations:

$$\frac{dx_1}{dt} = -\,(a_9 + 2a_{11}x_1 + a_{10}x_3 + a_4x_4 + a_5x_5)\,x_1 + a_{15}x_4^2 + a_{16}\,s(t)\,x_3 + 2a_8\,s(t),$$

$$\frac{dx_2}{dt} = -\,[a_6 + a_{12}x_3 + (a_1 + a_2 + a_{14})\,x_5]\,x_2 + a_4x_1x_4 + a_7\,s(t)\,r, \qquad (9)$$

$$\frac{dx_3}{dt} = -\,[a_{10}x_1 + a_{12}x_2 + a_{13}x_4 + a_{16}\,s(t)]\,x_3 + a_9x_1,$$

$$\frac{dx_4}{dt} = -\,(a_4x_1 + 2a_{15}x_4 + a_3x_5 + a_{13}x_3)\,x_4 + a_5x_1x_5 + a_{12}x_2x_3 + 2a_{14}x_2x_5 + a_7\,s(t)\,r,$$

where r is the H_2O mixture ratio (in ppmv), which is the control parameter of the model; all other parameters are unchanged. The function $s(t)$ parameterizes the diurnal variations of the photolysis rate (T is the duration of a day):

$$s(t) = \begin{cases} = 1, & t \in [Tn;\ Tn + T/2], \\ = 0, & t \in [Tn + T/2;\ T(n+1)],\ n = 1, 2, \ldots . \end{cases} \qquad (10)$$

If we follow the procedure of obtaining the low-order model described in Refs. 27 and 29, then for the mesospheric photochemical system we obtain that, according to the zero-order equations, there is only one slow variable x_1, all other variables being fast. However, zero-order equations for the variables x_2, x_4, and x_5 prove to be linearly dependent. Therefore, it is needed to consider equations of a higher-order approximation for the newly determined variable $x_f = x_2 + x_4 + x_5$. Solution of the corresponding set of algebraic equations for x_2, x_4, and x_5 (it is sufficient to take any two of three available equations) shows that $x_{4,5} \ll x_2$ and, consequently, $x_2 \approx x_f$. The latter approximate equality means that the equation for x_f actually determines the dynamics of x_2, when the fast dynamics of x_4 and x_5 is taken into account. The typical time x_2 (or x_f) is 10^4 s. Thus, the variable x_2, which is fast according to the zero-order equations, proves to be slow, as x_1, if considered properly. As a result, the low-order model of the mesospheric photochemical system describing the dynamic processes with the typical time of 10^4–10^6 s includes two equations for the slow variables x_1 and x_2:

$$\frac{dx_1}{dt} = -\,\alpha\,x_2 - [1 - s(t)]\,\mu\,x_2 + \delta\,s(t),$$

$$\frac{dx_2}{dt} = -\,\beta\,x_2^2/x_1^2 - \sigma\,x_2^2/x_1 + \gamma\,s(t)\,r. \qquad (11)$$

Here $\alpha = 2a_6$; $\mu = a_9$; $\delta = 2a_8$; $\beta = 2a_3\,a_6^2/(a_5\,a_4)$; $\sigma = 2a_6\,(a_1 + a_2)/a_5$; $\gamma = 2a_7$.

Let us emphasize once more that these two equations include the dynamics of fast variables x_3, x_4, and x_5, which are connected with the slow variables through the following equations:

$$x_4 \approx a_6\,x_2/(a_4\,x_1),\ x_5 \approx a_6\,x_2/(a_5\,x_1),$$

$$x_3 \approx a_9\,x_2/(a_{16})\ \text{(day) and}\ x_3 = \text{const (night)}.$$

The bifurcation diagrams for the complete model under study and its low-order version have qualitatively similar dynamic properties, which, in their turn, are similar to the results obtained in Refs. 35 and 37.

Thus, the fruitfulness of the approach consisting in the use of a low-order model for a studied search for regularities in a complex model was demonstrated in Refs. 27–29. In Ref. 7, the approach to construction of low-order models for arbitrary dynamic systems is described in detail. As noted above, this approach is based on the traditional separation of slow variables, accepting the variables with the long relaxation time as parameters of the model and the variables with the shorter relaxation time as being in the instantaneous equilibrium with the slow variables.

It should be noted that in Ref. 7 it is proposed to determine the relaxation times, according to which significant variables are selected in the photochemical systems, by zero-order equations, within the framework of separately considered equation for a corresponding reagent, although the typical time of variation of a variable with the evolution of the entire system may differ significantly from the relaxation time determined in such a way.

2. Qualitative analysis of the set of reactions of the purely oxygen atmosphere

The papers listed above indicate that the atmosphere as a chemical system is nonlinear to a high degree and its behavior can be described only by the correspondingly adequate methods. Besides, low-order models keeping the properties of complex chemical models can be constructed. Above in this paper, the low-order models resulted from the exhaustive systems of equations. The same purpose can be achieved from other initial point as well. As was mentioned in the Introduction, understanding of chemical processes cannot be thought complete, until the simplest systems of equations are studied from the viewpoint of nonlinear analysis. In the case of stratosphere, the initial point is the simplest ozone cycle in the oxygen atmosphere formulated by Champion in Ref. 39. We studied the purely oxygen atmosphere using methods of nonlinear dynamics, what is interesting, in principle, both from the viewpoint of atmospheric chemistry and from the viewpoint of the behavior of elementary systems in chemical reactors.

2.1. Set of reactions for the oxygen atmosphere

The reactions of the ozone cycle are considered by the methods of chemical kinetics within the framework of the so-called box model, which is usually used to describe chemical reactions in the atmosphere and corresponds to the situation of closed homogeneous chemical ideal-mixing reactor described by an autonomous system of nonlinear differential equations for reagent concentrations. In the language used at describing nonlinear dynamics systems, this situation corresponds to the case of a closed conservative system. Let us also note that the term “qualitative features” is then used not only in the sense which is traditional for the qualitative analysis (change of the character of the steady states or their number), but also for description of other situations considered as non-typical for the atmosphere, for example, when the concentration of some reagent becomes zero.

The system of reactions in the oxygen atmosphere[39] contains 12 reactions, including the reactions of photodissociation of molecular oxygen O_2 and ozone O_3, production of ozone in the three-particle collision (with O, O_2, O_3, and M as partners, where M is an arbitrary particle, not reacting with oxygen components), reactions inverse to ozone production (with O_2, O_3, and M as partners), reaction of ozone destruction in collision with atomic oxygen, and the reaction of recombination of oxygen atoms O (with O_2 and M as partners):

$$O_2 + h\nu \xrightarrow{J_2} O + O, \tag{12}$$

$$O_3 + h\nu \xrightarrow{J_3} O_2 + O, \tag{13}$$

$$O + O_2 + O_2 \xrightarrow{K_{2O_2} \equiv K_1} O_3 + O_2, \tag{14}$$

$$O + O_2 + O_3 \xrightarrow{K_{2O_3} \equiv K_2} O_3 + O_3, \tag{15}$$

$$O + O_2 + O \xrightarrow{K_{2O} \equiv K_3} O_3 + O, \tag{16}$$

$$O + O_2 + M \xrightarrow{K_{2M} \equiv K_4} O_3 + M, \tag{17}$$

$$O_3 + O_3 \xrightarrow{K_{-2O_3} \equiv K_5} O + O_3 + O_2, \tag{18}$$

$$O_3 + O_2 \xrightarrow{K_{-2O_2} \equiv K_6} O + 2O_2, \tag{19}$$

$$O_3 + M \xrightarrow{K_{-2M} \equiv K_7} O_2 + O + M, \tag{20}$$

$$O_3 + O \xrightarrow{K_3 \equiv K_8} 2O_2, \tag{21}$$

$$O + O + O_2 \xrightarrow{K_{4O_2} \equiv K_9} 2O_2, \tag{22}$$

$$O + O + M \xrightarrow{K_{4M} \equiv K_{10}} O_2 + M. \tag{23}$$

Consideration of these reactions leads to the system of three equations for concentrations of oxygen components O_2, O, and O_3 (let us denote them as x, y, and z, respectively):

$$\begin{gathered} \mathrm{d}x/\mathrm{d}t = J_3\, z - J_2\, x + 2K_8\, yz - \\ - (K_1\, x + K_2\, z + K_3\, y + K_4\, M)\, xy + \\ + (K_5\, z + K_6\, x + K_7\, M)\, z + (K_9\, z + K_{10}\, M)\, y^2, \\ \mathrm{d}y/\mathrm{d}t = J_3\, z + 2J_2\, x - K_8\, yz - \\ - (K_1\, x + K_2\, z + K_3\, y + K_4\, M)\, xy + \\ + (K_5\, z + K_6\, x + K_7\, M)\, z - (K_9\, z + K_{10}\, M)\, y^2, \\ \mathrm{d}z/\mathrm{d}t = -\, J_3\, z - K_8\, yz + (K_1\, x + K_2\, z + \\ + K_3\, y + K_4\, M)\, xy - (K_5\, z + K_6\, x + K_7\, M)\, z. \end{gathered} \tag{24}$$

The space of concentrations is three-dimensional. Because of the law of conservation of the number of atoms in the process of a chemical reaction, the concentrations of oxygen components must satisfy a certain equation

$$2x + y + 3z = A. \tag{25}$$

Therefore, it is sufficient to consider the reaction triangle (RT) determining the domain of concentration variability accessible to this system in the projection onto some plane. The methods for determination of steady states and the character of their stability on a plane have been well developed in the qualitative analysis (see, for example, Ref. 40).

Some blocks of the system of reactions (12)–(23) were considered earlier (see Refs. 41–43).

The system of equations for reactions (12), (13), (17), and (21) has the form

$$\begin{gathered} \mathrm{d}x/\mathrm{d}t = J_3\, z - J_2\, x + 2K_8\, yz - K_4\, Mxy, \\ \mathrm{d}y/\mathrm{d}t = J_3\, z + 2J_2\, x - K_8\, yz - K_4\, Mxy, \end{gathered} \tag{26}$$

$$\mathrm{d}z/\mathrm{d}t = -J_3 z - K_8 yz + K_4 Mxy.$$

The equation that is frequently used for the ozone concentration results from Eq. (26) after some approximations (see, for example, Ref. 41). The first one consists in exclusion of the equation for the O_2 concentration from the consideration because the concentrations of O and O_3 are small as compared to the concentration of O_2 at the altitudes corresponding to the position of the ozone layer. Other approximations deal with quantitative data on the rates and concentrations. The result is the following equation for the ozone concentration in the stratosphere:

$$\mathrm{d}z/\mathrm{d}t = 2J_2 x\left[1 - \frac{K_8 J_3 z^2}{K_4 J_2 x^3}\right]. \tag{27}$$

In Ref. 42, the atmosphere was divided into two layers with the boundary at the level of 30 km, and in every layer the ozone evolution was determined by Eq. (27) with the allowance for transport between the layers. For such a system, one steady solution was found with the character (steady node or saddle) depending on the terms characterizing the transport. In Ref. 43 the system of two equations for the concentrations of O and O_3 from Eq. (26) was studied, in which the concentration of O_2 was assumed constant. Such a system has the only steady state being a stable node, and its character does not change as parameters of the equation vary. In Ref. 41, the system (26) was considered with the addition of terms characterizing the sink of oxygen components O, O_2, and O_3 and the source of O_2. The system allows only one physically acceptable stable steady state, and damping oscillations about this state are excluded. Thus, in the previous researches, the qualitative structure of solutions proved to be sufficiently simple, but the complete phase portrait of even simplest system was not yet obtained. In Ref. 44, the system of reactions (12), (13), (17), and (21) was considered at $M = O_2$ and the additional stationary points in the reaction triangle were obtained. Particular sets of reactions from Eqs. (12)–(23) were analyzed in Refs. 45–47. References 48 and 49 are devoted to the roles of sources and sinks in the stability of the ozone cycle.

Remind that the steady states of the system of two differential equations

$$\dot{x} = P(x, y), \ \dot{y} = Q(x, y) \tag{28}$$

are determined by the equations

$$P = 0, \ Q = 0. \tag{29}$$

The type of the steady state is determined by the roots of the equation

$$\lambda^2 - T\lambda + \Delta = 0, \tag{30}$$

where

$$T = a_{11} + a_{22}; \ \Delta = a_{11} a_{22} - a_{12} a_{21};$$

$$a_{11} = \partial P/\partial y, \ a_{12} = \partial P/\partial z, \qquad a_{21} = \partial Q/\partial y, \ a_{22} = \partial Q/\partial z \tag{31}$$

and the derivatives are estimated for coordinates of the corresponding steady states.

2.2. Equations of the ozone cycle in the absence of radiation

Let us consider first a particular case of the night system,[46] in which reactions (14) and (21) proceed. This allows us to dwell on two points. This simple example gives us the possibility to find what consequences follow from the declaration that one variable is a constant. Besides, using this system as an example, let us illustrate how the information obtained from direct numerical solution of the system of equations corresponds to the information obtained from its qualitative analysis.

In the case of reactions (14) and (17), the system of kinetic equations has the form

$$\begin{aligned} \dot{x} &= k_1 x^2 y + 2k_8 yz; \\ \dot{y} &= -k_1 x^2 y - k_8 yz; \\ \dot{z} &= k_1 x^2 y - k_8 yz. \end{aligned} \tag{32}$$

Change of variables according to Ref. 50 as $\tilde{t} = \alpha t$, $\tilde{x} = \beta x$, $\tilde{y} = \gamma y$, $\tilde{z} = \delta z$, where $\alpha = k_8^2/k_1$, $\beta = \gamma = \delta = k_1/k_8$, allows the system to be reduced to a dimensionless form containing no parameters:

$$\begin{aligned} \dot{\tilde{x}} &= -\tilde{x}^2\tilde{y} + 2\tilde{y}\tilde{z}; \\ \dot{\tilde{y}} &= -\tilde{x}^2\tilde{y} - \tilde{y}\tilde{z}; \\ \dot{\tilde{z}} &= \tilde{x}^2\tilde{y} - \tilde{y}\tilde{z}. \end{aligned} \tag{33}$$

The concentration of O_2 is usually several orders of magnitude higher than concentrations of O and O_3. This allows us to believe that it is unchanged in the process of reaction. This approximation is often used in literature, and if we follow its logic in this case, then the system (33) should be replaced by the system, where $c = \tilde{x}^2$:

$$\begin{aligned} \dot{\tilde{y}} &= -\tilde{y}(c + \tilde{z}); \\ \dot{\tilde{z}} &= \tilde{y}(c - \tilde{z}). \end{aligned} \tag{34}$$

In the system (34), the right-hand sides of the equations include common factor $\tilde{y}$. The system

$$\begin{aligned} \dot{\tilde{y}} &= -(c + \tilde{z}); \\ \dot{\tilde{z}} &= (c - \tilde{z}) \end{aligned} \tag{35}$$

differs from Eq. (34) by the absence of the common factor, and its steady states are obviously the steady states of the system (34). The system (35) has no steady states in the finite part of the plane, however it has two singular points at infinity. In the case of the system (34), the steady points common for the system (35) either are complemented with the points arising from the equality of the common factor to zero, $\tilde{y} = 0$, i.e., in this case these are points on the $\tilde{z}$ axis. The behavior of systems (34) and (35) in the physical part of the plane (in the first quadrant) differs by the time dependence. For the system (34), the points on the $\tilde{z}$ axis are stable steady states, so at these points $\dot{\tilde{y}} = 0$, $\dot{\tilde{z}} = 0$. In the case of the system (35), the system approaches the points on the axis $\tilde{z}$ with nonzero rates.

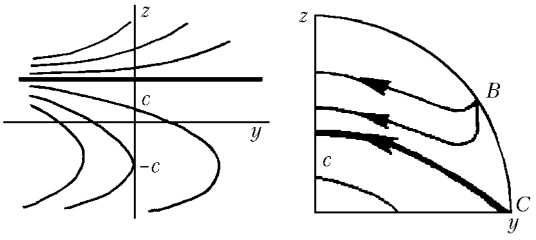
The systems (34) and (35) can be integrated exactly. The variables $\tilde{y}$, $\tilde{z}$ for them satisfy the equation

$$\frac{d\tilde{z}}{d\tilde{y}} = \frac{\tilde{z} - c}{\tilde{z} + c}, \tag{36}$$

whose solution under the initial conditions $\tilde{t} = t_0$, $\tilde{z} = z_0$, $\tilde{y} = y_0$ is the function

$$\tilde{y} = y_0 + (z_0 - c) + 2c \ln\left(\frac{\tilde{z} - c}{z_0 - c}\right). \tag{37}$$

This solution is shown in Fig. 1*a*. The straight line $\tilde{z} = c$ is an asymptote of the integral curves. The comparison of the exact solution (Fig. 1*a*) and the phase portrait of the system (Fig. 1*b*) convinces once more that the phase portrait gives full information on the system, except only for quantitative details insignificant for the qualitative analysis.



a *b*

Fig. 1. Comparison of the exact solution and the phase portrait of the systems (34) and (35), the thick curve is for the separatrix, *c* is its crossover point with the axis *z*: exact solution (*a*); fragment of the phase portrait (*b*); *B* and *C* are singular points at infinity.

In the case of the arbitrary concentration of O_2 (Eqs. (33)), the law of conservation of the number of atoms (25) should be taken into account. This allows us to derive a system of two differential equations for two selected variables from Eq. (33). Thus, the system describing the evolution of O and O_3 has the following form:

$$\dot{y} = (y/4)\,(-A^2 + 2Ay + (6A - 4)\,z - y^2 - 9z^2 - 6yz);$$
$$\tag{38}$$
$$\dot{z} = (y/4)\,(A^2 - 2Ay - (6A + 4)\,z + y^2 + 9z^2 + 6yz).$$

A fragment of the phase portrait corresponding to the quadrant with the positive concentrations is shown in Fig. 2. Comparison of Fig. 1*b* with Fig. 2 illustrates how the assumption on the constant concentration of O_2 affects the qualitative behavior of the system.

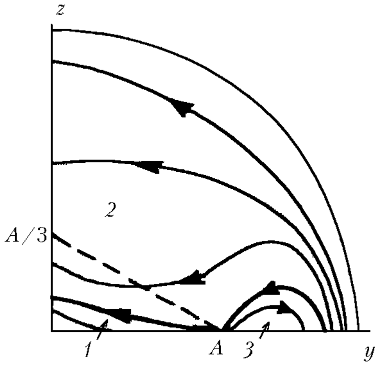


Fig. 2. Fragment of the phase portrait of the system (38): thick lines are for bifurcation curves, dashed line is the RT boundary.

The number and character of singular points remain unchanged, but their arrangement becomes different. The law of conservation at the arbitrary concentration of O_2 imposes restrictions onto the domain of variability of the concentrations, allowing them to be only within the RT. Only some part of the phase space limited by the straight line $3z_0 + y_0 = A - 2x_0 = B \le A$ in Fig. 2 proves to be allowable. Within the RT, the time behavior of the O and O_3 concentrations differs only quantitatively in the situations with the constant and variable concentration of O_2. However, qualitative changes may in principle appear, in physically significant areas, if situations are more complex.

Let us consider also the case of night atmosphere, when there are no reactions of photodissociation and a partner in the three-particle collision is a foreign particle. It includes four reactions: (17), (20), (21), and (23). It should be noted here that concentrations of the oxygen components differ by several orders of magnitude and the phase portraits (trajectories of variables in the phase space of the system) shown directly in real coordinates do not illustrate the behavior of the phase trajectories. Therefore, for illustration, it is convenient to pass to new variables. If such transformations are topological,[41] then the qualitative structure of the phase portrait (number and character of steady states) does not change. Let us pass to dimensionless variables as described in Ref. 50 using the scaling transformation

$$\tilde{t} = \alpha t,\ \ \tilde{x} = \beta x,\ \ \tilde{y} = \gamma y,\ \ \tilde{z} = \delta z,\ \ \tilde{M} = \mu M \tag{39}$$

in Eqs. (17) and (21). At such a transformation, the system of kinetic equations

$$\begin{aligned} dx/dt &= 2K_8\,yz - K_4\,Mxy,\\ dy/dt &= -K_8\,yz - K_4\,Mxy,\\ dz/dt &= -K_8\,yz + K_4\,Mxy \end{aligned} \tag{40}$$

with the use of $\beta = \lambda = \delta = \tilde{M}$, $\alpha = K_8/\tilde{M}$, and $\mu = K_4/K_8$ takes the form

$$\begin{aligned} d\tilde{x}/d\tilde{t} &= 2\tilde{y}\,\tilde{z} - \tilde{M}\,\tilde{x}\,\tilde{y}, \\ d\tilde{y}/d\tilde{t} &= -\,\tilde{y}\,\tilde{z} - \tilde{M}\,\tilde{x}\,\tilde{y}, \qquad (41) \\ d\tilde{z}/d\tilde{t} &= -\,\tilde{y}\,\tilde{z} + \tilde{M}\,\tilde{x}\,\tilde{y}. \end{aligned}$$

As is seen, the system (41) includes only one parameter $\tilde{M}$, whose value under atmospheric conditions at the altitude of 30 km equals 0.421829. The RT vertices are determined by the conserving value of A, and in the plane (y, z) they are $(A, 0)$ and $(0, A/3)$. At the altitude of 30 km $A = 1.464 \cdot 10^{17}$ cm^{-3}. In the coordinates $(y/10^{17}, z/10^{17})$, the phase portrait of the system (41) has the form shown in Fig. 3. The qualitative features of the phase portrait are clearly seen. At the same time, the number of steady states, the character of their stability, and the character of the trajectories, i.e., the information given by the phase portrait, keep unchanged at the transition to real values of the system parameters, as it is expected at topological transformations of variables. However, if it is shown on the real scales of the variables, the pattern of the trajectories is not that vivid.

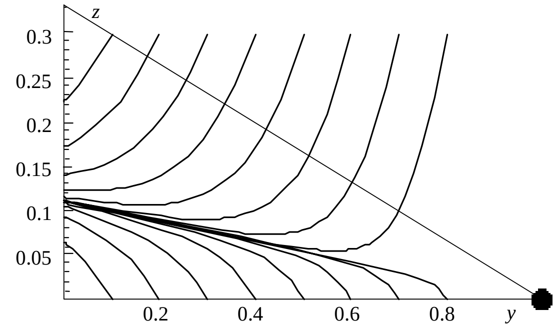


Fig. 3. Phase portrait of the ozone cycle reactions (17) and (21) (without the reaction of photodissociation) with a foreign particle as the third body in triple collisions ($y \to y/A$, $z \to z/A$). The axis z is a steady straight line; a saddle is located at the vertex $y = A$, $z = 0$.

Addition of some other reactions to the system, generally speaking, can change the type of nonlinearity of the system and, correspondingly, the structure of its phase space. Detailed analysis of changes of the phase portrait of the night system at addition of the reactions (20) and (23) to the reactions (17) and (21) is given in Refs. 43 and 46. The system of these four reactions is characterized by the presence of two steady states within the reaction triangle – a saddle is at the vertex $y = A$, $z = 0$ and the vertex $y = 0$, $z = 0$ is a complex singular point with a stable sector inside the RT. Allowance for all the reactions for the night case except for the reaction (23) gives the same qualitative pattern. Addition of the reaction of recombination of oxygen atoms (23) leaves only one singular point in the RT, namely, the point $y = 0$, $z = 0$ – a complex singular point with a stable sector inside the RT.

We have considered the case of the ozone cycle without radiation in that detailed manner to illustrate the fact that the phase portrait bears complete information on the system trajectories by showing the regions with different qualitative behavior of the trajectories depending on the initial conditions and the tendency of long-term variation of the solution. Let us emphasize that this information about a system cannot be obtained by other methods.

2.3. Complete set of reactions

In the full qualitative analysis of the system of equations of the ozone cycle in the oxygen atmosphere, all reactions were divided into four groups with different reactions of photodissociation: night case – no reactions of photodissociation, presence of one of the two reactions of photodissociation, and the full version (12)–(23). Each of these groups, in its turn, consisted of three parts with different partners in triple collisions: M is a foreign particle, or one of the oxygen components O_2, O, O_3, or the full version. For all the considered situations, all possible steady states were obtained and the character of their stability analyzed. Changes of the phase portraits at variation of the total number of oxygen particles A were analyzed as well.

In every group, two reactions were taken as a minimum set: production of ozone in a triple collision and ozone depletion by atomic oxygen plus the corresponding reactions of photodissociation. Then these reactions were supplemented with others up to exhaustion of all reactions in a group. Let us note the following features inherent in the system of reactions among the oxygen components. On the one hand, this system is highly nonlinear, exhibiting such features as multiple steady states and change of their number and the character of stability at variation of the system parameter A. At maximum, four steady states are possible inside the RT for the system of reactions (12), (14), and (21), among which two states are stable. The systems of reactions without the reaction of recombination of atomic oxygen showed bifurcations at variation of the parameter A. Thus, at the concentrations typical for the atmosphere, the system has a stable node inside the RT with the nonzero concentrations of all oxygen components and a saddle at the vertex $y = A$, $z = 0$. As A decreases, the stable node approaches the vertex $y = A$, $z = 0$ and reaches it at a certain value of A, so the single stable node remains at the vertex $y = A$, $z = 0$. These features evident for certain sets of reactions from the considered list disappear if all possible reactions are taken into account. A particular role in this case, play reactions of recombination of the atomic oxygen. If it would be possible to select reactions in the system, then in the chemical reactor we could observe many features of the oxygen system caused by its nonlinearity.

Comparison of all available phase portraits convinces us that the simplest system of reactions having the features of the system as a whole is the system of five reactions, namely, two reactions of photodissociation, reaction of ozone production in a three-particle collision, reaction of ozone destruction in collision with atomic oxygen, and the reaction of recombination of the atomic oxygen (the result obtained in co-operation with Gordov and Fazliev, the detailed description will be published later). It is just this system that can be used to construct the basic model of more general atmospheric photochemical systems.

The situations characteristic of observation in chemical reactors may be the following. First, in the cases without radiation or with radiation destructing only ozone, the state with the zero concentrations of ozone and atomic oxygen, i.e., with the presence of only molecular oxygen, is stable. In the cases with radiation destructing only molecular oxygen or both molecular oxygen and ozone, the state with nonzero concentrations of all the three oxygen components is stable. It is valid for both pure oxygen systems and systems including a foreign gas not reacting with the oxygen components with the allowance for all possible reactions. Bifurcation can take place in all cases except for the night one. It can be observed, if we neutralize the reactions of recombination of the atomic oxygen.

In general, as we take into account larger number of reactions, the structure of the phase portrait becomes simpler, and finally, with the allowance for all 12 reactions, we have only one steady state inside the RT – a stable node, the state with zero concentrations of the oxygen components. Figure 4 depicts the phase portraits of the complete system and the system without the reaction (23) for the constants corresponding to the altitude of 30 km, as well as the phase portraits of the minimum system with and without the reaction (23). Thus, the presence of the reaction (23) in the ozone cycle is of principal importance, because just it eliminates the possibility of obtaining the state with the zero concentrations of O_2 and O_3 at certain values of A.

As was already mentioned, the method for construction of low-order models proposed in Ref. 7 uses typical (in nonlinear analysis) separation of variables into groups with close and strongly different relaxation times. The basis for such a separation was formed in Ref. 7 by the relaxation times within the framework of the equations for every reagent. This approach is likely not universal for all atmospheric photochemical situations. Thus, for example, in the case of purely oxygen atmosphere for the stratospheric conditions, molecular oxygen is a slow variable, whereas atomic oxygen is a fast variable. The result of this approach is Eq. (27) for the ozone concentration, which determines the only steady state not subject to any qualitative changes at variations of the total number of oxygen particles A. Therefore, this equation can serve a low-order model for the system of reactions (12)–(22).

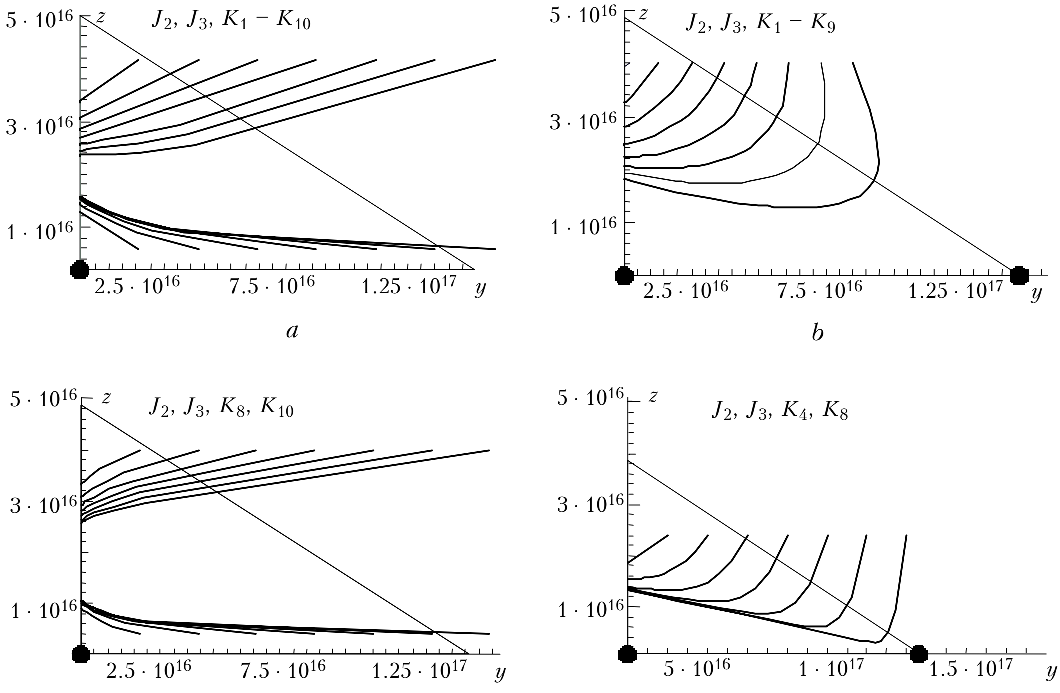


Fig. 4. Phase portraits of the full system of reactions and the system without the reaction of recombination of oxygen atoms (23) along with the corresponding phase portraits of low-order models under atmospheric conditions at the altitude of 30 km.

3. Low-order model of oxygen–hydrogen atmosphere

Above we have analyzed qualitatively the purely oxygen atmosphere, in which the object of study was the system of kinetic equations for three oxygen components.

To keep the visual character and the possibility of interpretation of the obtained results, it is important to find the compromise version, which allows various reagents reacting with the oxygen components to be included in consideration but, at the same time, keeps the advantages of qualitative analysis as to prediction. One of the possible ways, namely, simulation of additional substances and reactions through introduction of sources and sinks into the equations for oxygen components, was discussed in Ref. 48. Here we dwell on the other approach, in which the equations of the simple model follow from some extra reasons. The analysis of the dynamics of reagents in the oxygen–hydrogen atmosphere will be used for illustration of application of this approach to an actual problem.

3.1. Choosing simple model

In Ref. 53, we based on analysis of the oxygen–hydrogen atmosphere from Ref. 23 and believed that the corresponding set of reactions correctly represents the reality. The model in Ref. 23 is determined by the kinetic equations describing the dynamics of the oxygen–hydrogen system in the mesosphere; it accounts for the effect of the source of water vapor and sinks of oxygen and atomic and molecular hydrogen. The obtained equations were studied in Ref. 23 for the presence of multiple steady states with the positive result. The multiple steady states in the considered system appear due to the action of external effects (sources and sinks). We studied some hypothetical system as a simple model roughly describing the actual system to follow the conservation of the qualitative features of the simple model at transition to the realistic model. We also would like to follow how the features inherent in the ozone cycle in the oxygen atmosphere held at inclusion of the hydrogen components into the system.

As the simplest system, we took simplified system of reactions proposed in Ref. 51 for describing processes in the stratosphere and containing, in addition to purely oxygen reactions, some hypothetical reaction of hydrogen with the ozone. Syvorotkin and Sadovskii[51] related the ozone depletion in the stratosphere with the hydrogen blowing off the ozone layer due to the endogenous activity of the Earth. Realizing that actually this reaction was not ever found, we added it to the oxygen system, because the obtained system, on the one hand, allows exact qualitative analysis and, on the other hand, reflects some features of the oxygen-hydrogen system. This assumption *a posteriori* proved to be justified, because the simple model helped us to understand the realistic model.

So, we consider the following system of reactions:

$$\begin{gathered} O_2 + h\nu \xrightarrow{J_2} O + O, \\ O_3 + h\nu \xrightarrow{J_3} O_2 + O, \\ O_2 + O + M \xrightarrow{K_4} O_3 + M, \\ O_3 + O \xrightarrow{K_8} 2O_2, \\ H_2 + O_3 + M \xrightarrow{K_{11}} H_2O + O_3 + M. \end{gathered} \tag{42}$$

The kinetic equations describing the behavior of the concentrations have the form

$$\begin{gathered} \mathrm{d}x/\mathrm{d}t = -J_2 x - K_4 Mxy + J_3 z + K_{11} Mzh + 2K_8 yz, \\ \mathrm{d}y/\mathrm{d}t = 2J_2 x - K_4 Mxy + J_3 z - K_8 yz, \\ \mathrm{d}z/\mathrm{d}t = K_4 Mxy - J_3 z - K_{11} Mzh - K_8 yz, \\ -\mathrm{d}w/\mathrm{d}t = \mathrm{d}h/\mathrm{d}t = -K_{11} Mzh. \end{gathered} \tag{43}$$

The parameters x, y, z, h, and w denote the concentrations of O_2, O, O_3, H_2, and H_2O, respectively. In this system two laws of conservation work, corresponding to conservation of O and H atoms in the chemical reactions:

$$\begin{gathered} 2x + 3z + y + w = A_1; \\ 2h + 2w = B; \\ A_1 - B/2 = A. \end{gathered} \tag{44}$$

The system (43) has four steady states, three of which coincide with such states for pure oxygen atmosphere and one is introduced by the reaction with hydrogen.

The space of concentrations of the considered system is, generally speaking, five-dimensional. However, the laws of conservation (44) determine a three-dimensional plane in the space of concentrations.[52] Its intersection with the non-negative vectors $C_i = 0$ (C_i are concentrations of substances) gives a 3D reaction polyhedron, which can be visualized. It turned out that depending on the relations among the initial concentrations ($A_1 > B/2$, $A_1 = B/2$, $A_1 < B/2$) the system evolution could follow three scenarios. The steady states in all the cases have a character of complex singular points with stable or unstable sectors in certain planes. In the case that $A_1 > B/2$, the reaction polyhedron includes two steady states, one inside the polyhedron and one at its vertex. In other cases, the only steady state is at the polyhedron vertex, whereas other states lye beyond it and are non-physical because of negative coordinates.

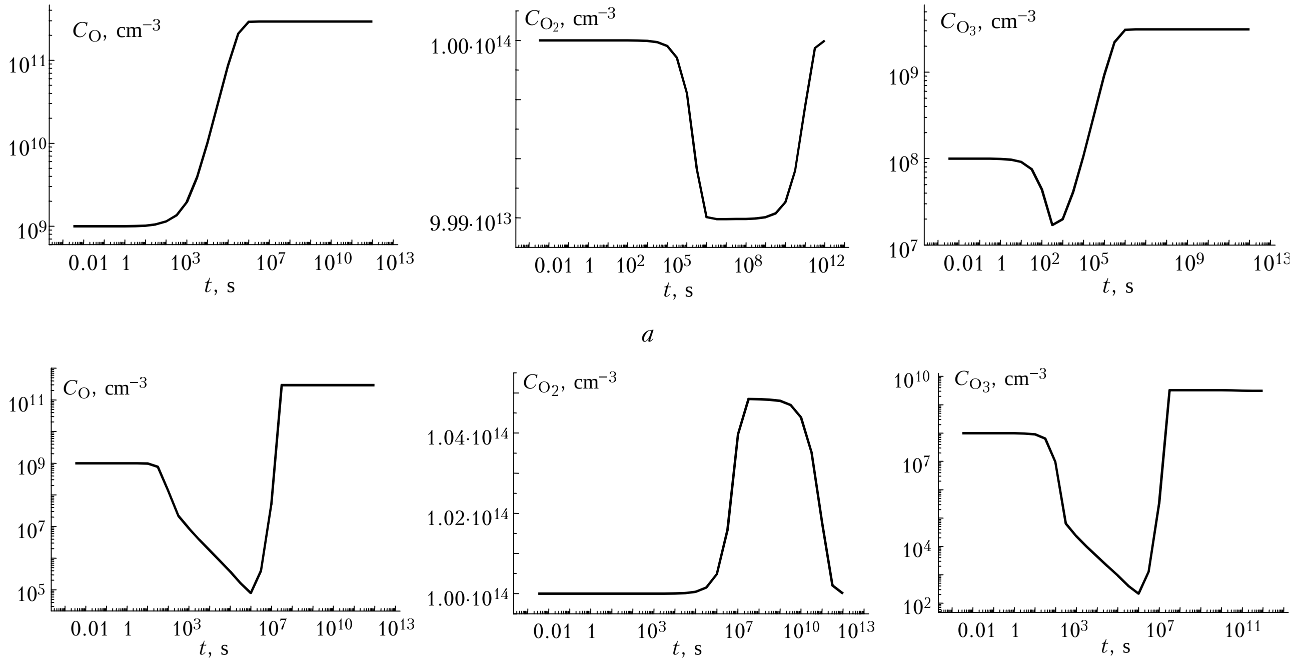
3.2. Comparison with the results of a realistic model

Thus, our simplified model (42), for which the complete and illustrative qualitative analysis is possible, shows the features in its behavior, which, in principle, may appear in the more realistic model. Direct comparison of the models is rather problematic. Actually, the realistic model[23] includes sources and sinks, whereas the model (42) obeys the laws of conservation. Besides, it includes only one reaction with hydrogen components, and therefore the behavior of the hydrogen-containing components in it cannot be compared with that in the realistic model.[23] However, analysis of the behavior of oxygen components in both models is possible and just it gives the basis for their comparison.

The time dependences of the O and O_3 concentrations were given in Ref. 53 along with the phase trajectories $z(y)$ for the simplified and the realistic models at several close values of the concentrations. The tendencies of concentration variations were similar in both models. Thus, it was shown that the qualitative features of realistic models could hold, in principle, in much simpler models available for complete analysis. Let us consider this situation in a more detail (see also Ref. 4).

According to the low-order model (42), there are two ways of the behavior of the oxygen components: one leading to nonzero concentrations of oxygen components, i.e., to the steady state inside the considered reaction polyhedron, and another leading to zero concentrations of the components and, correspondingly, the steady state at the polyhedron vertex. Keeping in mind that in the low-order model (42) there are two types of behavior delimited by the relation $A_1 = B/2$, we have performed more detailed calculations for the model from Ref. 23, expecting to find the corresponding boundary for it too. Toward this end, the system of differential equations determining the model from Ref. 23 was solved numerically at fixed values of sources and sinks, but at variations of the initial conditions for the variables H_2 and H_2O. Some calculated results are depicted in Fig. 5. The pattern shown in Fig. 5*a* corresponds to the concentrations of H_2 and H_2O in the mesosphere.

The behavior of concentrations of the atomic oxygen and ozone (Fig. 5*b*) is characterized by the presence of minimum with the following growth up to the steady values. The depth of the minimum depends on the initial concentrations of H_2 and H_2O and, in principle, can achieve zero values, whereupon further growth of the concentrations becomes impossible. The boundary between these types of behavior at the given values of the sources and sinks ($k_H = 10^{-3}$, $k_{H_2} = 10^{-2} k_H$, $f = 10^3$, $k_{O_2} = f/10^{14}$) and at the initial hydrogen concentration ~ 10^7 cm^{-3} is determined by the value of the water vapor concentration ~ $5 \cdot 10^{13}$ cm^{-3}, corresponding to the pressure of $1.8 \cdot 10^{-6}$ mbar. At the altitude of 70 km, this is roughly 20 times lower than the total pressure and an order of magnitude lower than the pressure of the saturating vapor at the corresponding temperature, but 2 to 3 orders of magnitude higher than the water vapor concentration existing under these conditions. At other values of the sources, sinks, and H_2 concentrations, the boundary, naturally, shifts. Note that these results were obtained with the use of the Mathematica software.



a

b

Fig. 5. Behavior of the concentrations of oxygen components in the model from Ref. 23 for several sets of the initial conditions: $[H_2]_0 = 10^8$ and $[H_2O]_0 = 10^9$ (*a*); $[H_2]_0 = 10^8$ and $[H_2O]_0 = 10^{13}$ (*b*).

Conclusion

In the literature, there are few papers, in which the system of equations describing the atmospheric chemical processes is analyzed from the viewpoint of nonlinear dynamics. This is caused by the nonlinearity of the corresponding kinetic equations, and the success of such analysis depends, to a high degree, on the possibility of constructing low-order models of the studied phenomena. The first papers in this field considered individual elementary (low-dimension) systems of the ozone cycle[41–43] and did not find some qualitative features in them. However, in recent papers, rather complex sets of reactions have demonstrated typical “nonlinear” features, such as multiple steady states, periodic oscillations, and appearance and disappearance of steady states at variations of system parameters. Such manifestations include transitions between the modes with the high and low content of NO_x; this effect was found in the troposphere in polluted regions and under conditions of winter stratosphere in high latitudes. Due to the construction of the low-order model of the corresponding chemical processes, the mechanism of this transition was explained. Another characteristic example is construction of the low-order model for the Antarctic stratosphere, which allowed bifurcations of the steady states to be followed up during the phenomenon of the ozone hole in 1987.

Return to analysis of the ozone cycle in the oxygen atmosphere[3,4,44–49,53] showed that the features caused by nonlinearity are inherent in it. In this connection, a particular role of the reaction of recombination of atomic oxygen was found. Introduction of this reaction suppresses both the presence of multiple states and appearance of bifurcations at variation of the total number of oxygen particles in the system (note that this reaction was ignored in Ref. 29). The low-order model of the oxygen atmosphere including five reactions may prove to be useful for further analysis. The low-order model of the oxygen–hydrogen atmosphere being, in fact, empirical one has, nevertheless, allowed the regions with different types of behavior of oxygen components to be determined within the realistic model.

Thus, both approaches to the study of low-order models, the one based on the exhaustive systems of kinetic equations for atmospheric reactions and another one on the equations for the elementary sets of reactions, provide for in-depth understanding of the atmospheric chemical processes.

Acknowledgments

The author is thankful to E.P. Gordov and A.Z. Fazliev for continuous and fruitful co-operation and constructive criticism.

This work was partly supported by the Russian Foundation for Basic Research, Grant No. 00–05–65209.

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