ON THE DYNAMICS OF A SIMPLE SYSTEM OF REACTIONS MODELING THE OXYGEN-HYDROGEN CYCLE IN THE MESOSPHERE

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Complete qualitative analysis of a few-variable model of the oxygen-hydrogen atmosphere (three reactions including oxygen constituents and a hypothetical combined reaction of ozone and hydrogen introduced by Syvorotkin and Sadovskii) is performed. Drastic difference in the concentration behavior has been revealed under definite combinations of the initial concentrations. The concentration behavior of the oxygen constituents found is similar to that which follows from a solution of the Young-Brasseur system describing processes in the mesosphere, the values of the corresponding parameters being comparable. Thus, it is shown that the phase portrait of the few-variable reaction system allows one to predict the regions of appearance of qualitative peculiarities in a more complicated model.

At present, analysis of evolution of the photochemical processes in the atmosphere is mainly based on direct calculations. The properties that are calculated are concentrations of the atmospheric components that, in turn, are determined by the set of reactions and reactants chosen. Generally speaking, this approach does not allow one to predict general tendencies of the concentration evolution while being capable of describing some specific process. At the same time, the methods of nonlinear dynamics provide a possibility of studying all the possible variants of the evolution, as well as predicting the appearance of one or other qualitative peculiarity. However, there are certain limitations in these methods because the procedures of qualitative investigations are well developed only for systems that have few equations.

In the case of purely oxygen atmosphere, the object of qualitative analysis is the system of two kinetic equations for three oxygen constituents.[1–6] Any increase in the number of reactants calls for an essentially larger number of equations. As a result, the problem arises on analyzing multidimensional phase portraits. This, almost necessarily, leads to the loss of the representation clarity, which is much attractive in the case of few-dimension systems allowing quite simple forecasting of the evolution.

To solve such a multidimensional problem we propose to use the approach conventional for physics and which is based on the seeking of a simplified model incorporating the basic features of the problem to be solved. In this context the main idea of the approach consists in investigation of few-variable systems of equations derived on the basis of some preliminary estimates. The validity of approximations applied is established by comparing the results obtained with those obtained using the system without approximations. Then, by making comprehensive qualitative analysis the prediction of qualitative changes for the few-variable model is carried out in order to seek those in a more realistic model. The fruitfulness of such an approach has been demonstrated in Ref. 7, when investigating a simple model of the stratospheric photochemical system over the Antarctic. That enabled revealing and description of some peculiarities in its actual behavior.

Dynamics of the oxygen-hydrogen system in the mesosphere has been considered in Ref. 8, where the kinetic equations, including the source of water vapor and sinks of the atomic and molecular hydrogen, have been examined when trying to reveal the presence of multiple steady states. The cause of their appearance may be an external action on the system that is being simulated by sources and sinks. Our investigation concerned with the effect of the non-linearity inherent in the system on its evolution.

As a few-variable model of the system under consideration, we have chosen the simplified system of reactions suggested in Ref. 9 for the stratospheric processes. This model considers, besides the purely oxygen reactions, some hypothetical combined reaction between the ozone and hydrogen as well. The authors[9] relate the ozone destruction in the stratosphere to blowing-through of the ozone layer with hydrogen resulting from the endogenous activity of the Earth. Qualitative analysis of such a simplified system of reactions allows one to elucidate if it really describes the ozone depletion and how close is the description of photochemical processes by this model to that in Ref. 8.

The model is defined by the following system of reactions:

$O_2 + h\nu \to O + O,$

$n_3 + h\nu \to O_2 + O,$

$O + O_2 + M \to O_3 + M,$

$O_3 + O \to 2O_2,$

$H_2 + O_3 + M - > H_2O + O_2 + M.$ $\qquad (1)$
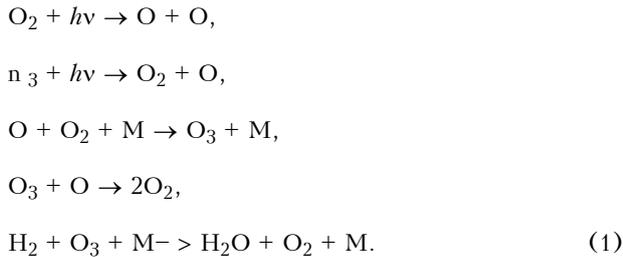
Let us denote the concentration of n_2, n, n_3, m_2, and m_2n as x, y, z, h, and w. This system must obey two laws of conservation that require conservation, in the chemical reactions, of the number of O and H atoms:

$2x + 3z + y + w = A,$

$2h + 2w = B.$ $\qquad (2)$

The system (1) has four isolated steady states, three of which coincide with those for the purely oxygen atmosphere and one is introduced by the reaction involving hydrogen. Besides, the system has a singular straight line comprising the steady states.

The space of states of the considered system is a five-dimension space. The conservation laws (2) define in it a three-dimension plane. Its intersection with non-negative vectors $C_i = 0$ (C_i are the concentrations) forms a three-dimension polyhedron of reactions (the ways of its construction are given in Ref. 10) that may already be visualized.

As it appears, the system evolution can follow three scenarios depending on the magnitudes of the initial concentrations ($A > B/2$, $A = B/2$, $A < B/2$).

Steady states have a character of complex singular points with stable or unstable sectors in definite planes except the point inside the reaction polyhedron, in the case with $A > B/2$, which is a stable node. Singular straight line within the three dimensional polyhedron coincides with one of its edge passing through its vertices ($x = 0$, $y = A$, $z = 0$, $h = B/2$, $w = 0$) and ($x = 0$, $y = A - B/2$, $z = 0$, $h = 0$, $w = B/2$). The reaction polyhedron and the steady states in the case of $A > B/2$ are shown in Fig. 1. In this situation there are two isolated steady states in the reaction polyhedron, the one within the polyhedron and the other its vertex ($x = 0$, $y = A$, $z = 0$, $h = B/2$, $w = 0$).

The inner state in the three dimensional polyhedron, as was mentioned above, behaves as a stable node, while the state at the vertex as a saddle. The singular straight line includes the above saddle point and manifests itself as a separatrix. In other words, if the concentration of oxygen particles exceeds the concentration of particles involving hydrogen, the steady state is characterized by non-zero concentrations of oxygen constituents and water vapor whereas the hydrogen appears to be exhausted. In the case of $A \le B/2$ the only isolated steady state, the node, is located at a vertex of the polyhedron ($x = 0$, $y = 0$,

$z = 0$, $h = B/2 - A$, $w = B/2$) whereas the rest states are out of the polyhedron. The latter states are non-physical because of their negative coordinates. The range of stability of the singular straight line in this case lies within the polyhedron and the phase trajectories terminate on this line. In other words, in the steady state the O_2 and O_3 concentrations are equal to zero and the concentrations of n, m_2, and m_2n depend on the initial conditions.
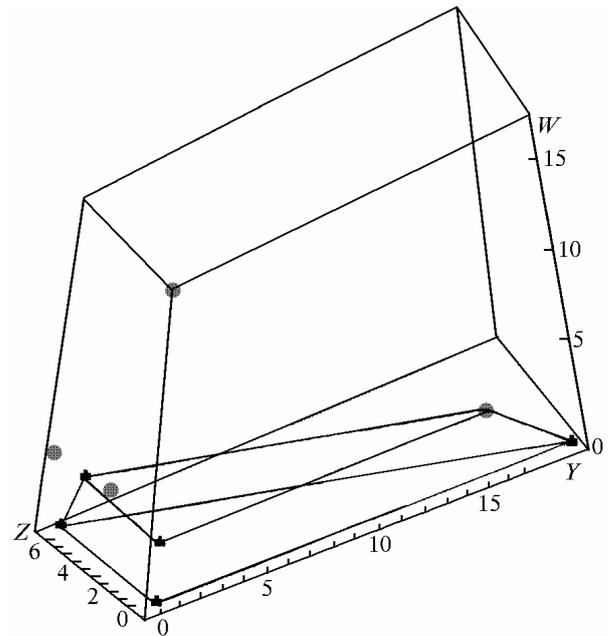
FIG. 1. The polyhedron of reactions describing the few-dimension oxygen-hydrogen system (1) with steady states, in the case of $A > B/2$.

The phase trajectories in the case of $A > B/2$, in the plane y, z, are shown in Fig. 2 for two characteristic values of the concentration w.

For the sake of presentation clarity the values of the rate constants and the constants determining the conservation laws have been taken close to unity when constructing the phase portraits shown in Fig. 2. As known, the topological peculiarities of the phase portraits are independent of the numerical values of constants within a wide range. However, given realistic values of the rate constants and concentrations, these peculiarities may appear to be indistinguishable because of the significant differences of the scales. For example, at the values of constants chosen for the mesosphere in Ref. 8 the same phase portrait takes the form shown in Fig. 3 ($w = 0.1$). The correspondence between the phase portraits presenting the illustrative and real situations may be followed up quite easily.

Comparison of the few-variable model (1) for which the complete and pictorial qualitative analysis is possible with the comprehensive model[8] can be performed by checking the presence of the specific
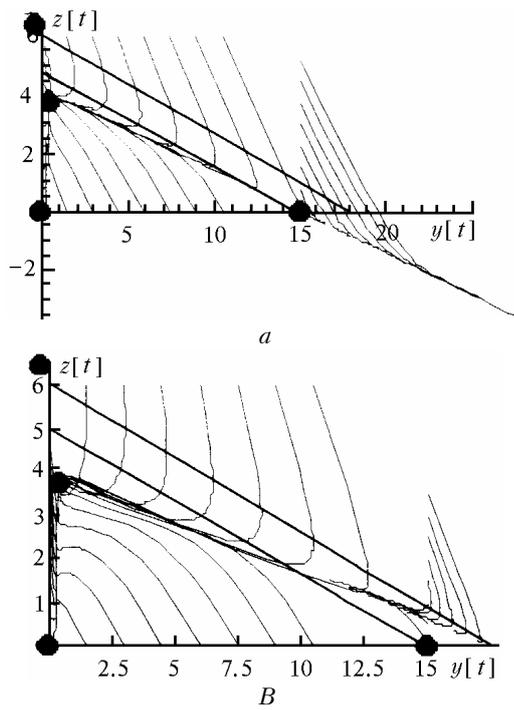
FIG. 2. Phase portraits of the few-dimension model (1), in the plane y, z for two characteristic values of concentrations w (A > B/2): w = 0 (a) and w = 3 (b).

features, predicted within the framework of the few-variable model, in the more complex model.[8] The one-to-one comparison of the models is impossible since there are sources and sinks in the model from Ref. 8 whereas the model (1) considers the conservation laws. Besides, there is only one reaction in the model (1) involving the hydrogen constituents and therefore the behavior of the hydrogen-containing constituents cannot be compared to those in the model from Ref. 8. However, the comparison of the behavior of the oxygen constituents is possible and is of interest from the view point of constructing the basic model of the oxygen-hydrogen atmosphere.
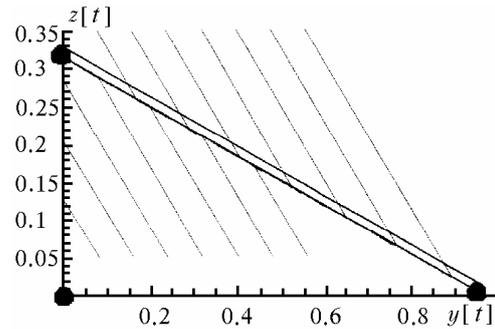
FIG. 3. Phase portrait of the reaction system (1) in the plane y, z with the rate constants from Ref. 8 under mesospheric conditions for concentration w = 0.1 (concentrations are normalized to A).

Figure 4 presents the O and O_3 concentrations as functions of time and the phase trajectories z(y) for the simplified and realistic models in the case of A > B/2. It can be seen that the tendencies of their changes are similar in both models.
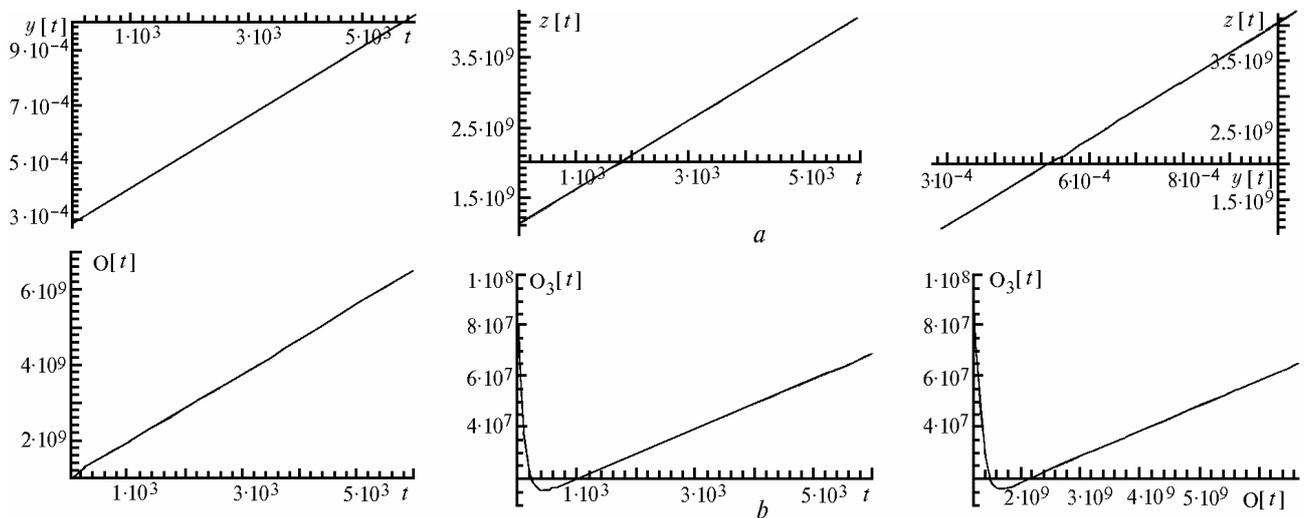
FIG. 4. Concentrations of O and O_3 as functions of time and the phase trajectories z(y) for the few-dimension (1) and realistic[8] models in the case of A > B/2: model (1), w = 10^9, B = 2 · 10^9 (a) and model,[8] h = 10^8, w = 10^9 (b).

Thus, it is shown, by the example of the oxygen-hydrogen atmosphere, that the qualitative peculiarities of realistic models may retain in few-variable models. This gives grounds for constructing a few-variable basic model of the oxygen-hydrogen atmosphere. We suppose to continue the study of all reactions involving hydrogen constituents in order to determine their contribution into the appearance of multiple steady states and their stability. Analysis of the relaxation times is also planned to be done to choose the most

important reactions. It is just the solution of these problems that will give a chance to formulate the basic model of the oxygen-hydrogen atmosphere which is sufficiently simple and at the same time retains the qualitative peculiarities of more realistic models. The basic model of that sort will allow one to establish long-term trends in the behavior of concentrations of the oxygen constituents and to forecast the possible catastrophic changes.

ACKNOWLEDGMENT

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