

PROGRAM SHELL FOR SOLVING PROBLEMS IN ATMOSPHERIC CHEMISTRY

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Received April 1, 1997*

Program shell for qualitative analysis of the kinetic equations of atmospheric chemistry is described. Statistical models of the atmosphere along with a list of elementary chemical reactions serve as initial data to run the shell. For the selected model of the atmosphere and the set of reactions, the system of kinetics equations is outputted in the interactive mode. Using the Mathematica application package, this system is analyzed qualitatively.

INTRODUCTION

At present a central problem of chemical kinetics of atmospheric gases is to describe the behavior of concentrations of minor gas components in different atmospheric layers, first of all, ozone in the stratosphere. Researchers in this field have put a lot of effort into solving fundamental global and regional meteorological and ecological problems through the construction of models for chemical processes to solve climatic problems and the refinement of chemical reaction cycles including those that control over the exchange processes with the underlying surface (the land or the ocean). A means for solving these problems is qualitative analysis of the systems of kinetic equations of atmospheric chemistry that describe all possible scenarios for the evolution of atmospheric gas composition.

The software support in atmospheric chemistry is developed in the NASA, National Center of Atmospheric Research of USA, and in England as part of the National University Program on Global Atmospheric Modeling.

However, the fact that the chemical code is subordinate to a dynamic consideration of problems on global climatic change makes one to simplify radically the kinetic models in atmospheric chemistry. Most simplifications call for fundamental substantiation.

There are also a number of program products for solving chemical kinetics problems, among them commercial products MAPLE, DASAL, and CRAMS (see Ref. 1) that can be used to formulate the systems of kinetic equations for chemical reaction cycles and to analyze these systems qualitatively. Among freeware programs on chemical kinetics, the Program of the Polytechnic Institute of New York (see Ref. 2) should be mentioned along with the Program ASAD on atmospheric chemistry (produced by UGAMP, see Ref. 3) oriented to formulate the systems of kinetic equations based on families of reactions.

In the present paper, the behavior of the minor atmospheric gas components is analyzed by selecting chemical-reactions versus the altitude range. In so doing, either elementary reactions can be selected that form chemical conversion cycles for the examined substances or families of reactions. Here, we implemented the approach based on the selection of elementary reactions, neglected the spatial transport of substances, and analyzed individual atmospheric layers (considered as a homogeneous closed system) at a fixed temperature. A series of works (see Ref. 4 and the references therein) on qualitative analysis of low-order systems, mainly, oxygen atmospheres, made for the development of the program shell.

Next steps are connected with techniques for solving the problems of chemical kinetics and can be implemented algorithmically. They are first of all formulation of the conservation laws, selection of independent variables, and construction of the system of kinetic equations for these variables. To solve these problems, a block of the program shell was developed to operate with data bases on atmospheric chemical reactions and atmospheric models.

The second software block comprises the problem formulation in the interactive mode of operation to solve analytically or numerically the formulated system of kinetic equations.

The user can analyze qualitatively kinetics of atmospheric chemical processes with the help of the application package Mathematica, namely, to find stable states, to make a phase portrait of two- or three-dimensional systems, two- or three-dimensional projections for higher-order systems and to investigate the vicinity of the selected stationary point.

The software comprises a hypertext reference manual with instructions for operation with the shell, brief description of principles of atmospheric chemistry and qualitative analysis, and comments to the data bases.

In the first section of our paper algorithms for formulation of kinetic equations are discussed. Data structure and program shell are described in the second section. Some potentialities of the shell are illustrated in the third section by the example of a simple model of oxygen atmosphere.

A protocol of program shell operation is presented, a phase portrait of the vicinity of a stationary point is shown along with a plot of separatrix in projections of atomic oxygen and ozone concentrations and projections onto different planes of the system phase portrait for large deviations from the equilibrium.

1. KINETIC EQUATIONS IN ATMOSPHERIC CHEMISTRY

Chemical processes occurring at different altitudes and latitudes in the Earth's atmosphere are subjects of atmospheric chemistry. Physical regularities, geological structure, climatic conditions, and anthropogenic effect on ecosystem cause a wide variety of substances that take part in these processes and hence a great number of reactions the substances enter.

To analyze the chemical processes occurring in the atmosphere, a set of reactions typical of the examined conditions should be formulated.

The formulation of the set of reactions makes it possible to construct a system of kinetic equations and conservation laws.^{2,5} To write the kinetic equations, stoichiometric matrices for reactants (M^r) and products (M^p) should be constructed along with the column S defining a complete set of substances that take part in chemical reactions



The order of the stoichiometric matrices is $n \times m$, where n is the number of substances and m is the number of reactions taken into account. Here, k is the column of reaction rate constants. The system of kinetic equations for concentrations of substances can be written with the help of stoichiometric matrices in the form

$$\frac{ds_j}{dt} = \sum_{i=1}^n (m_{ij}^p - m_{ij}^r) k_i \prod_{h=1}^m S_h^{m_{ih}^r} \quad (2)$$

Here, S_h is the concentration of the h th substance from the column S and m_{ij} are the elements of stoichiometric matrices.

To formulate the conservation laws, molecular matrix M should be constructed to connect the column substances S with the chemical elements E they comprise.⁵ The number of rows in this matrix is equal to the number of substances and the number of columns – to the number of elements. The element m_{ij} ($m_{ij} \geq 0$) of the molecular matrix indicates the weight of the j th element comprising the i th substance. In

general, the conservation laws for chemical elements (integrals of motions) are defined by relations

$$M^T S = C_e, \quad (3)$$

where e is the number of chemical elements. The number of the conservation laws is equal to the number of chemical elements. In addition to Eq. (3), the conservation laws

$$XS = C, \quad (4)$$

appear when the number of independent reactions is less than their maximum number, that is, when the rank of stoichiometric matrix is less than the maximum rank. These additional conservation laws are determined by reaction kinetics. They can be formulated based on the equation

$$\Gamma_S X = 0 \quad (5)$$

under conditions of orthogonality of X and rows of the matrix M

$$XM = 0. \quad (6)$$

A feature of problems in atmospheric chemistry is that only three reaction types are largely considered, namely, bimolecular, trimolecular, and photolytic. For this reason, the initial system of kinetic equations comprises terms of the order no higher than cubic

$$\frac{ds_i}{dt} = \sum_{j=1}^n \left(a_j^i + \sum_{k=1}^n \left(b_{jk}^i + \sum_{p=1}^n \Gamma_{jkp}^i s_p \right) s_k \right) s_j. \quad (7)$$

Tensors a , b , and Γ can be easily found from Eqs. (2). Elimination of variables with the help of the conservation laws that relate linearly the concentrations of substances does not increase the nonlinearity order of the system of kinetic equations, but decreases the number of equations by the number of eliminated chemical elements. We note that arbitrary selection of variables being eliminated allows us to eliminate slowly varying concentrations, for example, O_2 and N_2 . The reaction rate constants are determined from tables of chemical reactions.

2. PROGRAM SHELL STRUCTURE

The program shell comprises the data, interactive data processing algorithms, output of the system of kinetic equations, and problem formulation for its subsequent qualitative analysis.

The data required to run the program shell are statistical models of the atmosphere⁶⁻⁸ comprising information about vertical and latitudinal distributions of the temperature and concentrations of typical atmospheric gases as well as a table of chemical reactions of atmospheric gases, including reaction rate

constants. It should be noted, that in Refs. 3 and 10 the temperature dependence of the rate constants of bimolecular reactions is defined as follows:

$$k_{\text{bimol}} = A (T/300)^n \exp(-W/T)$$

In reference manual,¹¹ it is specified by the formula

$$k_{\text{bimol}} = A_1 \exp(-E_{\text{act}}/RT)$$

$$k_{\text{trimol}}^0 = k_0^{300} (T/300)^l,$$

For trimolecular reactions,¹¹ we have where A , A_1 , k_0^{300} , and W are the tabular constants, E_{act} is the activation energy, and R is the gas constant. Different definitions of the reaction rates led to two versions of the reaction table in the shell. Analytical dependences are lacking for photolytic reactions; therefore the rate constants of photolytic reactions are tabulated as functions of the altitude and solar zenith angles.⁹

The algorithm includes the following procedures:

- selection of the statistical model of the atmosphere (for numerical calculations) and the list of chemical reactions;

- selection of the set of reactions describing the examined chemical processes (construction of the matrix of stoichiometric coefficients);

- formulation of the conservation laws for closed systems and the list of variables being eliminated (construction of the molecular matrix);

- compilation of the list of variables being eliminated for open systems;

- assignment of the altitude range (when doing numerical calculations);

- derivation of the kinetic equations;

- definition of job on qualitative analysis with the application package Mathematica 2.0;

- job processing with the application package Mathematica.

The utility of the shell supports operation with user's files and setting of external models of the atmosphere and tables of chemical reactions.

The program shell includes the following elements of qualitative analysis of the system of equations (7): finding of stationary concentrations, testing of the stability of stationary states, arrangement in the hierarchy of relaxation times to the equilibrium, making the phase portrait or its 2D- or 3D-projections, making the phase portrait in the vicinity of stationary points, and analyzing temporal dependences of concentrations of substances when the system deviates from its stable state. Numerical calculations are done with the operators NSolve, FindRoot and NDSolve of the application package Mathematica. We succeeded in derivation of analytic

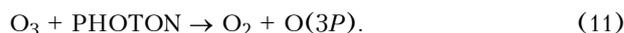
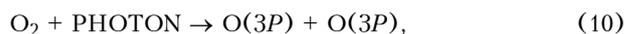
solutions for stationary concentrations and relaxation times for some low-order models.

External view of the program shell is displayed in Fig. 1.

At the left of the interface, the basic table of elementary reactions is shown and at the right of the interface – the table with the set of examined reactions. Reactions of different types are tabulated in different tables. The atmospheric models are specified in menu Model. Derivation of equations and executed procedures are specified in the menu Kinetics, whereas the parameters that specify the precision of calculations and the initial conditions are set in the menu Format.

3. EXAMPLE. KINETICS OF THE OXYGEN ATMOSPHERE

By way of example illustrating the system operation, let us analyze four reactions of the Chapman cycle



The system of kinetic equations for concentrations of substances has the form

$$\frac{d\text{O}(3P)}{dt} = +2j_2\text{O}_2 + j_3\text{O}_3 - k_1\text{O}(3P)\text{O}_3 - k_4\text{O}(3P)\text{O}_2\text{N}_2; \quad (12)$$

$$\frac{d\text{O}_2}{dt} = -j_2\text{O}_2 + j_3\text{O}_3 + 2k_1\text{O}(3P)\text{O}_3 - k_4\text{O}_2\text{O}(3P)\text{N}_2; \quad (13)$$

$$\frac{d\text{O}_3}{dt} = -j_3\text{O}_3 - k_1\text{O}(3P)\text{O}_3 + k_4\text{O}_2\text{O}(3P)\text{N}_2, \quad (14)$$

where k_1 , k_2 , j_2 , and j_3 are the reaction rate constants.

In the protocol of program execution, an example is given of the output of stationary states, conservation law, and relaxation times (see Appendix). The examined set of reactions obeys one conservation law and has one stable state with concentrations of:

atomic oxygen of $1.445 \cdot 10^8$,
molecular oxygen of $7.349 \cdot 10^{16}$, and
ozone of $9.917 \cdot 10^{12}$.

The conservation law is described by the relation

$$\text{O}(3P) + 2\text{O}_2 + 2\text{O}_3 = \text{const}, \quad (15)$$

which specifies the plane of reaction triangle. The relaxation times have characteristics hierarchical scales from several seconds to several weeks.

Atmospheric chemistry

File Model Data Reactions Kinetics Format ?

Oxygen reactions

Number of reactions-206

Copy Number of bimolecular reactions-7 m->N2,O2

Reaction
O(3P) + OH -> O2 + H
O(1D) + N2O -> N2 + O2
O(1D) + O2 -> O(3P) + O2
O(1D) + O3 -> O2 + O(3P) + O(3P)
O(1D) + O3 -> O2 + O2
O3 + HONO -> O2 + HONO2
OCIO + O3 -> ClO3 + O2
OH + ClO -> HCl + O2
OH + HO2 -> H2O + O2
OH + O3 -> HO2 + O2

n	Reaction
348	O(1D) + O2 -> O(3P) + O2
349	O(1D) + O3 -> O2 + O(3P) + O(3P)
350	O(1D) + O3 -> O2 + O2
92	O2 + PHOTON -> O(3P) + O(3P)
93	O3 + PHOTON -> O2 + O(3P)
94	O3 + PHOTON -> O2 + O(1D)
102	O2 + PHOTON -> O(3P) + O(1D)

FIG. 1

Qualitative analysis of the system of kinetic equations gives us the information whether or not the hierarchy of the atmospheric component concentrations remains unchanged at different altitudes and how the concentrations of the atmospheric gases behave and the temporal scales of their variations. In this case, structurally two main points can be distinguished:

- small deviations from the stationary state that differ by several tens of percent; these deviations are most often caused by natural factors;

- large deviations caused by various catastrophic factors, primarily anthropogenic.

Figure 2 shows the phase portrait of the system behavior for small deviations from the stationary state. The first temporal scale is associated with fast variations of the atomic oxygen concentration (vertical straight lines in the figure). The second temporal scale is associated with relaxation of ozone and atomic oxygen concentrations to their equilibrium values. In the phase portrait, this corresponds to the motion along the separatrix AB .

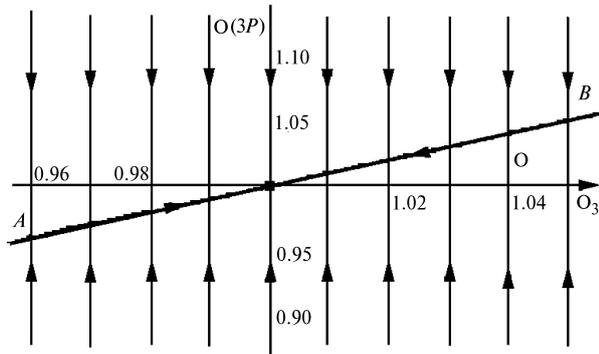


FIG. 2. Phase portrait of the system behavior for small deviations from the equilibrium (by 5% for ozone and 10% for atomic oxygen). Coordinate axes O_3 and $O(3P)$ are scaled by the corresponding stationary concentrations. The coordinates of the stable state are $(1, 1)$.

Figure 3 shows the separatrix for large system deviations from the equilibrium in the plane of atomic oxygen and ozone concentrations in logarithmic scale. The characteristic times taken to obtain specified values of concentrations are also indicated in the figure. In analogy with the case of small deviations, the point with the given ozone and atomic oxygen concentrations approaches the separatrix in a very short time and then moves along it for a long time.

Figure 4 shows projections of the phase portrait in the plane of reaction triangle onto the plane of concentrations of oxygen components ($O(3P)$, O_3), ($O(3P)$, O_2), and (O_3 , O_2). As can be seen from Fig. 4, for large deviations from stationary concentrations the state of the chemical system approaches the separatrix. The time required to reach the separatrix is of the order of several seconds.

Figures 2–4 illustrate the stability of the oxygen atmosphere model described by the set of reactions (8)–(11) for small and large deviations.

Enlarging the set of reactions may lead to a wider spectrum of possible scenarios for the behavior of kinetic systems which can be studied with the help of the suggested information-computation system.

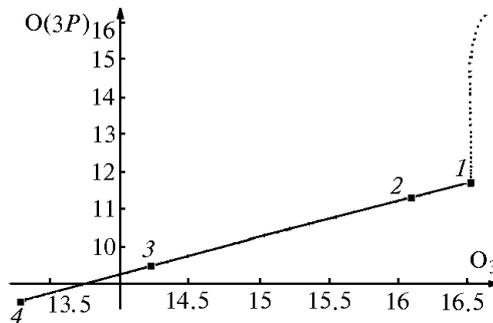


FIG. 3. Position of the separatrix for large deviations of $O(3P)$ and O_3 from the equilibrium. The time required to reach point 1 is ten minutes, point 2 – two months, point 3 – 15 years, and point 4 – 1500 years.

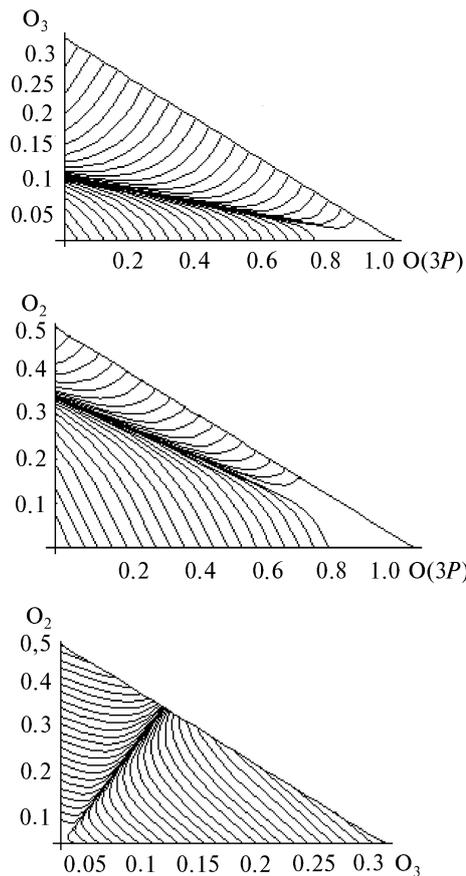


FIG. 4. Phase portraits of the oxygen atmosphere (reactions (8)–(11)). Two-dimensional projections. The coordinate axes are scaled on the integral of motion. The stationary state has the coordinates ($O(3P) \sim 10^{-9}$, $O_2 \sim 0.5$, $O_3 \sim 10^{-4}$).

CONCLUSION

In the present paper, we have touched only on the main points of implementation of the information-computation system for qualitative analysis of problems in atmospheric chemistry. The precision of computations and graphics software are beyond the scope of this paper, because they are largely determined by the potentialities of the application package Mathematica. The system will be extended to solve the problem on the spatial distribution of the minor gas components in the atmosphere.

ACKNOWLEDGMENT

The authors are grateful to the Russian Foundation for Basic Researches for the support (Grant 95-05-66201).

APPENDIX

Protocol of execution of the program shell Atmospheric Chemistry

General information

Number of analyzed reactions 4

Bimolecular reactions 3

$O_2 + PHOTON \rightarrow O(3P) + O(3P)$

$O_3 + PHOTON \rightarrow O_2 + O(3P)$

$O(3P) + O_3 \rightarrow O_2 + O_2$

Trimolecular reactions 1

$O(3P) + O_2 + N_2 \rightarrow O_3 + N_2$

Heterogeneous reactions—#h

Variable compounds 3

$O(3P)$, O_2 , O_3 .

Steady compounds 1

N_2

Atmospheric model USA—Polar Latitudes—Summer
Altitude—31

Kinetic Equations

$dO(3P)/dt = + j92 * O_2 + j92 * O_2 + j93 * O_3 -$

$- bk295 * O(3P) * O_3 - tk73 * O(3P) * O_2 * N_2$

$dO_2/dt = - j92 * O_2 + j93 * O_3 + bk295 * O(3P) * O_3 +$

$+ bk295 * O_3 * O(3P) - tk73 * O_2 * O(3P) * N_2$

$dO_3/dt = - j93 * O_3 - bk295 * O_3 * O(3P) +$

$+ tk73 * O_2 * O(3P) * N_2$

Steady states and stability

Conservation law(s)

$2 O_2 + 3 O_3 + O(3P) = 1.47 \cdot 10^{17}$

Stationary States

$O_3P \quad O_2 \quad O_3$

$1.445 \cdot 10^8 \quad 7.349 \cdot 10^{16} \quad 9.917 \cdot 10^{12}$

Relaxation Times

{0.03524, $1.725 \cdot 10^{16}$ }

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