Computing in the "Atmospheric Chemistry" information-calculating system

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The "Atmospheric Chemistry" information-calculating system (ICS) is intended for analyzing the concentrated systems, whose dynamical behavior is described by kinetic equations. The basic parameters of the atmospheric chemical system analyzed in an ICS are the atmospheric model, surface albedo, and zenith angle. The problems solved include the calculation of rate coefficients of photochemical reactions at a given height in the atmosphere or with the given radiation flux, derivation of kinetic equations and integrals of motion based on the given set of reactions, determination of concentrations of time-dependent components, etc. For the Chapman cycle and oxygen—hydrogen atmosphere, test calculations were carried out, the results of which qualitatively coincide with the earlier calculations.[1,2]

Introduction

Internet representation of the information resources and programs aimed at making calculations in the atmospheric chemistry has appeared almost simultaneously with the advent of the worldwide web. Among the Internet sites and ftps there are a great number of files describing the atmospheric chemical processes and programs for solving some problems characteristic of this subject domain. Below, we present a brief overview of the existing information resources on the problems in atmospheric chemistry. Then we describe the resource we have created and compare the results calculated for two chemical systems obtained with the "Atmospheric Chemistry" ICS with the ways used to solve these problems in Refs. 1 and 2.

The problems of determining the dynamics of concentration of most important atmospheric components are quite typical in the atmospheric chemistry. The factors that influence the dynamics are not only chemical processes and solar radiation in the atmosphere, but also the dynamic processes causing air mass transfer, convection, etc. Many authors have attempted to solve these problems. There have been created such software products as ASAD: Chemical Modelling Software[3] to derive kinetic equations within reaction classes; Chemistry Tool Kit[4] to organize and map data; the SLIMCAT[5] program package describing a 3D transfer model, whose parameters can be the 3D global climatic model data; TOMCAT,[6] which is a 3D chemical component transfer model connected with the ECMWF data. The latter model integrates the tropospheric chemistry scheme, which involves about 50 contaminants. A more detailed description of the software resources and data can be found in the "Atmospheric Chemistry" ICS in the links to the resources.[7]

The above software and information resources are, as a rule, organized as file sets or program codes, which a user must install at his/her computer. Within the ICS, there is a different approach to the arrangement the user's work with the information resources and the software. The necessity of creating the Internet-accessible information-calculating systems is caused by the development of modern infrastructure in science. The way the computers and information technologies support and strengthen scientific potential has received several names (Grid, e-Science, etc.[8]). Technically, the work we are presenting here should be considered within these approaches.

The "Atmospheric Chemistry" ICS has been modified several times at different stages of its development.[9–14] Initially, the ICS was client oriented. It was a separate executable file written in Visual Basic. The data for the system was stored in the Microsoft Excel table format. Based on the user-defined reactions, a system of kinetic equations was derived in the shell, and after that a user could specify requirements for this system's solution. The final result was the program[9] for the Mathematica 3.0 interpreter. Within this software, a user could analyze the kinetic equations. It should be noted that a similar approach was implemented in Ref. 15.

A later ICS version was server-based[10,11] and included a module for statement and solution of the problems of atmospheric chemical component dynamics. It used the DBMS Interbase for OS Linux to store the data. User web-interface for data storage was based on a dialog operating system, which involved the use of the CGI and SSI technologies. Organization of data in this second version had some disadvantages. One of them was insufficient data structuredness. For example, the substances that were involved in reactions were stored as symbols and had no underlying chemical structure. This complicated

the analysis of chemical composition of a substance, and the latter was essential in building up stochiometric matrices in deriving the kinetic equations. There were no instruments for working either with ions or isotopes. Besides, it was impossible for a user to enter his/her own reactions and their related data, which narrowed the user's productivity in the reaction choice module.

The above drawbacks were eliminated in the new site version, which we have constructed under the INTAS project on creating a portal for the atmospheric sciences.[12–14,16] The "Atmospheric Chemistry" information-calculating system is an interactive system for analyzing the atmospheric chemical processes in a box model. Within the frames of this model, a user can formulate a problem and quantitatively analyze it.

The following modules are the main ICS' parts:

1. The reaction choice module.

2. The module for specifying physical parameters (altitude, albedo, etc.).

3. The module for deriving a system of kinetic equations.

4. The module for stating and solving the problems of dynamics of the atmospheric chemical components.

The resource takes aim at the users who are seeking quantitative information on kinetics of the atmospheric chemical processes. The static part of this information resource is accessible to all Internet users. The dynamic part, which a user creates to solve the problems once stated, is accessible for that user only. With this site, to make problem solving possible, a user must first get registered with the ATMOS portal (http://atmos.iao.ru). The registration procedure aims at relating certain ICS resources to a particular identified user. When registered, a user can introduce his own resources: input molecules, isotopes, and ions new for the system, compose reactions among them, enter reaction rate coefficients, statistical atmospheric models, etc.

1. Problem statement in the "Atmospheric Chemistry" ICS

1.1. Data handling

Simulation of the atmospheric chemical processes requires a proper organization of the data on substances, data on reactions these substances take part in, and data on the medium where the substance transformations occur. A detailed description of the database can be found in the monograph.[1]

Data handling involves two steps. The first step is formation of a reaction by the user if the required reaction is unavailable with the ICS or if the reaction is available, but the rate coefficient needs to be changed. The second step is choosing the reactions for further analysis by the kinetic theory. A detailed description of these steps can be found in the "Help" section of the ICS.

Data work involves the following operations to the chemical entities.

1. Input and removal of atoms, ions, and isotopes.

2. Composition of molecules from atoms and deleting molecules.

3. Formation of the structure of physicochemical properties of substances.

4. Formation of the cycles of atmospheric chemical reactions.

5. Input/removal of, and modifications to reactions and cycles.

The user selects the reactions from the database of chemical reactions (currently available is the data on atmospheric chemical reactions,[17] the stratospheric reactions data,[18,19] and reaction data presented by Seinfield and Pandis[20]). The choice can be based on reaction type (bimolecular, trimolecular, photolysis reactions) or on substance (to be searched through all the reactions available in the database). Reactions of any type can be arranged in cycles. There is a separate table that stores links to cycled reactions.

1.2. Specifying physical parameters

To determine the environment for user chosen reactions, we have created the interface that allows simulation of two scenarios: development of the reaction process a) at a specified altitude and b) under user defined conditions, that is, with settings of temperature and spectral dependence of radiation intensity affecting the chemical system.

The spectral dependence of the radiation intensity is determined by the simulation details. For laser radiation sources it will be enough to set a laser type and its spectral characteristics. In simulating the atmospheric process with settings of the altitude for which the reaction rate coefficient is calculated, the radiation intensity is calculated within the Chou and Lee[21] approach using statistical atmospheric model data.[22]

1.3. Deriving kinetic equations

Behavior of the atmospheric chemical systems is quantitatively analyzed based on the kinetic equations generated in the ICS for a user's set of chemical reactions and/or reaction cycles. Generation of kinetic equations implies that a user specifies the type of a chemical system. For open systems, it is possible to include into a reaction set incomplete reactions (with known reagents, but unknown products) or sources and sinks. In the ICS, when the kinetic equations have been derived, the conservation laws can be found (if any), and the reaction rate coefficients calculated (calculation of the photolysis reaction rate is most difficult, because it needs the atmospheric conditions or the spectral dependence of the radiation intensity to be set). With the conservation laws available, the user can choose to exclude some variables from consideration by reducing the number of analyzed nonlinear differential equations. At the step of deriving the equations, the reaction rate coefficients are determined from the user's model settings.

2. Solving problems in the ICS

2.1. Solution of kinetic equations

Kinetic equations are studied and solved numerically. To solve differential equations, the Sundials program package[23] is applied that uses the Newton–Krylov method. The computation procedure implemented in it requires the absolute and relative computing accuracy to be specified. The input data for the package are kinetic equations, time interval for which the answer is needed, initial conditions, and the number of points characterizing the temporal evolution of the chemical components in the solution. The interface for data entering is, as a rule, implemented as a table with the forms for entering. The output data are the obtained solutions and the diagnostics of the Sundials program package. The latter gives the information on the overall number of steps, total number of function calls, the total number of the Sundials calls, number of Jackobian evaluations, number of nonlinear iterations, number of nonlinear divergences occurred, etc.

In this section, we apply the system's capacities to two sets of chemical reactions taken from literature. As is well known, the ozone formation cycle is an essential part of all atmospheric photochemical models. The main chemical processes leading to ozone formation and destruction were first studied by Chapman[24] in 1930 and included photochemical reactions between oxygen constituents.

A qualitative analysis of the equation system suggested by Chapman for the oxygen atmosphere was systematized by Gordov et. al.[1] They performed a complete classification of the states of a reaction system in the oxygen atmosphere, the latter assumed a nonlinear closed conservative system. This study reveals the following features inherent in a reaction system between the oxygen constituents. On the one hand, the system is highly nonlinear and shows such features of this system as multiple stationary states and their variation in number and stability, when the system experiences changes. On the other hand, these features, being so explicit for some of our reaction sets, seem to get lost if we consider all possible reactions. A special role in disappearance of the manifestations of nonlinearity belongs to recombination reactions of the atomic oxygen.

To demonstrate the system's functionality, we have chosen two problems as examples: a simplified Chapman cycle[1] and the oxygen–hydrogen system.[2]

2.2. Closed system. The system with a photodissociation reaction of molecular oxygen

This case involves three reactions (see below): photodissociation of molecular oxygen (1), generation of ozone in three-particle collisions (2), and ozone destruction in collisions with the oxygen atoms (3). An oxygen molecule is the third particle in the ozone generation reaction. Among the reaction sets in the

oxygen atmosphere, this set has the richest phase portrait structure. In the reaction triangle, there are four stationary states, two at the triangle vertices and two inside the triangle. Of these four, two states are stationary (Fig. 1a).

Depending on the initial conditions, the system develops to the either of these states. If we denote the concentrations of the oxygen components O_2, O, O_3 as x, y, and z, respectively, then the conservation law can be written in the form

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

and the system's phase portrait can be presented in the plane of the either set of two variables.

At an A value change, the situation within the reaction triangle changes as well; there remain two stationary states, from which the state with the zero ozone concentration is stable (Fig. 1b).

J_2, K_1, K_8, $A = 10$
the vertex $y = A$, $z = 0$ is a stable node;
the vertex $y = 0$, $z = A/3$ is a saddle;
inside the reaction triangle, there is a stable node and a saddle.

a

J_2, K_1, K_8, $A = 1$
the vertex $y = A$, $z = 0$ is a stable node;
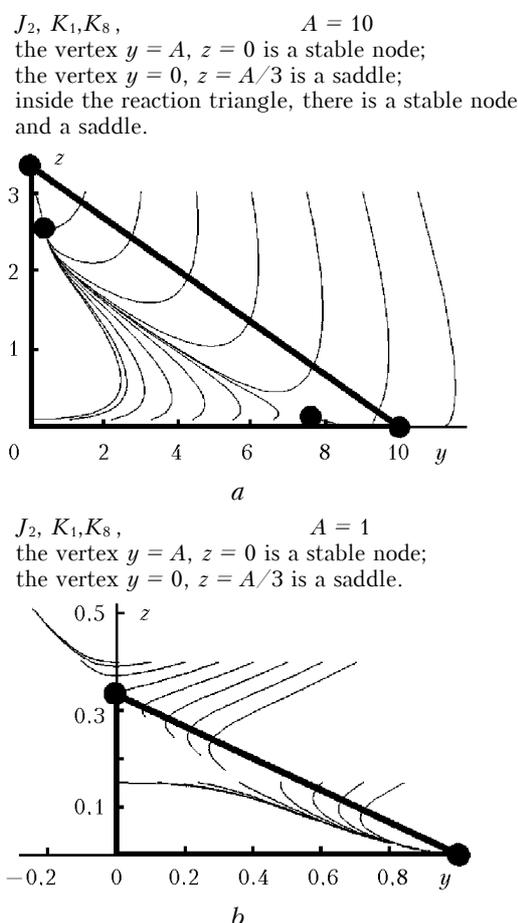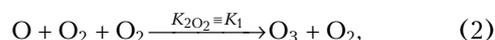the vertex $y = 0$, $z = A/3$ is a saddle.

b

Fig. 1. Phase portraits for the reaction systems (1)–(3).

Note that for clarity, the phase portraits in Fig. 1 are obtained with the scaling transformation ($y/10^{17}$, $z/10^{17}$). The bifurcation A value is located between the values for which the phase portraits are given:

$$O_2 + h\nu \xrightarrow{J_2} O + O, \tag{1}$$

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

$$O_3 + O \xrightarrow{K_3 \equiv K_8} 2O_2. \qquad (3)$$

Now let us find out how this information can be obtained in the "Atmospheric Chemistry" information system.

The particular feature of the case we are considering is the absence, in the ICS, of the photodissociation reaction for molecular oxygen in the form it appears in Eq. (1). The reaction was introduced into the ICS reaction database by a user as it is allowed by the system functions.

Below, there is a list of reactions and data sources, from which the information on reaction rates is taken:

Reaction	Source
$O_3 + O \rightarrow O_2 + O_2$	JPL NASA-14
$O_2 + O_2 + O \rightarrow O_3 + O_2$	IUPAC-2002
$O_2 + photon \rightarrow O + O$	User-defined

To compute the reaction rate coefficients, we have chosen the conditions from the model developed in the USA[22] and corresponding to the altitude of 1 km for a mid-latitude summer.

Stationary states with positive coordinates found outside the ICS are given in Table 1.

Table 1. Coordinates of the stationary states of reaction system (1)–(3)

State number	O_2	O	O_3
1	$7.25378 \cdot 10^{16}$	399.814	$4.41486 \cdot 10^{14}$
2	0.0	$1.464 \cdot 10^{17}$	0.0
3	0.0	0.0	$4.88 \cdot 10^{16}$
4	192.0	$1.464 \cdot 10^{17}$	$3.09193 \cdot 10^{-15}$

State 1 is located inside the reaction triangle and is a stable node. States 2 and 3 are located at the triangle vertices and, being a stable node and a saddle, correspond to the presence of only oxygen and only ozone, respectively. The state 4, being also a saddle, almost coincides with the state 2 forming a node-saddle. The picture of the stationary states is similar to that shown in Fig. 1a. Within the ICS, the coordinates of state 1 are determined as critical concentrations at a sufficiently long computation time. Coordinates of nonstationary states cannot be found in this way.

Specification of different sets of the initial conditions allows building up of the phase portraits in the neighborhood of the stationary states. The example given below shows a picture of phase paths characteristic of the most part of the reaction triangle, namely, the phase paths tending to stable node 1 located near the vertex $[O_3] = A/3$. However first, the paths approach the separatrix of the saddle 4 (Fig. 2a). Numerical study of the problem is reduced to solution of kinetic equations in the neighborhoods of the considered points. The settings of the initial concentrations for the analysis of the first stationary point are shown in Table 2.
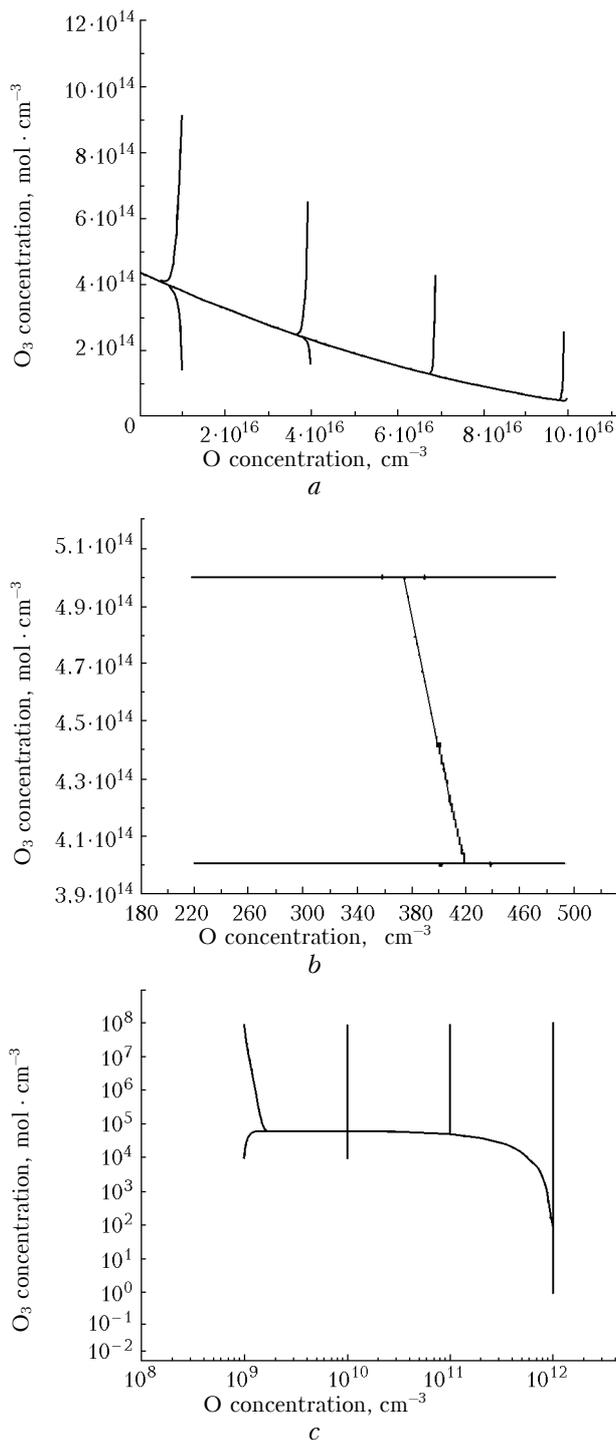

Fig. 2. Phase portraits of system (1)–(3) in different parts of the phase space; $A = 1.464 \cdot 10^{17}$ (*a*, *b*); paths tending to the stable node 1 along the separatrix of saddle 4 (see Table 1) shown at different scales; $A = 10^{12}$ (*c*); path tendency to the stable node at the reaction triangle vertex with only the atomic oxygen.

As is seen from Fig. 2b, at $A = 10^{12}$, phase paths starting at different parts of the reaction triangle tend to the vertex ($[O_3] = 0$, $[O] = A$), which in this case is the only stable stationary state (compare to Fig. 1b).

Table 2. The initial concentrations for the solution variants for the system (1)−(3) in Fig. 2

Variant No.	At 1 km altitude				At 30 km altitude (Fig. 2c)	
	(Fig. 2a)		(Fig. 2b)			
	O	O_3	O	O_3	O	O_3
1	10^{16}	10^{15}	200	$5 \cdot 10^{14}$	10^9	10^8
2	$4 \cdot 10^{16}$	10^{15}	300	$5 \cdot 10^{14}$	10^{10}	10^8
3	$7 \cdot 10^{16}$	10^{15}	400	$5 \cdot 10^{14}$	10^{11}	10^8
4	10^{17}	10^{15}	500	$5 \cdot 10^{14}$	10^{12}	10^8
5	10^{16}	10^{14}	200	$4 \cdot 10^{14}$	10^9	10^4
6	$4 \cdot 10^{16}$	10^{14}	300	$4 \cdot 10^{14}$	10^{10}	10^4
7	$7 \cdot 10^{16}$	10^{14}	400	$4 \cdot 10^{14}$	10^{11}	10^4
8	10^{17}	10^{14}	500	$4 \cdot 10^{14}$	10^{12}	10^4

2.3. Open systems. The oxygen-hydrogen system

The model suggested by Yang and Brasseur[2] describes the oxygen–hydrogen system typical of the mesosphere. It involves 14 chemical and photochemical reactions supplemented with the mesospheric water vapor source and the sinks of atomic hydrogen and molecular hydrogen and oxygen. Only two of these parameters (k_H and f) are assumed independent; the relation between them and other parameters is shown in Table 3.

Table 3. Parameters of sources and sinks that supplement the oxygen−hydrogen reaction system given in Table 4

Substance	Sink, s^{-1}	Source, $cm^{-3} \cdot s^{-1}$
[H]	k_H	
[H_2]	$k_{H_2} = C\, k_H$	
[H_2O]		$F = 2f$
[O_2]	$k_{O_2} = f/10^4$	

The space of the parameters (k_H, f) is divided into subspaces, in which the system has different number of stationary states, from zero to three. For $k_H = 10^{-6}$ s^{-1} and at the change of $\text{Log}\,f$ from zero to five, there is a region of three stationary states, that is, the specified value of f corresponds to three values of concentrations, for example in Ref. 2, Fig. 5.

To reproduce this situation within the "Atmospheric Chemistry" system, we have chosen the atmospheric conditions at the altitude of 75 kilometers.
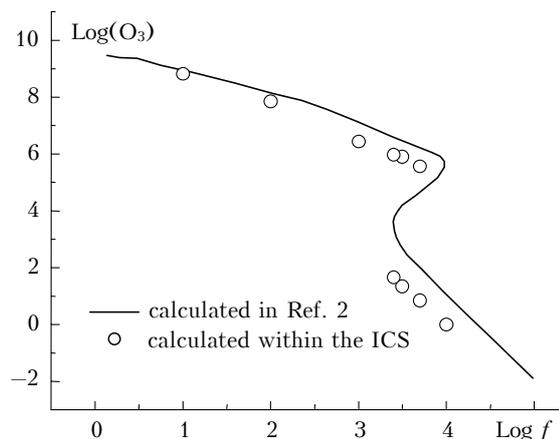
This choice brings us to the reaction rates shown in Table 4.

Then, having formed the initial conditions and the values for (k_H, f) specified, we determine the

stationary concentrations of the involved substances by the values of critical concentrations at a sufficiently large computation time, which gave out one point on the diagram of $\text{Log}\,O_3$ dependence on $\text{Log}\,f$ (Fig. 3).

Table 4. The rates of reactions of the oxygen−hydrogen system at the altitude of 75 km

Bimolecular reactions	Reaction rate coefficient
$O_3 + O \rightarrow O_2 + O_2$	$2.192 \cdot 10^{-16}$
$OH + O \rightarrow O_2 + H$	$4.057 \cdot 10^{-11}$
$HO_2 + O \rightarrow OH + O_2$	$8.319 \cdot 10^{-11}$
$O_3 + H \rightarrow OH + O_2$	$1.274 \cdot 10^{-11}$
$HO_2 + H \rightarrow H_2 + O_2$	$5.600 \cdot 10^{-12}$
$HO_2 + H \rightarrow OH + OH$	$7.200 \cdot 10^{-11}$
$OH + H_2 \rightarrow H_2O + H$	$2.047 \cdot 10^{-16}$
$HO_2 + OH \rightarrow O_2 + H_2O$	$1.718 \cdot 10^{-10}$
$HO_2 + H \rightarrow H_2O + O$	$2.192 \cdot 10^{-16}$
Trimolecular reactions	
$N_2 + O_2 + O \rightarrow N_2 + O_3$	$2.163 \cdot 10^{-34}$
$N_2 + O_2 + H \rightarrow HO_2 + N_2$	$2.887 \cdot 10^{-32}$
Photolysis reactions	
$O_3 + photon \rightarrow O_2 + O$	0.0949
$H_2O + photon \rightarrow OH + H$	0.0002
$O_2 + photon \rightarrow O + O$	$1.035 \cdot 10^{-8}$

Fig. 3. Comparison of the data calculated within the ICS with that by Yang and Brasseur.[2]

To obtain the points for the upper and lower curve branches, we used two variants of the initial conditions (Table 5).

Though the reaction rates in our computations and in the computations of Yang and Brasseur have some divergences, agreement between the results, especially the presence of a large number of stationary states, can be regarded as satisfactory.

Table 5. The initial concentration values used in calculation of the oxygen−hydrogen system behavior depending on the source and sink parameters

Variant No.	H	H_2	H_2O	HO_2	O	O_2	O_3	OH
1	10^7	10^8	10^9	10^6	10^9	10^{14}	10^8	10^6
2	$4 \cdot 10^{10}$	$2.8 \cdot 10^8$	$4.69 \cdot 10^{11}$	$3.56 \cdot 10^5$	$3.76 \cdot 10^4$	10^{14}	1	1.38

N.A. Lavrent'ev et al.

Vol. 18, No. 7 /July 2005/ Atmos. Oceanic Opt. 537

Conclusions

The work describes the "Atmospheric Chemistry" ICS, which allows one to analyze the component distribution behavior in a concentrated chemical system with the user set physical conditions.

The ICS has a number of auxiliary services that allow, for example, the database with reactions and the related substances to be enriched in the "Databases" section. The "Reactions" section provides a user with the information on atmospheric chemical reactions and allows him/her to compose arbitrary reaction sets for their further analysis. The "Medium" section allows atmospheric and other conditions external for the chemical system, such as temperature, spectral behavior of the radiation intensity, etc. to be specified in different ways. Kinetic equations for open or closed chemical systems can be derived in the "Kinetics" section. The same section also stores conservation laws (if any) and allows one to calculate the reaction rate coefficients. The "Analysis" section allows one to perform numerical solution of the generated kinetic equations. For solution of differential equations, we used the Sundials program package. Calculated results can be presented in both tabular and graphical forms.

Some of the technical toolkits that we used in the ICS creation are the following. For the database implementation, a freeware DBMS MySQL is chosen. The PHP script language is used to perform the SQL query calls for manipulations with the database, to construct dynamic pages of the user and administrative interfaces, to transfer, and to process the data. The Apache server is chosen to be the web-server. This set of toolkits is available on both Windows and Linux platforms, which ensures the system's functioning on a server with either of the operation systems.

Acknowledgments

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