KinSim: A Research-Grade, User-Friendly, Visual Kinetics Simulator for Chemical-Kinetics and Environmental-Chemistry Teaching

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ABSTRACT

KinSim is a research-grade, interactive, user-friendly, open-source, and visualized software for kinetic modeling of environmental chemistry and other applications. Students without any computer programming background and limited knowledge on environmental chemistry can use KinSim, which also includes multiple features and functionality dedicated to reducing users' workload and preventing users from creating errors in modeling, KinSim is particularly suitable for in-classroom and homework teaching applications. Students can choose from several pre-programmed mechanisms and initial conditions for important environmental chemistry problems, and only clicking a few buttons is needed to perform a simulation and obtain graphs with concentrations and chemical fluxes. The mechanism and initial conditions can be edited very easily to study other cases. Feedback from its use in courses shows the effectiveness of KinSim in facilitating students to conduct computer experiments to gain familiarity with environmental chemical systems and helping them gain deeper understanding of complex emergent behavior of the systems. KinSim's accuracy and speed are similar to those from other software packages used in research, and at least 15 published peer-reviewed papers have used it.

GRAPHICAL ABSTRACT

INTRODUCTION

Chemical kinetics, a core branch of physical chemistry, serves as an indispensable tool for the

30 research of the evolution of chemical systems, including our natural environment.[1] Environmental chemistry applies chemical kinetics, as well as other chemical theories and techniques, to tackle several global challenges such as environmental pollution,[2–5] public health,[2,4] and global change.[3,5] Education in environmental chemistry is thought to be necessary to increase students' awareness of these challenges and their engagement into facing these challenges.[6,7]

35 However, environmental chemistry education has its own difficulty: the composition of and processes in nature are inherently highly complex and far more challenging than typical problems taught in chemistry classes, which usually consider only a few species and 1–2 variable physical parameters at a time. For instance, chemical kinetics taught in physical chemistry classes often only includes elementary-reaction problems for integration or slightly more complex problems that can be

40 solved by steady-state or other approximations.[8] In contrast, one of the simplest and most well-known environmental chemistry problems, ozone depletion, cannot be understood with a mechanism containing fewer than 6 reactions.[9]

Studying/demonstrating these relatively complex problems usually needs a chemical kinetic solver that integrates a system of ordinary differential equations (ODEs) representing rate equations. Many

45 open-source solvers often provide little more than source code and limited graphical user interface (e.g., ODEINT).[10] Therefore, programming and translation of a mechanism into ODEs are usually necessary. However, the former is beyond many students' competences and the latter is laborious and can easily create errors. Commercial kinetic solvers often are expensive and still not fully adapted for environmental chemistry teaching, and thus require programming skills in some occasions (see an

50 example for FACSIMILE).[11] While it is possible for instructors to use options such as those above only for illustration of time-evolutions of environmental chemical systems in class, it is highly beneficial to

students' learning if they can directly experiment with environmental chemistry problems themselves by chemical kinetic modeling.

In this paper, we present an open-source chemical kinetic simulator, KinSim, whose development we led for both environmental chemistry research and teaching. It is a research-grade software that has been not only used in various environmental chemistry and chemical kinetics research projects[12–17] (resulting in >15 published peer-reviewed papers), but also used without the need for any programming in class thanks to a number of its student-friendly features/functionalities as shown below. In addition, the applications of KinSim can be easily extended to problems in areas such as indoor air chemistry,[18] chemistry of planetary atmospheres,[19] and combustion.[20]

DESCRIPTION

The version of KinSim presented in this paper is v4.0. It is run in Igor Pro,[21] a powerful but inexpensive analysis and graphic package (a free-trial version is fully functional for 30 days, which may be sufficient for many class applications; a multiple-computer coursework license costs US$125, an individual student license US$75). KinSim consists of several embedded windows, i.e., a control panel, a few tables for setting up the mechanism, the initial condition, and other parameters and inputs for the simulation, and a few graph windows for output plots (Figure 1). These embedded windows, along with related functionalities, are described in the following subsections.
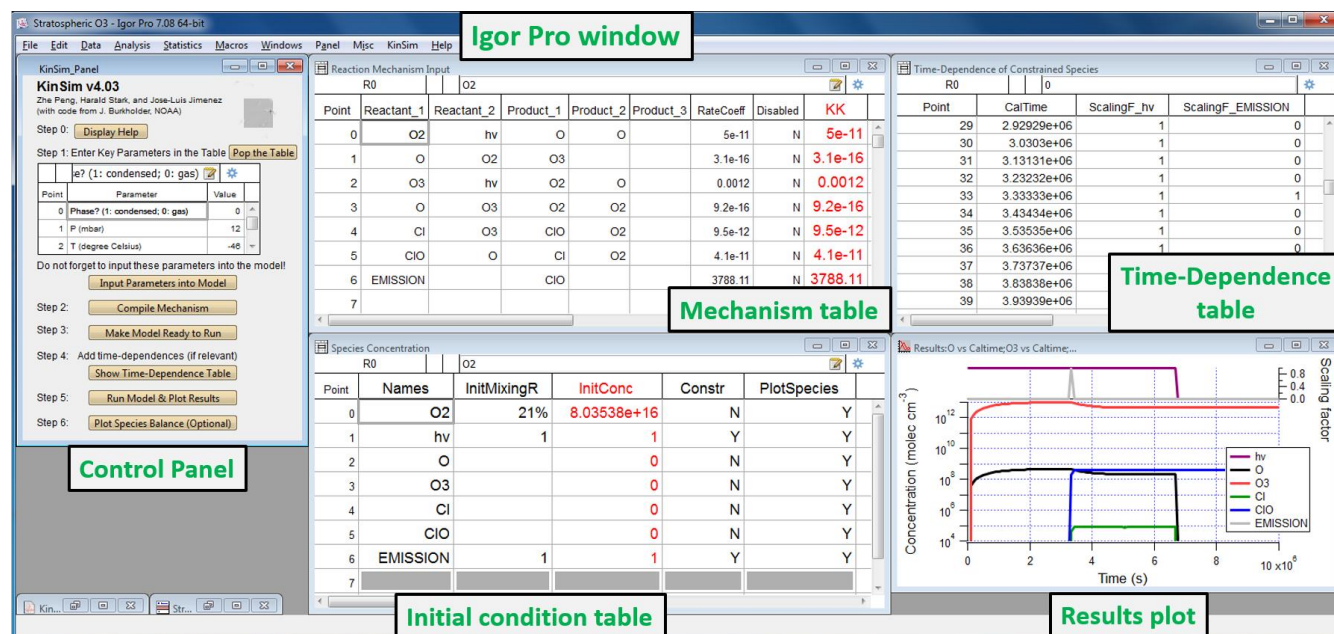
Figure 1. Screenshot of the layout of KinSim for the stratospheric ozone case study in this paper. The control panel (left), the tables for mechanism input (top middle), initial concentrations (bottom middle), and time-dependence setup (top right), and an output plot (bottom right) are included. Different parts of this layout are denoted by text in green.
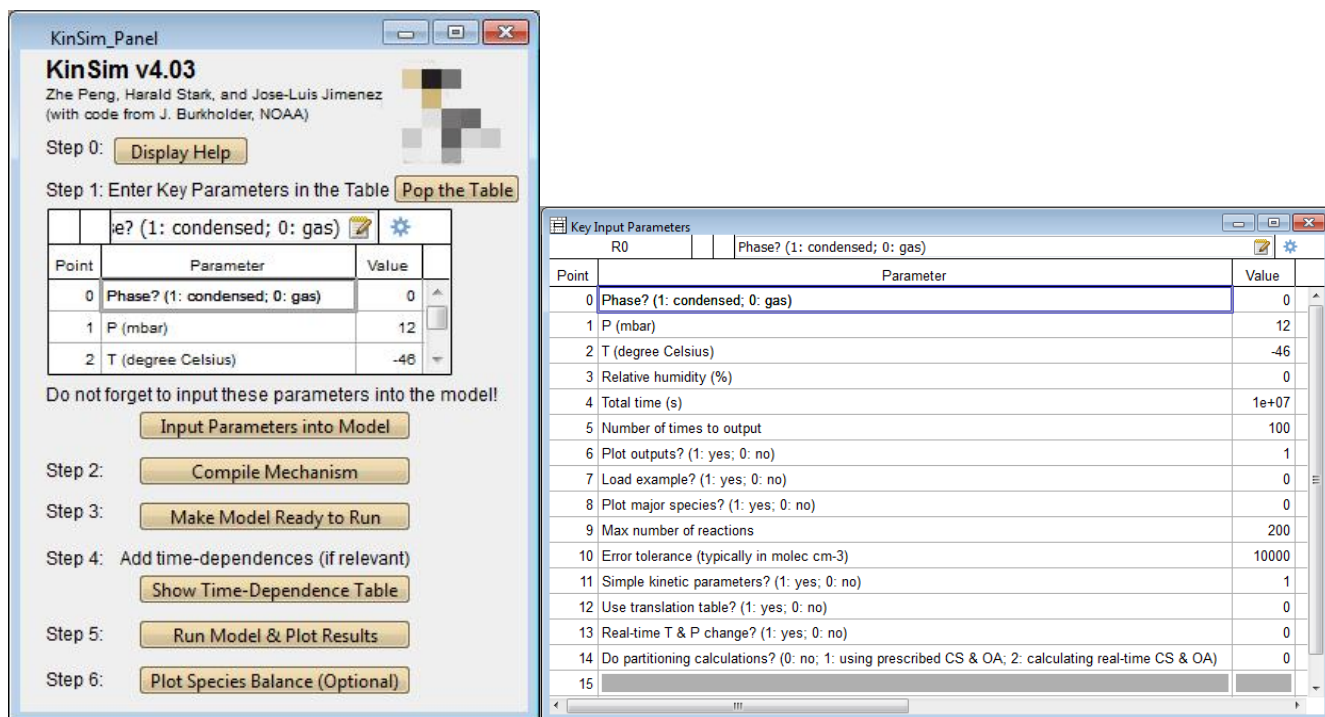

Figure 2. Screenshots of the control panel and the popped parameter-setting table for the stratospheric ozone case study.

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Control Panel

The control panel (Figure 2) is the part of KinSim that users interact with to run their simulations. Every button on the panel corresponds to a key functionality. An online manual, which is regularly updated and contains a link to download the latest version of KinSim, can be displayed on Step 0.

80   Steps 1–5 are essential for running simulations, while Step 6 is optional. To run a simulation, it is only needed to click the buttons in order. The software can determine which buttons are appropriate to be clicked based on the current status of model setup and disable those that should not be executed. This presents a clear guideline of what the next step is and prevents inexperienced students from inadvertently damaging the model setup. Both aspects are particularly important in ensuring a

85   smooth practice of kinetic modeling in class, when the students are doing their own simulations on their laptop computers and where time constraints and any confusing aspects can interfere with the pedagogical objectives.

Users can set the simulation parameters in the embedded table on the panel (Figure 2), or click "Pop the Table" button and set them in a larger table. Besides common parameters for chemical

90 kinetics modeling, e.g., pressure, temperature, and simulation time, some functionalities can be activated to facilitate students' use of the simulator. For instance, "Load examples" (Parameter No. 6) can be turned on to have a simple example for Steps 2–4; "Simple kinetic parameters" can be activated to directly use only first or second order rate coefficients (without temperature dependence). That greatly facilitates in-class simulations, while the more accurate but complex Jet Propulsion

95 Laboratory[22] and IUPAC[23] formats of kinetic parameters (commonly used in gas-phase chemical kinetics) can be used if desired (see "Mechanism" subsection). The main phase of the simulated system can also be set to gas or condensed, with molecules cm^{-3} and mol L^{-1} as basic concentration units, respectively (see "Initial Concentrations" subsection).

Mechanism

100 For many simple applications, only the reactants, products, and rate coefficient of each applicable reaction need to be entered in the "Reaction Mechanism Input" table. When the button for Step 2 (mechanism compilation) is clicked, the subroutines calculating the derivative terms for the ODEs corresponding to the mechanism are automatically generated, to be used during numerical integration (Step 5, see "Outputs" subsection).

105 A few special processes (photolysis and emission of specific species, and dilution of the whole reactant and product mixture) can be entered in the mechanism table in very simple ways, and they are transparently handled by the simulator without requiring any programming skills from the user. Individual chemical reactions can be disabled in the reaction table. When a reaction is disabled, that reaction will not be taken into account in the integration, but no change to the reaction list is needed.

110 This feature is particularly useful in class or for homework when the effects of certain reaction(s) in the system need to be studied. For example, students can be polled in class about the effect of disabling or enabling a reaction, and then a simulation can be quickly run to illustrate the results of these actions. This type of experiment challenges the students to understand the dynamics at play in a given system (see Example Case Study 3 in SI). Various reactions or groups of reactions can be

115 enabled and disabled easily without the risk of damaging the simulation setup.

Initial Concentrations

In gas-phase systems, the basic concentration unit is molecules cm^{-3} (omitted in inputs for simplicity). Other convenient mixing ratio units are also allowed, e.g., parts-per-million, billion, or trillion by volume (ppm, ppb, and ppt, respectively) for gas-phase species and µg m^{-3} ("ug/m3" in the inputs) for particle-phase species. In the presence of the species named "H2O" in the mechanism, its concentration is automatically entered in % by the simulator according to relative humidity, temperature, and atmospheric pressure input in the key parameter table in the control panel. When the button for Step 3 is clicked, all initial concentrations are converted in molecules cm^{-3} and shown in the "Init Conc" column in the "Species Concentration" table (Figure 1). In condensed-phase systems, the basic concentration unit switches to mol L^{-1}.

Two other features set up in this table can be also useful in class: one is constraining species concentration (the "Constr" column). If set to "Y", the concentration time series of a species during the integration can be kept constant at its initial concentration (for a time-varying constrained concentration, see the "Time Dependence" subsection). This functionality is often needed in when trying to simulate chemistry constrained by a set of experimental conditions and results. This can be performed with KinSim without any user programming, which facilitates the use of more realistic examples in courses. Another useful feature is to avoid plotting species of less interest in the graphs. This can be easily controlled in the "Plot Species" column, or with a main parameter table setting for the major species (N_2, O_2).

Time Dependence

If no special processes or constrained species are specified previously, Step 4 is automatically skipped to avoid potential confusion to inexperienced users. Otherwise, for each of special processes and constrained species in the mechanism, a scaling factor time series needs to be set up in the "Time Dependence" table (Step 4). The simulator sets these time series to 1 for all times during the initialization of this table. In many cases, this table then does not require further attention. In the example shown in this paper the scaling factor of for the emission of a key reactant is set to 0 (no emission) for all time steps and to 1 (full emission rate) for one time-step. This allows investigating the

impact of the rapid injection of a species in the system. Simulation of diurnal cycles in the atmosphere is another example of a process that can be simulated with this feature.

145 ## Outputs

With the model set up, clicking the button for Step 5 will start the integration of ODEs using the backward differential formula method.[24] Integration is almost always completed instantly for typical system sizes for teaching purposes. After the integration, time series of species concentrations (and scaling factors of special processes and constrained species, if relevant) are automatically plotted

150 (Figure 3a). The solver uses variable internal time-steps chosen by the numerical solution needs of a given problem, but for simplicity the output is reported only at equally spaced time steps as specified in the key parameter table. By default, this plot is in linear scale, but can be easily modified to use a logarithmic scale in Igor Pro as needed (e.g., with a log left axis as in Figure 3b).

Step 6 is an optional post-processing step that plots the chemical fluxes that control the

155 concentration of a chosen species. If it is called, the software analyzes the production and loss rates of a given species due to all the reactions in which it appears as a reactant or a product, and plots these rates as a function of time (Figure 3c, d). This is a very useful tool to analyze the roles of different reactions and of other reactant species in the time evolution of a given species.

(a)

(b)

(c)

(d)
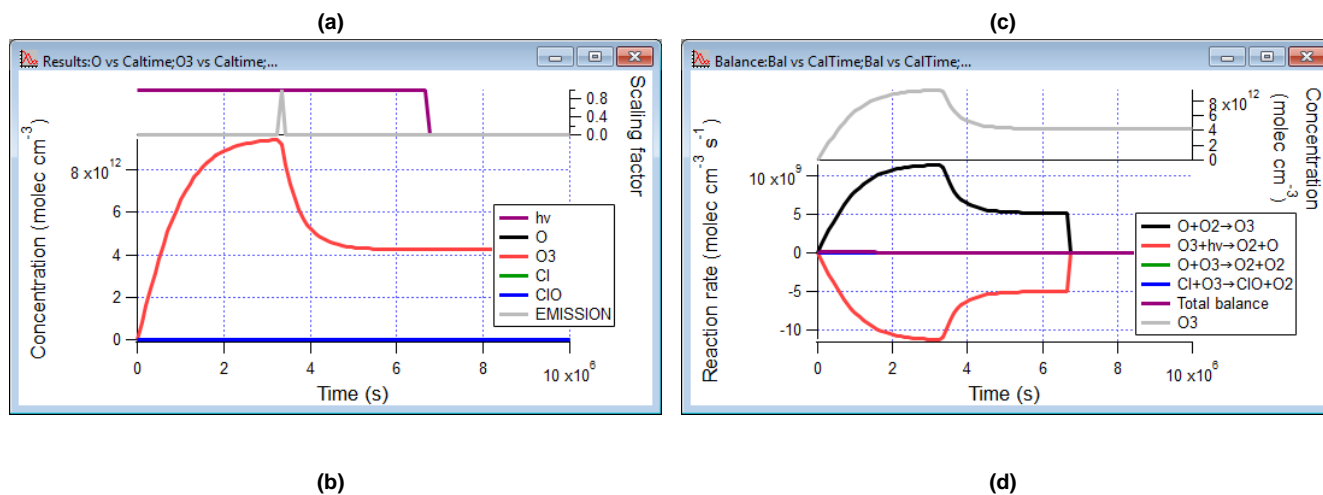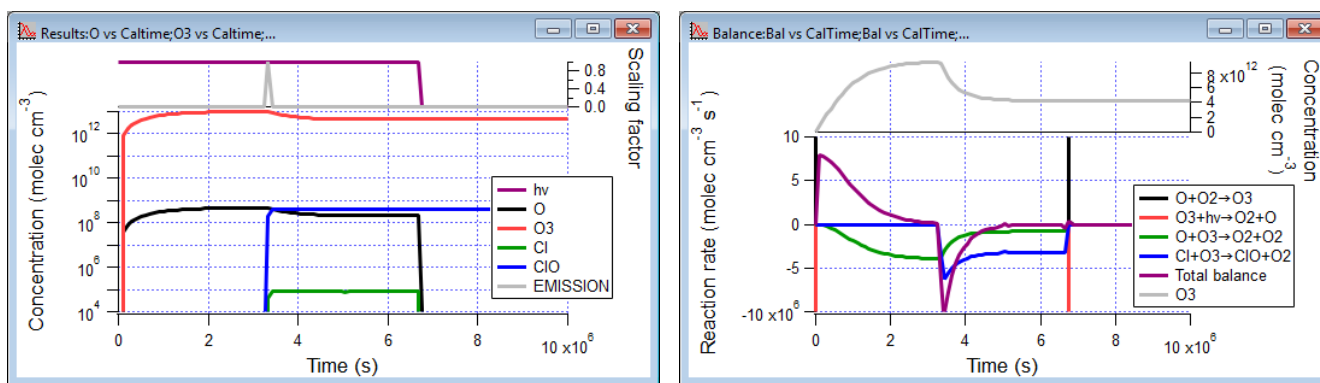
Figure 3. Output windows for the stratospheric ozone case study: (a) time series of species concentrations and scaling factors of special processes (photolysis and emission) in linear scale (those of O, Cl, and ClO are all very low and almost overlap); (b) same plot as (a) with concentrations in logarithmic scale, which allows examining the controlling role of minor species on ozone concentrations; (c) Ozone production and loss rates due to different reactions (full scale) that shows that ozone production and loss are always in approximate balance; (d) same plot as (c) with smaller reaction rates zoomed in, which allows evaluating the effect of critical reactions in the system.

A CASE STUDY: STRATOSPHERIC OZONE HOLE

We demonstrate the usage of KinSim in class through a simplified case study of the stratospheric ozone hole, a well-known and relatively simple problem. A case for an altitude of ~30 km is simulated. Temperature, atmospheric pressure, and relatively humidity are adopted from the textbook of Seinfeld and Pandis (see Figure 2 for the parameter setting).[9] Total reaction time is set to 10^7 s (~4 months), i.e., comparable timescale as the ozone hole evolution within a year.

The first four reactions in the mechanism table (Figure 1) constitute the Chapman mechanism,[9] which represents the interconversion of O, O_2, and O_3 in the stratosphere. $Cl+O_3 \rightarrow ClO+O_2$ and $ClO+O \rightarrow Cl+O_2$ are the most important reactions of catalytic stratospheric O_3 destruction. The rate coefficients (including photolysis frequencies) are set per ref [9]. The last process in the table is an emission of ClO. This is done for simplicity of this initial example, as ClO is a relatively stable Cl-containing intermediate with a significant concentration. However, an initial concentration of a chlorofluorocarbon and its photolysis reaction can be easily added for a more realistic simulation. To highlight the impact of the introduction of chlorine containing species (Cl_x) on O_3, the emission is assumed to be abrupt, i.e., occurring only at ~1/3 of the total reaction time (peaking at the 33rd of the 100 time steps of the output time series). KinSim treats the emission changes between the 32nd and 33rd times to output (from 0 to full) and between the 33rd and 34th (from full to 0) linearly. The ClO

emission rate is set to a value corresponding to a total emitted concentration of 1 ppb. Photolyses are shut down since the 67th times to output to mimic polar winter without light.

The simulation results in Figure 3 clearly shows that the introduction of Cl_x species (at a stratospherically-relevant amount, 1 ppb)[25] substantially and rapidly decreases the O_3 concentration (Figure 3a). From Figure 3c, d, students can easily observe that the O_3 decrease is caused by two effects: a decrease in O atoms, which reduces the formation of O_3 via $O + O_2$, and the $Cl + O_3$ reaction that destroys O_3 directly. The O atom concentration is lowered by $ClO+O \rightarrow Cl+O_2$ (Figure 3b), but is also affected by other reactions. Students then may try analyzing the production and loss rates of O and O_3 using other ClO emission rates/patterns, different patterns of photolysis simulating different seasons, or by disabling individual reactions. All of these are easy to do within KinSim and allow students to gain a more solid understanding on the chemistry of this system.

We also include more case studies for tropospheric, aerosol, and aquatic chemistries in SI to show other functionalities of KinSim and its suitability for modeling of various environmental chemistry problems.

STUDENT FEEDBACK AND CONCLUSIONS

Students who used KinSim as part of the Advanced Atmospheric Chemistry course at the University of Colorado-Boulder between 2015 and 2017 were surveyed (see SI for the details of the survey results). Overall, students rated KinSim very positively and deemed it a very useful tool for atmospheric chemistry learning, particularly understanding complex kinetic problems. Although most of the students surveyed had little background in chemical kinetic modeling before the class, they were generally able to use KinSim well in class and found many functionalities/features in KinSim friendly to inexperienced users. About 90% of the surveyed students intend to use KinSim if chemical kinetic problems become relevant in their future graduate research. The seamless transition between teaching and research applications is a key feature of KinSim. In summary, KinSim is a user-friendly and useful chemical kinetic simulator for both atmospheric chemistry teaching/learning and research.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI:

10.1021/acs.jchemed.XXXXXXX.

A ZIP archive containing KinSim source code (IPF), example case study setup files ready for loading (ITX, including the one for the ozone hole case in the main paper) and a text document presenting the description of the other case studies and example exercises for students (PDF)

Details of students' feedback about KinSim use in teaching (PDF)

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