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Multiphase Kinetic Multilayer Model Interfaces for Simulating Surface and Bulk Chemistry for Environmental and Atmospheric Chemistry Teaching

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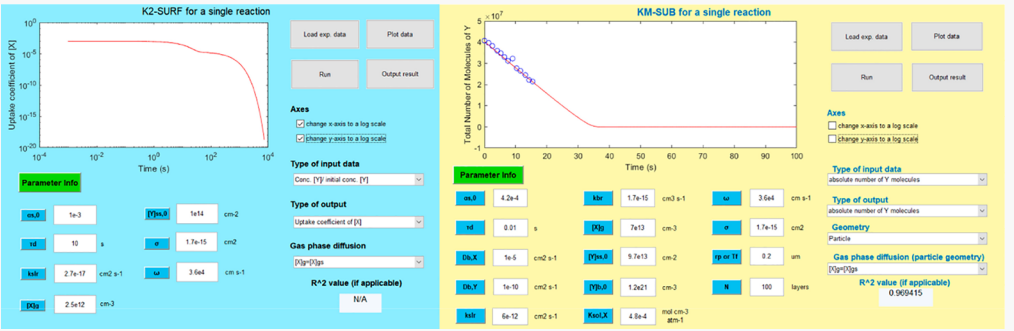

ABSTRACT: This paper presents MATLAB user interfaces for two multiphase kinetic models: the kinetic double-layer model of aerosol surface chemistry and gas−particle interactions (K2-SURF) and the kinetic multilayer model of aerosol surface and bulk chemistry (KM-SUB). Each interface has simple and user-friendly features that allow undergraduate and graduate students in physical, environmental, and atmospheric chemistry classes to learn about multiphase chemistry modeling without prior computer programming or modeling experience. It is easy to input parameters, and the simulation results are promptly displayed in the interface; thus, these model interfaces are particularly suitable for in-classroom and homework teaching applications. The model input parameters include surface and bulk reaction rate coefficients, surface accommodation coefficient, and gas and bulk diffusivities, while model outputs include gas uptake coefficient and surface and bulk concentrations. Students can use the K2-SURF interface to simulate surface processes and the KM-SUB interface to simulate surface and bulk processes. Example simulations were performed for each interface to present atmospherically relevant applications and to demonstrate its versatility for exploring model sensitivity on various kinetic parameters. The K2-SURF interface was used to show how the rate of ozone uptake by an organic surface and temporal evolution of surface concentrations are affected by the surface accommodation coefficient, desorption lifetime, and surface reaction rate coefficient. Additionally, the KM-SUB interface was applied to demonstrate how bulk diffusivities impact the degradation kinetics of oleic acid particles, so that students can learn how the phase state (liquid vs semisolid vs glassy solid) impacts multiphase chemical kinetics. The developed K2-SURF and KM-SUB interfaces are effective tools for modeling surface and bulk reactions in college-level educational settings, helping students to obtain a deeper understanding of the complex behaviors of heterogeneous and multiphase systems.

KEYWORDS: *Upper-Division Undergraduate, Graduate Education/Research, Environmental Chemistry, Computer-Based Learning, Atmospheric Chemistry, Kinetics, Physical Chemistry*

1. INTRODUCTION

As climate change and air pollution become a more critical issue in the Anthropocene,[1] education on global challenges pertaining to the environment has become increasingly crucial. To address emerging global environmental challenges, it is imperative for students to be equipped with modern tools and skill sets.[2] For example, college-level environmental chemistry classes today encourage students to engage with global challenges using scientific concepts.[3] The classes of environmental[4,5] and atmospheric chemistry[6−8] often apply the basics of chemical kinetics, a branch of physical chemistry that describes mass transport and chemical reactions. Especially, students in atmospheric and environmental chemistry classes learn how atmospheric aerosol particles and droplets undergo multiphase reactions that can lead to chemical transformation of air

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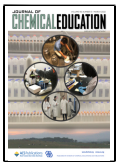

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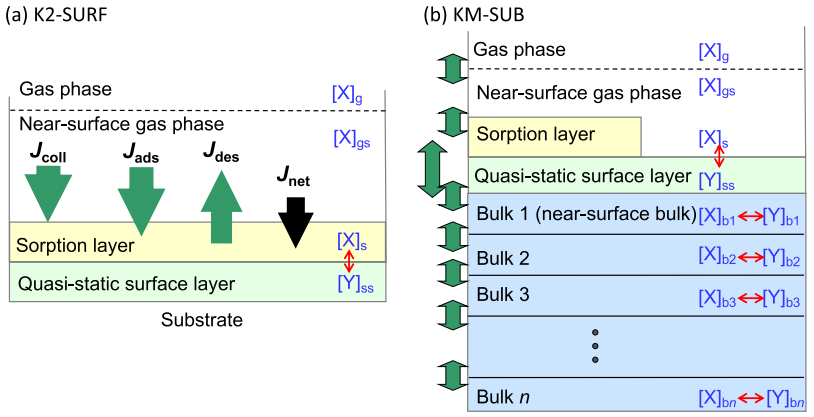

Figure 1. Schematic diagram of (a) K2-SURF and (b) KM-SUB: Compartments, transport fluxes (thick green arrows), and chemical reactions (thin red arrows) of volatile species X and nonvolatile species Y.

pollutants such as chlorine formation on polar stratospheric clouds for ozone hole chemistry as well as uptake of sulfur dioxide and sulfate formation in aqueous droplets in polluted air. Quantitative evaluation of such multiphase processes is critical in better understanding of aerosol effects on climate, air quality, and public health in the Anthropocene.[9−11] Instructors can supplement their environmental and atmospheric chemistry curriculum with technological tools such as computational models. Previous studies have shown that visualizing models of chemistry can enhance teaching effectiveness and that the incorporation of computational modeling into the curriculum increased student's interest in chemistry.[12,13] The usefulness of visualization in chemical education has been demonstrated in the field of quantum chemical calculations,[14,15] but there has been limited model applications of chemical kinetics in environmental chemistry teaching.[16]

Computational models are very powerful in simulating multiphase chemical kinetics and they are also useful in experimental laboratories for data analysis and processing of kinetic experiments. Thinking with models enables chemists to visualize the important entities and processes as well as to support the processes of reasoning and constructing knowledge.[17] It also allows chemists to go beyond qualitative descriptions of processes and to predict concentrations which may not be observable during experiments. It has been shown that students' and even the experts' use of chemical models can improve their understanding of concepts and that visualization in chemistry can help them recognize the importance of applying modeling tools.[18] Therefore, a comprehensive understanding of models and modeling is helpful for students' learning of chemistry,[13] providing major positive impacts on their perception of chemical concepts and their cultivation of critical-thinking skills.[19,20] However, most undergraduate students and many of the graduate students majoring in environmental and atmospheric chemistry have limited experience in computational modeling. The lack of formal education and exposure to scientific computation and modeling is quite common for students majoring in chemistry.[21] Many students in environmental chemistry lack knowledge and experience in computational codes because they do not have sufficient classroom opportunities to become familiar with the fundamentals of computational methods. As a consequence, when students come to the point that they need to apply a modeling program, they often use it as a black box without being aware of model assumptions and limitations, leading to misinterpretation of model results.

For the description of atmospheric aerosol processes, traditionally a resistor model has been applied with some key assumptions including homogeneous mixing within particles and steady-state conditions.[7,22] To overcome these limitations, the Pöschl-Rudich-Ammann (PRA) kinetic model framework was developed which encompasses chemical reactions and mass transport using a flux-based approach with a series of rate equations and parameters.[23,24] On the basis of the PRA framework, Shiraiwa et al. have developed multiphase kinetic models: the kinetic double-layer model of aerosol surface chemistry and gas-particle interactions (K2-SURF)[25] to describe uptake of gaseous species and chemical transformation of surface compounds and the kinetic multilayer model of aerosol surface and bulk chemistry (KM-SUB)[26] to treat bulk diffusion and reaction in the condensed phase. Both models can be applied for particle and film geometries. Each model has an original MATLAB code, but neither of them had graphical user interfaces, posing limits for those without an extensive background in computational modeling. The development of user-friendly interfaces would be critical for making the model readily accessible for such students[16,27−29] so that they could use these computational tools for environmental and atmospheric chemistry in-classroom activities and homework assignments.

In this paper, we present K2-SURF and KM-SUB user interfaces that are in MATLAB and intended for users to interact with both models in educational settings. It is recommended for students to have prior knowledge in college-level general chemistry concepts including chemical kinetics. However, the interfaces' user-friendly features do not require prior experience with programming, computational modeling, or aerosol science. By interacting with the multiphase kinetic models K2-SURF and KM-SUB, students can learn how certain kinetic parameters affect multiphase chemical reactions in atmospheric aerosols and films. The simulations performed with the K2-SURF and KM-SUB interfaces can be utilized in undergraduate physical and atmospheric chemistry classes as well as graduate chemistry courses that teach kinetics, catalysis, or multiphase atmospheric chemical reactions. Instead of having students memorize facts from a textbook, instructors can provide supplementary educational resources for visualizing and predicting kinetic parameter trends. Students can either work on these simulations independently or collaboratively. The K2-SURF and KM-SUB models have been applied extensively to atmospheric aerosol

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research, resulting in a number of peer-reviewed publications,[30−38] which serve as good references for students and instructors who may incorporate the model interfaces into their curriculum as well as for researchers who may apply these models for their research.

2. MODEL DESCRIPTIONS

2.1. K2-SURF

The K2-SURF model simulates gas−surface interactions involving volatile (X) and nonvolatile species (Y). K2-SURF can treat gas-phase diffusion, surface accommodation, reversible adsorption and desorption, and surface reactions.[9] As shown in the schematic diagram in Figure 1a, the model layers include the gas phase, near-surface gas phase, sorption layer, and quasi-static surface layer. The K2-SURF model interface presented in this study considers a single surface reaction between X and Y. Note that it does not treat bulk processes, which is the subject of KM-SUB.

K2-SURF includes seven input parameters, as shown in Table 1. The surface accommodation coefficient of X, $\alpha_{s,0}$, is the probability that a molecule of X will stick on an adsorbate-free surface upon collision.[16] τ_d is the desorption lifetime representing how long it takes for a molecule to desorb from a surface, and k_{SLR} is the second-order rate coefficient for a reaction between X and Y. $[X]_g$ and $[Y]_{ss,0}$ are the initial gas-phase and surface number concentrations of X and Y, respectively. σ is the effective molecular cross section of X, and ω is the mean thermal velocity of X. If gas-phase diffusion is being treated, the gas-phase diffusion coefficient of X also needs to be inputted into K2-SURF.

K2-SURF describes surface uptake using a flux-based approach by treating fluxes (in $cm^{-2}\ s^{-1}$) of collision ($J_{coll,X}$), adsorption ($J_{ads,X}$), and desorption ($J_{des,X}$):

$$J_{coll,X} = [X]_{gs}\omega_X/4 \quad (1)$$

$$J_{ads,X} = \alpha_{s,X}J_{coll,X} \quad (2)$$

$$J_{des,X} = \tau_{d,X}^{-1}[X]_s \quad (3)$$

where $[X]_{gs}$ is the near-surface gas-phase concentration of X. Gas-phase diffusion can also be treated in K2-SURF using a flux-based approach for particles and a coated wall flow tube as described in previous publications.[24,39] This may result in $[X]_{gs}$ being depleted compared to $[X]_g$ for certain parameter sets. In the presence of surface reactions, the surface reaction rate or loss rate of X on the surface $L_{s,X}$ (in $cm^{-2}\ s^{-1}$) can be described as

$$L_{s,X} = k_{SLR}[X]_s[Y]_{ss} \quad (4)$$

The uptake coefficient γ_X is the fraction of collisions of a gas molecule X with a surface that leads to uptake:

$$\gamma_X = \frac{J_{ads,X} - J_{des,X}}{J_{coll,X}} \quad (5)$$

The model outputs include γ_X, $[X]_s$, $[Y]_{ss}$, and $[X]_{gs}$ when gas-diffusion is considered. Students can learn further details of K2-SURF in Shiraiwa et al. (2009).[25]

Table 1. K2-SURF Model Parameters with Unit and Definition[a]

parameter	unit	definition	value and range
$\alpha_{s,0}$		surface accommodation coefficient of X on an adsorbate-free substrate	10^{-3} ($1-10^{-5}$)
τ_d	s	desorption lifetime of X	10 ($10-10^{-4}$)
k_{SLR}	$cm^2\ s^{-1}$	second-order rate coefficient for surface layer reaction of X with Y	2.7×10^{-17} ($2.7 \times 10^{-14} - 2.7 \times 10^{-19}$)
$[X]_g$	cm^{-3}	gas-phase number concentration of X	2.5×10^{12}
$[Y]_{ss,0}$	cm^{-2}	initial surface number concentration of Y	10^{14}
σ	cm^2	effective molecular cross section of X in the sorption layer	1.7×10^{-15}
ω	$cm\ s^{-1}$	mean thermal velocity of X in the gas phase	3.6×10^4
D_g	$cm^2\ s^{-1}$	gas-phase diffusion coefficient of X	

[a]Value and range represent the base case scenario and sensitivity simulations, respectively, as presented in section 4.1.

2.2. KM-SUB

Figure 1b illustrates the model layers, fluxes, and chemical reactions in KM-SUB.[26] KM-SUB simulates surface and bulk processes involving volatile and nonvolatile species by considering gas-phase diffusion, gas-surface transport (reversible

Table 2. KM-SUB Model Parameters with Unit and Definition[a]

parameter	unit	definition	
$\alpha_{s,0}$		surface accommodation coefficient of X on an adsorbate-free substrate	4.2×10^{-4} ($1-10^{-5}$)
τ_d	s	desorption lifetime of X	0.01
k_{SLR}	$cm^2\ s^{-1}$	second-order rate coefficient for surface layer reactions of X with Y	6.0×10^{-12}
k_{BR}	$cm^3\ s^{-1}$	second-order rate coefficient for bulk reactions of X with Y	1.7×10^{-15} ($1.7 \times 10^{-13} - 1.7 \times 10^{-17}$)
$D_{b,X}$	$cm^2\ s^{-1}$	bulk diffusion coefficient of X	10^{-5} (liquid), 10^{-7} (semisolid), 10^{-10} (solid)
$D_{b,Y}$	$cm^2\ s^{-1}$	bulk diffusion coefficient of Y	10^{-10} (liquid), 10^{-15} (semisolid), 10^{-20} (solid)
$[X]_g$	cm^{-3}	gas phase number concentration of X	7.0×10^{13}
$[Y]_{ss,0}$	cm^{-2}	initial surface number concentration of Y	9.7×10^{13}
$[Y]_{b,0}$	cm^{-3}	bulk number concentration of Y	1.2×10^{21}
$K_{sol,X}$	mol cm^{-3} atm^{-1}	partitioning coefficient of X	4.8×10^{-4}
ω	$cm\ s^{-1}$	mean thermal velocity of X in the gas phase	3.6×10^4
D_g	$cm^2\ s^{-1}$	gas-phase diffusion coefficient of X	
σ	cm^2	effective molecular cross section of X	1.7×10^{-15}
r_p	μm	particle radius	0.20
n		no. of bulk layers	100

[a]Value and range represent the base case scenario and sensitivity simulations, respectively, as presented in section 4.2.

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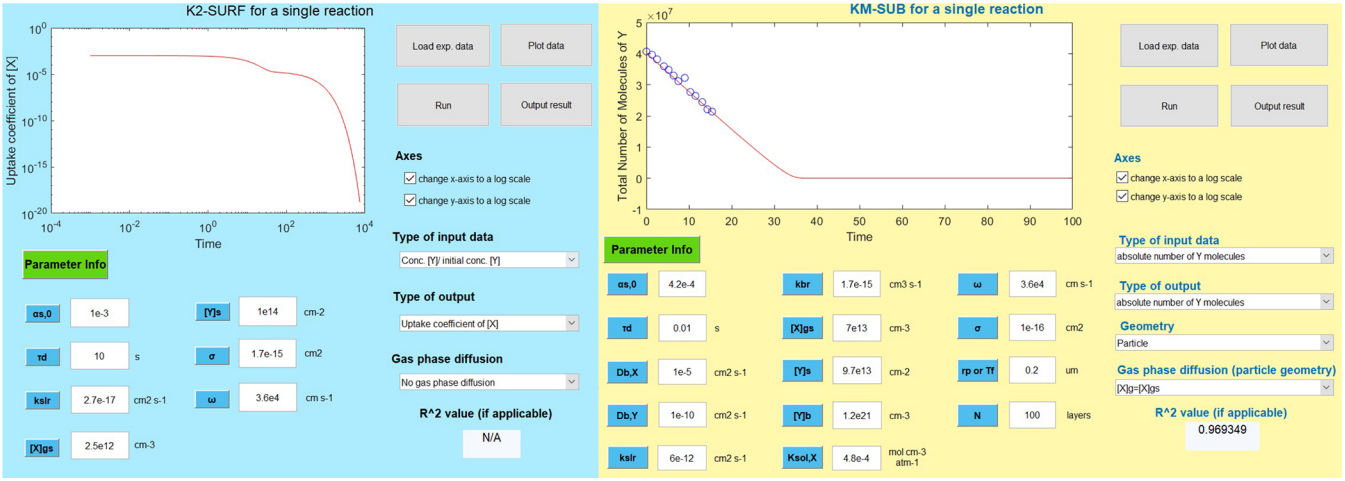

Figure 2. K2-SURF (left) and KM-SUB (right) interfaces on MATLAB. Each includes a figure panel for displaying simulation results (top left), buttons for running model simulations and checkboxes for axes scaling (top right), adjustable model parameters (bottom left), selection boxes for input/output, gas-phase diffusion, and geometry options, and an R^2 value if applicable (bottom right).

adsorption), surface layer reactions, surface-bulk transport, bulk diffusion, and bulk reactions.[6] The bulk is split into a number of n bulk layers, each of which is assumed to be homogeneously mixed. Bulk reactions can occur in each layer and Fickian diffusion between layers is treated using a flux-based approach. The KM-SUB model interface presented in this study considers single surface and bulk reactions between X and Y.

Table 2 lists model input parameters. In addition to the parameters introduced in K2-SURF, there are seven new parameters including bulk diffusion coefficients of X and Y ($D_{b,X}$, $D_{b,Y}$), a second-order bulk reaction rate coefficient between X and Y (k_{BR}) and a partitioning coefficient of X ($K_{sol,X}$). KM-SUB can simulate a particle or film geometry by considering the particle radius (r_p) or the film thickness (T_f). The KM-SUB model outputs include surface and bulk concentrations, surface and bulk mass accommodation coefficients, absolute numbers of molecules, and concentration profiles of volatile and nonvolatile species. Further details of the KM-SUB model including fluxes and rate equations can be found in Shiraiwa et al. (2010).[26]

3. USER INTERFACE DESCRIPTIONS

The K2-SURF and KM-SUB user interfaces were developed with MATLAB version R2020b, which is a platform that engineers and scientists often use for data analysis, programming codes, and computing algorithms. Each interface requires a folder containing the following files in order to run: a MATLAB code file, a MATLAB figure file, a text file containing parameter definitions, and an Excel.xlsx file containing sample experimental data points. Each folder also contains a text file with detailed instructions of how to open the interface. It is important that these instructions are followed as otherwise error messages may appear when the code is run. Figure 2 shows the windows that display when users run the K2-SURF and KM-SUB MATLAB code files.

To begin modeling on either interface, the "Load exp. data" button is pressed to import any data points from an Excel.xlsx file. The user is required to input the file name and number of data points in the spreadsheet. Then, users can change the values for any parameter on the bottom-left region of the window. To learn more about what each parameter represents, users can either click on the names of the individual parameters or press the "Parameter Info" button to view a list of definitions for every parameter. These features are particularly helpful for students because they do not have to memorize for what each symbol stands. The MATLAB codes for each interface are provided in the Supporting Information. The K2-SURF and KM-SUB parameters and definitions are listed in Table 1 and Table 2, respectively.

The types of input and output can be changed with the drop-down lists on the bottom-right corner. Users can also adjust gas-phase diffusion options using a drop-down list. Users can assume that gas-phase diffusion is unimportant and that the gas phase and near-surface gas phase will have the same concentrations ("$[X]_g = [X]_{gs}$"). Alternatively, gas-phase diffusion can be included using a flux-based approach for different experimental geometries ("Flow tube," or "Spherical particles") in K2-SURF and can also be included for spherical particles ("gas phase diffusion correction included") in KM-SUB. If students choose to include gas-phase diffusion, they are subsequently prompted to enter a gas-phase diffusion coefficient (in $cm^2\ s^{-1}$). The KM-SUB interface also has a geometry option ("Particle" or "Thin film (Note $[X]_g = [X]_{gs}$)") which can be changed depending on the geometry of the experiment being modeled. Users can also switch between logarithmic and linear axis scales by checking or unchecking the boxes under the bold "Axes" heading, respectively. By default, these boxes are unchecked, meaning that the axes are linear.

Once all the desired adjustments are made, users can press "Plot data" to generate a graph containing all their imported data points. Then, the "Run" button is pressed to produce a curve to model the chosen type of output. The number of time points is 999 as this number is sufficient for producing high-quality time resolution in a logarithmic space. The x-axis always represents time in seconds, and the y-axis always represents the chosen output type. If the selected input and output options are the same, an R^2 value displays on the bottom-right and the imported data points are included with the modeled curve. Otherwise, the R^2 value and imported data points are not displayed on the interface windows. The "Run" button does not generate a curve if data points are not loaded or plotted on the interface beforehand. After running the interface, users can press "Output result" to export results into a new Excel.xlsx file that contains all

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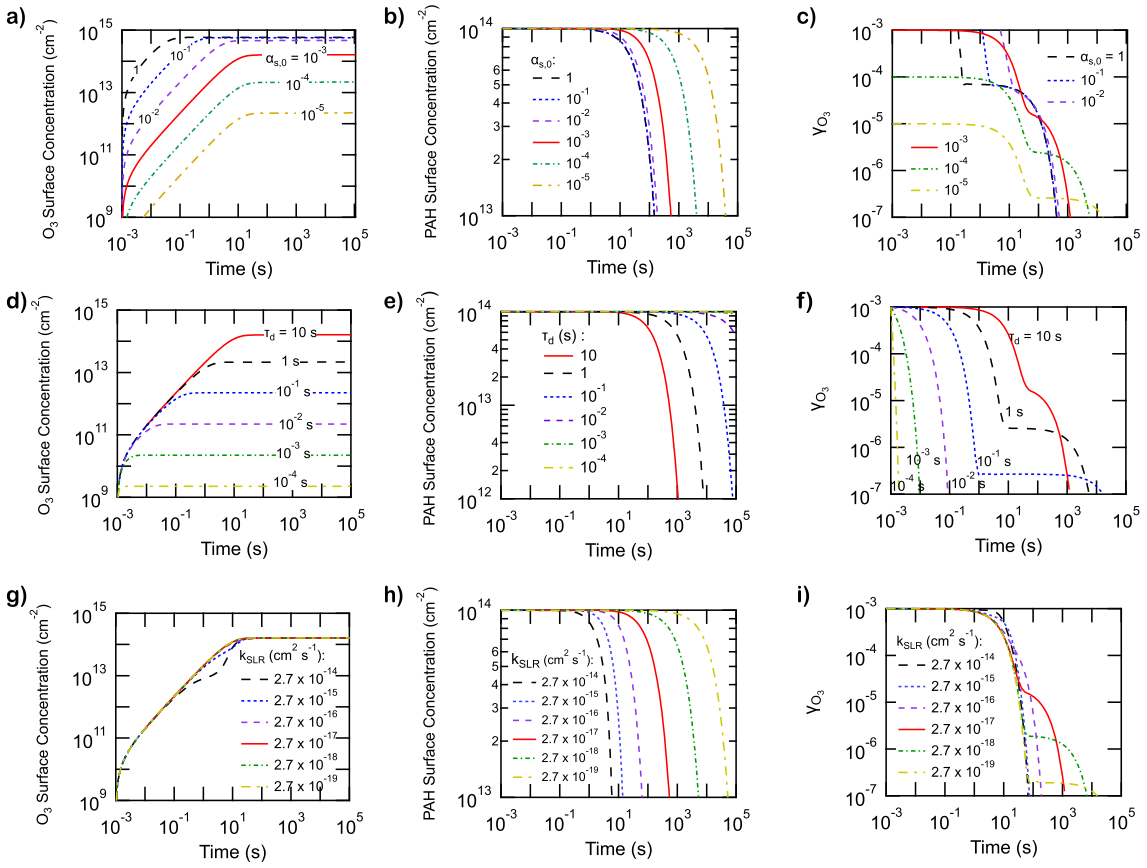

Figure 3. K2-SURF model simulations for ozone uptake by PAH: temporal evolution of (a,d,g) O_3 surface concentration $[O_3]_s$, (b,e,h) PAH surface concentration $[PAH]_{ss}$, and (c,f,i) O_3 uptake coefficient γ_{O3}. The base case scenario (red lines in all panels) is simulated with model parameters listed in Table 1 and (a,b,c) $\alpha_{s,0}$, (d,e,f) τ_d, (g,h,i) k_{SLR} were varied to show their sensitivities.

999 time points from the modeled curve (note that this function works well in Windows but not in Mac computers).

4. EXAMPLE SIMULATIONS

4.1. K2-SURF

Between the two interfaces presented in this paper, it is recommended for students to start with K2-SURF; this model is simpler and thus more suitable for those who are just beginning to learn heterogeneous aerosol kinetics. On the basis of a previous kinetic modeling study of PAH ozonolysis on aerosol particles,[25] example simulations were conducted with the K2-SURF MATLAB interface using the parameter set listed in Table 1. The outputs of interest were ozone uptake coefficients, surface concentrations of ozone (X), and surface concentrations of PAH (Y). The axes were set to logarithmic scales, and the type of gas-phase diffusion was left at its default setting, "$[X]_g = [X]_{gs}$" The Excel.xlsx files for each curve's data points were exported, and figures were created with Igor Pro 8. These figures could also be reproduced with Excel and MATLAB. Three kinetic parameters ($\alpha_{s,0}$, τ_d, k_{SLR}) were varied in increments of a factor of 10 to demonstrate the effects of each kinetic parameter on surface concentrations and uptake coefficients to better understand surface processes.

Figure 3 shows the simulation results of surface concentrations of O_3 and PAH as well as O_3 uptake coefficients, with various values of $\alpha_{s,0}$, τ_d, and k_{SLR}. Focusing on the base case scenario (red lines), the ozone uptake coefficient γ_{O3} exhibits an initial plateau up to ~1 s (Figure 3c) due to adsorption of ozone onto relatively clean surfaces as O_3 surface concentration $[O_3]_s$ increases (Figure 3a). As the desorption of adsorbed molecules starts to occur, γ_{O3} decreases and reaches a second plateau when reversible adsorption and surface reactions are balanced (e.g., $J_{ads,X} - J_{des,X} \approx L_{s,X}$) and $[O_3]_s$ reaches steady-state conditions. Following the second plateau, γ_{O3} decreases significantly as surface reactions proceed leading to a decrease of surface PAH concentrations $[PAH]_{ss}$ (Figure 3b).

Students can also use the K2-SURF model as a supplementary resource for learning how adsorption, desorption, and collision fluxes influence ozone uptake. In fact, the uptake coefficients in Figure 3 can all be explained using eqs 1−5. $J_{ads,O3}$ is proportional to $J_{coll,O3}$ and $\alpha_{s,0}$ (eq 3), so a large $\alpha_{s,0}$ can increase the initial γ_{O3}: as shown in Figure 3c, the initial γ_{O3} increases by an order of magnitude as $\alpha_{s,0}$ also increases by an order of magnitude. A higher $J_{ads,O3}$ will result in more O_3 molecules being adsorbed on the surface (Figure 3a), which over time will lead to faster PAH surface depletion through reactions and therefore lower PAH surface concentrations (Figure 3b). On the other hand, lower $\alpha_{s,0}$ and hence lower adsorption fluxes can decrease $[O_3]_s$ and thus decrease the surface reaction rate $L_{s,O3}$ (eq 4), increasing the time for $[PAH]_{ss}$ to decrease.

As $\tau_{d,O3}$ increases, the desorption flux $J_{des,O3}$ decreases and hence $[O_3]_s$ increases (Figure 3d). This leads to higher $L_{s,O3}$ (faster surface reaction), resulting in faster decay of $[PAH]_{ss}$ (Figure 3e). Under steady-state conditions of $[O_3]_s$ ($d[O_3]_s/dt = J_{ads,O3} - J_{des,O3} - L_{s,O3} \approx 0$), γ_{O3} can be expressed as $\gamma_{O3} \approx L_{s,O3}/J_{coll,O3}$. Thus, higher $L_{s,O3}$ would translate into higher γ_{O3} as shown in Figure 3f. On the other hand, shorter $\tau_{d,O3}$ leads to

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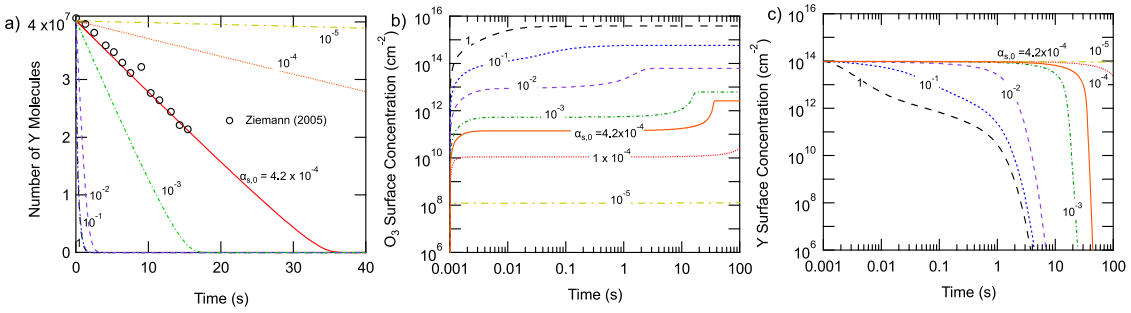

Figure 4. (a) KM-SUB modeled and measured (Ziemann, 2005)[40] temporal evolution of the absolute number of oleic acid molecules upon ozonolysis of oleic acid particles. KM-SUB modeled temporal evolution of surface concentrations of (b) O_3 and (c) oleic acid with $\alpha_{s,0}$ in the range of 10^{-5}−1. The red lines represent the base case scenario with $\alpha_{s,0} = 4.2 \times 10^{-4}$ in liquid particles.

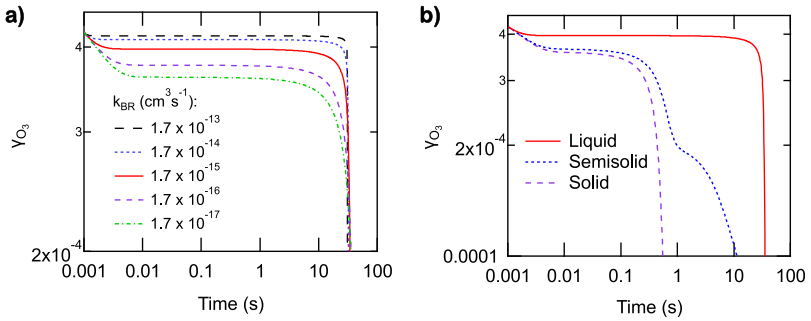

Figure 5. (a) The uptake coefficient of O_3 γ_{O3} by oleic acid particles simulated using KM-SUB with bulk reaction rate coefficients k_{BR}. (b) The simulated γ_{O3} with different particle phase states for liquid ($D_{b,x} = 10^{-5}$ cm^2 s^{-1}, $D_{b,y} = 10^{-10}$ cm^2 s^{-1}), semisolid ($D_{b,x} = 10^{-7}$ cm^2 s^{-1}, $D_{b,y} = 10^{-15}$ cm^2 s^{-1}), and solid ($D_{b,x} = 10^{-10}$ cm^2 s^{-1}, $D_{b,y} = 10^{-20}$ cm^2 s^{-1}).

lower $[O_3]_s$ and $L_{s,O3}$, and hence lower γ_{O3}, increasing the amount of time to decay PAH. k_{SLR} does not significantly affect $[O_3]_s$ (Figure 3g), as $[O_3]_s$ is mostly determined by the balance of $J_{ads,O3}$ and $J_{des,O3}$. As k_{SLR} increases, $L_{s,O3}$ increases, resulting in higher γ_{O3} under steady-state conditions (Figure 3i) and therefore faster decay of PAH (Figure 3h). At lower k_{SLR}, it takes a longer time for $[PAH]_{ss}$ to decrease with lower $L_{s,O3}$ and γ_{O3}.

The learning goal of the application of the K2-SURF interface is for students to learn about the interplay of adsorption, desorption, and surface reaction on overall gas uptake and heterogeneous kinetics. To support achieving this goal, an example worksheet is included in the supplement, which can be utilized for discussion classes or for homework. It guides students to conduct model simulations with given input parameters to obtain O_3 surface concentrations with different $\alpha_{s,0}$ values. These simulations will help students gain a quantitative understanding of the impact of surface accommodation on resulting surface concentrations. These deep analyses are helpful in a classroom setting because they allow students to apply their knowledge in basic chemical kinetics to real-world atmospherically relevant scenarios.

4.2. KM-SUB

After students get acquainted with K2-SURF for simulating surface processes, KM-SUB can be used to simulate surface and bulk processes. Here we exhibit exemplary simulations for multiphase reactions between ozone and oleic acid particles, in comparison to experimental data from Ziemann (2005).[40] This reaction system has been studied extensively, serving as a model system of multiphase processes in atmospheric aerosols.[41] In addition, multiphase processes are important and relevant for a variety of environmental processes such as stratospheric ozone chemistry for ozone hole formation, haze formation in urban air pollution, and acid rain formation.[5−7,9] By learning and simulating this model system of oleic acid ozonolysis, students will learn the basis and relevance of multiphase aerosol processes on real-world environmental issues.

The KM-SUB model outputs include absolute number of oleic acid (Y) molecules, surface concentrations of ozone (X) and oleic acid, ozone uptake coefficients, and bulk concentration profiles of ozone and oleic acid. Gas-phase diffusion was ignored with the gas-phase ozone concentration of 7.0×10^{13} cm^{-3} (corresponding to 2.8 ppm at 1013 hPa and 298 K) and the setting of "$[X]_g = [X]_{gs}$," was used in the interface. The particle radius was set to 200 nm. The values of other parameters for the base case scenario are listed in Table 2. $\alpha_{s,0}$, k_{BR}, $D_{b,X}$, and $D_{b,Y}$ were varied to showcase how ozone uptake coefficients and concentration profiles were affected. The Excel.xlsx files for each curve's data points were exported, and figures were created with Igor Pro 8.

Figure 4a illustrates the base case model results of KM-SUB (with $\alpha_{s,0} = 4.2 \times 10^{-4}$ in liquid particles) for absolute numbers of oleic acid molecules, showing a very good agreement with the experimentally observed decay. Students can compare computational simulations to experimental data and evaluate the effectiveness and limitations of computational modeling. As shown with the red line in Figure 4b, the surface concentration of ozone exhibits a rapid initial increase from zero to a plateau level of $[O_3]_s \sim 10^{11}$ cm^{-2}, which is determined by the combination of reversible adsorption, surface reaction, and surface-to-bulk transport driven by the chemical reaction in the bulk. After ~30 s, $[O_3]_s$ gradually increases with the decay of oleic acid as shown by the decay of the surface concentration of oleic acid (Figure 4c). Figure 4 also includes modeled lines

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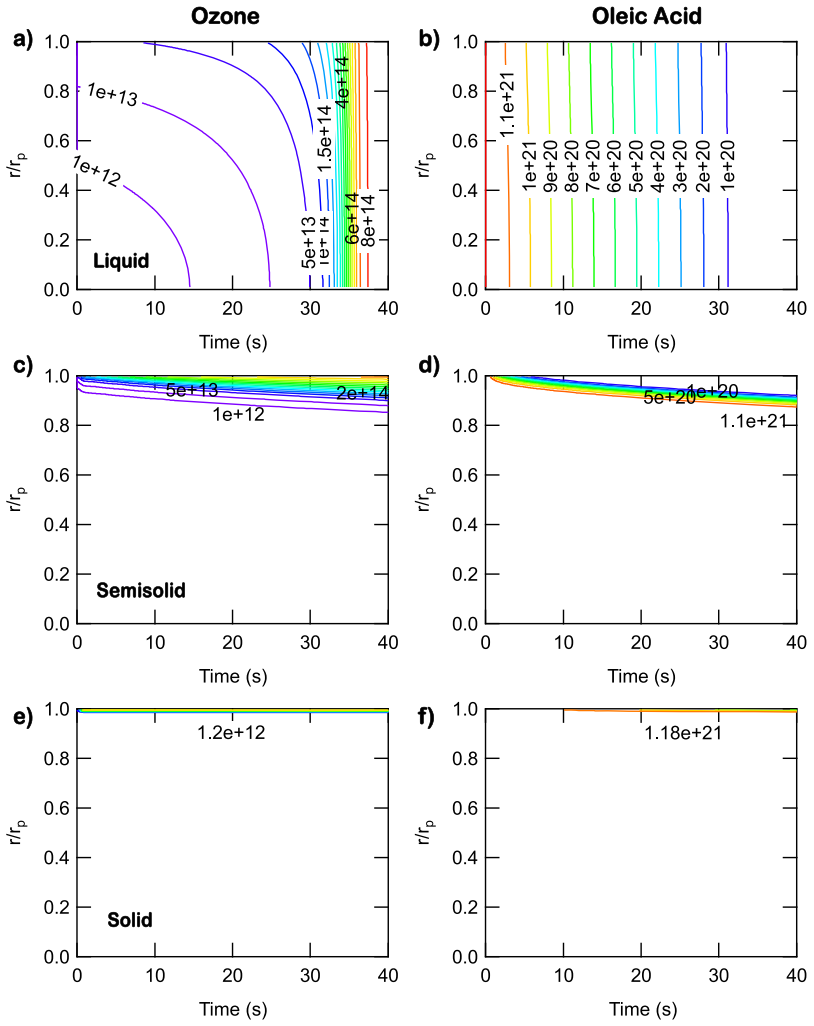

Figure 6. Modeled temporal evolution of bulk concentration profiles for model base case 1 for (a,c,e) ozone and (b,d,f) oleic acid in three different phases: (a,b) liquid, (c,d) semisolid, and (e,f) solid. The colored lines represent bulk concentrations in cm^{-3} from low (blue) to high (red). The *y*-axis indicates the radial distance from the particle center normalized by the particle radius, ranging from the particle core ($r/r_p = 0$) to the near-surface bulk ($r/r_p = 1$).

simulated with a wide range of $\alpha_{s,0}$. Higher $\alpha_{s,0}$ indicates larger accommodation of O_3 into oleic acid particles, leading to faster depletion of oleic acid and larger $[O_3]_s$. Students can also attempt to model the effects of k_{SLR} and τ_d on surface concentrations using the KM-SUB interface.

Figure 5 shows the temporal evolution of γ_{O3}, indicating that γ_{O3} stays constant in the course of reaction and eventually decreases rapidly when oleic acid is depleted. The effect of k_{BR} on γ_{O3} is demonstrated in Figure 5a. γ_{O3} decreases upon a decrease of k_{BR}, as a lower k_{BR} value corresponds to slower bulk reactions to deplete oleic acid and hence a lower overall uptake of O_3. This pattern is similar to the relationship between k_{SLR} and γ_{O3} on the PAH surface demonstrated with K2-SURF.

Additional KM-SUB simulations were performed to demonstrate the impact of particle phase state (liquid vs semisolid vs solid) on ozone uptake. Each phase state corresponds to a pair of bulk diffusion coefficients as shown in Table 2, which is based on a previous kinetic modeling study that investigated gas uptake and chemical aging of amorphous semisolid organic aerosols.[42] As shown in Figure 5b, γ_{O3} is lower for semisolid particles and the lowest for solid particles due to kinetic limitations of bulk diffusion. Retarded bulk diffusion limitations prevent ozone from diffusing into the particles and oleic acid from diffusing from the inner bulk to the surface. Students who are new to the KM-SUB interface can ease into this more complex model by simulating surface concentrations and ozone uptake coefficients, which they will have previously outputted using K2-SURF, before investigating other outputs such as bulk concentrations.

To better understand kinetic limitations and visualize concentration gradients, the bulk concentration profiles of O_3 and oleic acid can be plotted as shown in Figure 6. For the liquid phase, O_3 initially exhibits concentration gradients up to ~30 s as controlled by the interplay of interfacial mass transport with bulk diffusion and chemical reaction. The ozone concentration gradient decreases gradually with the decay of oleic acid and the related decrease of chemical loss; as the chemical loss by reaction with oleic acid rapidly decreases after ~30 s, the ozone concentration gradient swiftly relaxes and then becomes well mixed throughout the particle bulk due to rapid bulk diffusion.[26] Despite the presence of O_3 concentration gradients, oleic acid is effectively well-mixed as the concentration of oleic acid is several orders of magnitude larger than that of ozone and oleic acid diffuses rapidly in a liquid matrix (Figure 6b).

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In semisolid particles, O_3 exhibits a strong concentration gradient due to fast bulk reaction and slow bulk diffusion (Figure 6c), which causes a reverse strong gradient for the bulk concentration of oleic acid in the bulk close to the surface (r/r_p > ~0.9; Figure 6d). For solid particles with very low diffusivity, both ozone and oleic acid exhibit steep concentration gradients near the surface, whereas the inner particle bulk remains nearly unchanged: O_3 penetrates only into the near-surface bulk, and thus the chemical consumption of oleic acid is also restricted to the near surface bulk (r/r_p > 0.99; Figure 6e,f). Through this exercise of generating and interpreting contour plots of O_3 and oleic acid concentration profiles, students can further justify the ozone uptake coefficient simulation results and learn more about bulk reaction and diffusion processes in atmospheric aerosol particles.

The learning objective of the application of the KM-SUB interface is for students to learn about the impact of bulk diffusion and reactions on multiphase kinetics of gas uptake and chemical transformation of particles. We provide an example worksheet in the supplement for students to learn the impact of different phase states on surface concentration, uptake coefficient, and the rate of chemical transformation. When example simulations are implemented in an educational setting, it is imperative for students to cross-reference different types of simulations because they collectively explain various multiphase aerosol processes.

CONCLUSIONS

This paper presents K2-SURF and KM-SUB user interfaces that allow students with a college-level chemistry background to gain a quantitative understanding of heterogeneous and multiphase aerosol processes. The K2-SURF interface can model surface processes such as the gas uptake and chemical transformation of surface compounds, and the KM-SUB interface can simulate multiphase processes including bulk reaction and diffusion. Because of their user-friendly features, none of the interfaces require prior knowledge in computer programming languages or atmospheric aerosol science. Students can have a deeper understanding of surface and bulk processes and learn the concept of kinetic limitations by varying various kinetic parameters and observing how they affect uptake coefficients and surface and bulk concentration profiles.

The K2-SURF and KM-SUB interfaces can serve as educational tools for undergraduate and graduate level physical and atmospheric chemistry courses that cover concepts such as kinetics, heterogeneous catalysis, and multiphase chemical reactions. These tools can also help students become more comfortable with computational modeling and more aware of how assumptions and limitations deviate from experimental data. These tools have been applied to undergraduate and graduate research (Chem 180, 280 at UC Irvine) and independent research (Chem 199 at UC Irvine); students provided very positive feedback, regarding them as very helpful tools for understanding complex multiphase kinetic problems. In addition, they can be used as an in-class tool for courses such as Environmental Chemistry as well as Gas-Phase and Multiphase Atmospheric Chemistry for instructors for demonstration and can also be used for homework assignments for students to conduct additional simulations. For this purpose, an example worksheet is attached in the Supporting Information, consisting of three problems each for K2-SURF and KM-SUB simulations. This worksheet can be utilized for discussion classes or for homework, helping students to conduct simulations to better understand the concept of multiphase kinetic modeling.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.1c00931.

K2-SURF User Interface Files: MATLAB code and figure files, .txt file with parameter definitions, and Excel.xlsx spreadsheet with simulated data for surface concentration ratios over time (ZIP)

KM-SUB User Interface Files: MATLAB code and figure files, .txt file with parameter definitions, and Excel.xlsx spreadsheet with Ziemann's experimental data for absolute number of Y molecules over time (ZIP)

Worksheet example (PDF)

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Notes

The authors declare no competing financial interest.

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