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Aerosol Uptake Described by Numerical Solution of the Diffusion−Reaction Equations in the Particle

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The reactive uptake of gases by a particle is explored by numerically solving the associated partial differential equations. These equations explicitly couple the diffusion and reaction of multiple species in the particle. This approach makes it possible to calculate the concentration of each reactant within the particle as a function of both time and position and to examine the impact of concentration gradients on the rate of uptake. The effect of liquid diffusion on the rate of uptake is explored for a reference reaction (O_3 + oleic acid particles) as a function of the particle size and the liquid-state concentration of the species taken up from the gas phase. Diffusion within the particle is found to significantly limit uptake for large particles and the large gas-phase concentrations often used in laboratory experiments, although it is typically less important under atmospheric conditions. This numerical approach to solving the diffusion−reaction equations is also used to modify the common electric circuit resistance model for heterogeneous uptake to make it more applicable when diffusion within the particle is limiting.

Introduction

Much recent work in atmospheric chemistry has focused on identifying and characterizing the composition and chemistry of aerosol particles. These aerosols are both natural and anthropogenic in origin and can significantly impact the climate, local air quality, and human health.[1] The manner in which aerosols are studied in both the troposphere and the stratosphere has advanced, including the increasingly widespread use of aerosol mass spectrometers.[2−6] It is now possible to obtain detailed information about particle size and composition on a near real-time basis and to correlate these data with measurements of ambient trace gas concentrations. The interactions of gas-phase species with aerosol particles are not well understood, however. The ability of gas-particle reactions to change the composition, size, reactivity, and hygroscopicity of particles has made this an active area of investigation.[7−9] The complexity and diversity of aerosols found in the atmosphere make it difficult to characterize the kinetics of such gas-particle reactions. However, recent laboratory studies in which the composition of reacted particles is quantitatively monitored have made it possible to measure the rate of uptake of a gas-phase species by aerosol particles.[10−12] These studies have offered insight into the complex processes governing the uptake of gas-phase species by particles with application to both laboratory systems and authentic atmospheric particles.

One convenient method used to interpret experiments measuring the uptake of a gas-phase species, X, by a condensed-phase species, Y, is the electric circuit resistance, or "resistor," model.[13−15] In this model, the rate of each process contributing to the overall rate of uptake, including gas-phase diffusion, thermal accommodation and reaction at the surface, and solvation and reaction in the bulk, is represented by a conductance, Γ. The inverse of each conductance, $1/\Gamma$, represents a resistance to uptake, and these individual terms can be combined in series or in parallel to represent the overall resistance to uptake, $1/\gamma$.

To date, the resistor model as generally employed has not included diffusion of the liquid reactant in the particle, although Worsnop et al.[16] have recently generalized it for this purpose. In light of recent experimental results[11] that show the importance of these diffusion processes, we have numerically solved the corresponding coupled differential equations. We use this numerical solution as a benchmark against which to evaluate the ability of the resistor model to describe the rate of reactive uptake for a range of particle sizes and diffusion rates. We also derive a modified resistor model, the accuracy of which is verified by using our coupled PDE approach. This model requires orders of magnitude less computational time than the general numerical solution, yet it proves to be more accurate than current resistor models in describing the rate of uptake when limited by diffusion within the particle.

Mathematical Treatment

The general solution for the time-dependent concentration profiles within a reactive particle can only be obtained by considering the simultaneous diffusion and reaction of each species present within the particle.[17−19] Here, we will evaluate the simplified case of only two reactants, one of which originates in the gas phase and is taken up by the particle, the other of which is initially present in the particle. However, the approach outlined below can be generalized to more complex systems containing a larger set of reactants and reactions.

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The uptake of a species, X, from the gas phase by a particle containing a species, Y, is governed by reaction and diffusion within the particle:

$$\frac{\partial[\mathrm{X}]}{\partial t} = D_{\mathrm{X}}\nabla^2[\mathrm{X}] - k_2[\mathrm{X}][\mathrm{Y}] \qquad (1)$$

$$\frac{\partial[\mathrm{Y}]}{\partial t} = D_{\mathrm{Y}}\nabla^2[\mathrm{Y}] - k_2[\mathrm{X}][\mathrm{Y}] \qquad (2)$$

where D_X and D_Y are the diffusion constants (cm^2 s^{-1}) of the respective species (in Y), and k_2 is the second-order rate coefficient (M^{-1} s^{-1}) for the reaction between X and Y. Although other processes can contribute to the rate of uptake, we assume that they are fast and are therefore not rate-limiting.

The standard resistor model used to describe heterogeneous uptake makes two assumptions that allow these diffusion−reaction equations to be solved analytically. The first assumption is that the species X is in steady state, i.e., [X] is not a function of time. The other assumption is that [Y] is not a function of the position within the particle. These approximations are valid only when (a) X reacts so quickly with Y that it does not have the opportunity to diffuse very deeply into the particle, and (b) Y diffuses quickly enough with respect to reaction that [Y] is uniform throughout the particle. It should be noted that the latter assumption is not valid for viscous species and consequently the resistor model fails.

In the approach outlined below, we solve the set of coupled partial differential equations (eqs 1 and 2) numerically so that the assumptions described above are avoided. Nevertheless, to simplify the equations we assume that the particles are spherical such that they can be rewritten in spherical polar coordinates as

$$\frac{\partial[\mathrm{X}]}{\partial t} = \frac{D_{\mathrm{X}}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial[\mathrm{X}]}{\partial r}\right) - k_2[\mathrm{X}][\mathrm{Y}] \qquad (3)$$

$$\frac{\partial[\mathrm{Y}]}{\partial t} = \frac{D_{\mathrm{Y}}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial[\mathrm{Y}]}{\partial r}\right) - k_2[\mathrm{X}][\mathrm{Y}] \qquad (4)$$

We have solved this set of equations using the numerical method of lines technique in Mathematica (v 4.1.0.0, Wolfram Research). In solving these equations, we have made the following simplifying assumptions: (1) that the concentration of X at the surface of the particle is in equilibrium with the gas-phase concentration, (2) that the flux of X at the center of the particle is zero, and (3) that the flux of Y at both the center and the surface is zero. In addition, we have specified that the particle exists initially as a pure droplet of Y with the equilibrium concentration of X at the surface. These assumptions are expressed in the corresponding boundary and initial conditions, namely: (1) $[X]_{surf} = H_X P_X$ (where H_X is the Henry's Law constant for X in Y, and P_X is the pressure of X), (2) $\partial[X]/\partial r|_{r=0} = 0$, (3) $\partial[Y]/\partial r|_{r=0} = \partial[Y]/\partial r|_{r=a} = 0$ (where a is the radius of the particle), (4) $[Y](t = 0) = [Y]_0$, and (5) $[X](t = 0) = H_X P_X\,\delta(r - a)$ (where δ is the unit step function).

Effect of Diffusion within the Particle. To investigate the effect of diffusion of Y within the particle on the uptake of X, we varied the diffusion constant, D_Y, over a wide range. Unless otherwise indicated, the values of all other relevant parameters were chosen to represent a specific reference reaction (O_3 with oleic acid particles), where $a = 1$ μm, $H_X = 0.3$ M atm^{-1}, $P_X = 1 \times 10^{-4}$ atm, $D_X = 1 \times 10^{-5}$ cm^2 s^{-1}, and $k_2 = 1 \times 10^6$ M^{-1} s^{-1},[20] with the values used for H_X and D_X being estimated from similar systems.[21−23]

Figure 1 shows the concentration of Y calculated as a function of both the radial position within the particle and the reaction time for two different values of the diffusion constant: $D_Y = 1 \times 10^{-7}$ cm^2 s^{-1} (1a and 1b) and $D_Y = 1 \times 10^{-10}$ cm^2 s^{-1} (1c and 1d). It is evident in Figure 1a and 1b that the diffusion of Y is faster than the rate of reaction with X and therefore a uniform concentration of Y is maintained even as it reacts. Figure 1c and 1d demonstrate the effect that a smaller D_Y has on the concentration profile. A gradient in [Y] is established within the particle, although the reaction still goes to completion as X diffuses inward. In this case, the reaction rate is slower, and the slow diffusion of Y within the particle acts as an additional resistance to the reactive uptake of X from the gas phase.

The effect of this resistance can be seen in Figure 2 where the total concentration of Y in the particle is plotted as a function of time for the two values of D_Y. In the limit of fast diffusion ($D_Y = 1 \times 10^{-7}$ cm^2 s^{-1}), the resistor model predicts a decay that is linear in $\sqrt{[Y]/[Y]_0}$ vs time,[10−11] namely:

$$\sqrt{\frac{[\mathrm{Y}]}{[\mathrm{Y}]_0}} = 1 - \left(\frac{3P_{\mathrm{X}}H_{\mathrm{X}}\sqrt{D_{\mathrm{X}}k_2}}{2a\sqrt{[\mathrm{Y}]_0}}\right)t \qquad (5)$$

The initial rate of reactive uptake, Γ_{rxn}, can then be obtained from the slope of the data in Figure 2:[10,11,14]

$$\Gamma_{\mathrm{rxn}} = \frac{4H_{\mathrm{X}}RT}{\bar{c}}\sqrt{D_{\mathrm{X}}k_2}\sqrt{[\mathrm{Y}]_0} = \left(\frac{8RTa}{3\bar{c}P_{\mathrm{X}}}[Y]_0\right)(slope) \qquad (6)$$

where R is the gas constant, T is the temperature, and $\bar{c}$ is the mean speed of the gas. Fitting all of the data to eq 5 in this manner provides a more precise measure of the rate of uptake than is obtained from just the initial slope of [Y] vs time.

On the other hand, when diffusion is slow (as is the case for $D_Y = 1 \times 10^{-10}$ cm^2 s^{-1}), the resistor model and eq 5 are no longer valid as demonstrated by the nonlinear plot in Figure 2. Although the plotted function possesses the correct slope initially, it slows at later times due to the slow diffusion. Since experimental data often contain sufficient scatter to obscure this nonlinear behavior, a linear fit may still appear to accurately describe the rate of decay. If we use such a linear regression to obtain an average slope for the slow diffusion data in Figure 2, we find that it is approximately seven times smaller than the slope for the fast-diffusion data. This slowing is due solely to the decrease in D_Y since all other parameters, including the rate constant and the particle size, are the same in both cases. Consequently, the resistor model underestimates Γ_{rxn} by a factor of 7 if it is used to estimate the initial slope from the average slope.

Diffusion, Particle Size, and Surface Concentration. To explore the role of diffusion, we calculated $[Y(r,t)]$ as a function of both the particle size and the diffusion constant, D_Y. The slopes obtained from a linear-least-squares fit to eq 5 were calculated using the resistor model as in Figure 2, and each was divided by the slope at $t = 0$ (when diffusion is not limiting). These normalized slopes, shown in Figure 3, therefore represent the slowing effect that decreased diffusion has on the rate of uptake as calculated with the resistor model. When diffusion is fast ($D_Y \geq 10^{-7}$ cm^2 s^{-1}) and the particles are larger than 0.5 μm, there is little dependence on size (less than 5% deviation), and the normalized rate approaches an upper limit of one. Under these conditions, the resistor model does a good job of describing reactive uptake. Interestingly, this rate also approaches a lower limit (∼0.1) when diffusion is slow

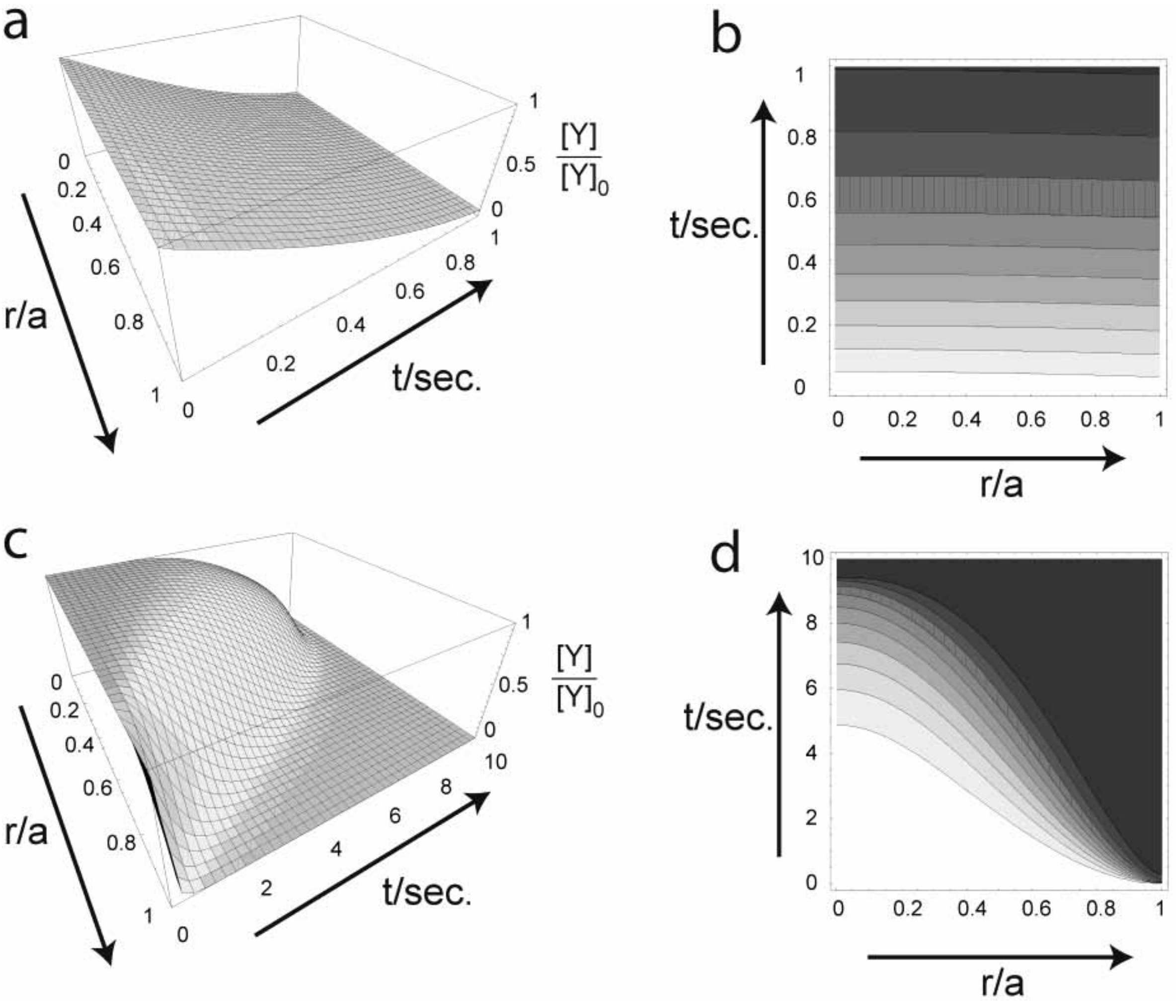

Figure 1. Calculated concentration profiles of the condensed-phase species, Y, as a function of time and position within the particle. Parameters used are: $D_X = 1 \times 10^{-5}$ cm^2 s^{-1}, $k_2 = 1 \times 10^6$ M^{-1} s^{-1}, $H_X = 0.3$ M atm^{-1}, and $a = 1$ μm. (a) and (b): $D_Y = 1 \times 10^{-7}$ cm^2 s^{-1}. Fast diffusion of Y results in a well-mixed particle. (c) and (d): $D_Y = 1 \times 10^{-10}$ cm^2 s^{-1}. Slow diffusion of Y results in a concentration gradient within the particle, and the rate of reaction is slower than in (a) and (b).

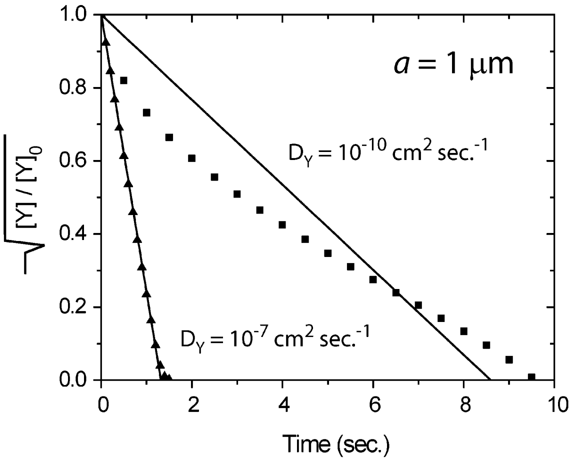

Figure 2. Calculated decays of [Y] as a function of time for two values of D_Y: 1×10^{-7} cm^2 s^{-1} and 1×10^{-10} cm^2 s^{-1} All other parameters are as in Figure 1. Straight lines represent best fits of the resistor model and provide estimates of the average rates of uptake using all of the data.

($D_Y \leq 10^{-11}$ cm^2 s^{-1}). In this case, the decay represents the rate of reaction limited by the diffusion of X since it determines reactant mixing. Here, the resistor model fails to include the effects of small D_Y and indicates a rate of reaction that is an order of magnitude too small.

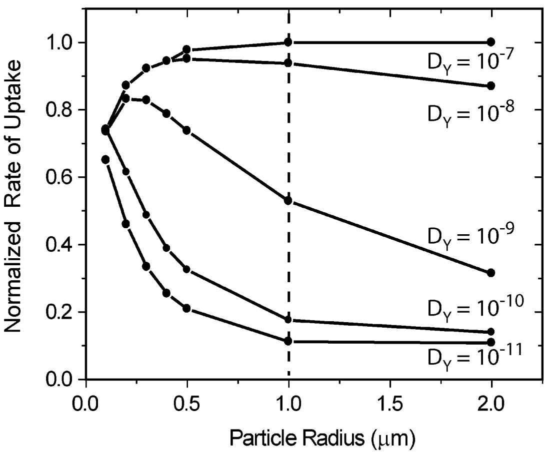

Figure 3. The dependence of the rate of uptake on the radius of the particle and the diffusion coefficient, D_Y, where the rate has been normalized by its value at $t = 0$. As expected, the larger particles are affected more by slow diffusion than are the smaller ones. The dashed line indicates the 1 μm particle size used in Figures 1 and 2. All parameters other than D_Y and a are the same as in Figure 1.

Though the decrease in the rate evident for smaller particle sizes ($a < 0.5$ μm) and fast diffusion ($D_Y \geq 10^{-9}$ cm^2 s^{-1}) may seem counter-intuitive, it can be understood in terms of the large degree of surface curvature. When X enters a small

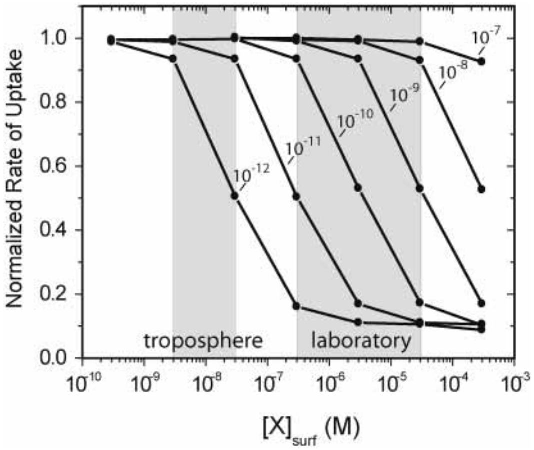

Figure 4. The dependence of the normalized rate of uptake on the diffusion coefficient, D_Y (in cm^2 s^{-1}), and the surface concentration, $[X]_{surf}$. The effect of D_Y is much more pronounced under laboratory conditions than those typical of the troposphere.

particle, it "sees" the surface in more directions and thus can escape more easily before reaction occurs than if it enters a flat surface. This observation has been discussed previously by Hanson et al.[24] and explains why uptake coefficients measured for flat surfaces in the lab must be corrected when applied to small spherical particles.

The effect of D_Y is also related to the gas pressure, P_X, because the surface concentration of X, $[X]_{surf}$, is assumed to be at its Henry's Law equilibrium value ($= H_X P_X$). We calculated $[Y(r,t)]$ as a function of both $[X]_{surf}$ and D_Y and then used the resistor model to determine the normalized rate of uptake, as in Figure 3. These rates, shown in Figure 4, demonstrate the strong dependence on D_Y when $[X]_{surf}$ is high (3×10^{-4} M). Because laboratory studies are generally conducted at such high concentrations in order to complete the reaction in minutes instead of days, diffusion may limit the rate of reaction under these circumstances. Thus, for many reactions the effects of diffusion may have to be taken into account to obtain useful uptake coefficients from laboratory experiments, but they will not be as significant under atmospheric conditions where partial pressures are often orders of magnitude lower.

Validity of the Resistor Model. The conventional resistor model assumes that the uptake of X is not limited by the diffusion of Y within the particle. We are now in a position to determine under what conditions this assumption is valid by comparing the results of the resistor model to our numerical solutions. In Figure 5 we show the minimum value of D_Y required to use the resistor model while incurring no more than 10% error in the calculated value of the rate of uptake. This minimum D_Y is plotted as a function of particle size for $[X]_{surf}$ ranging from 10^{-7} M to 10^{-4} M. It should be emphasized that the most general solution to the diffusion−reaction equations requires that the full dependence on all of the relevant parameters, H_X, D_X, P_X, D_Y, k_2, and a, be taken into consideration, and thus Figure 5 is strictly valid only for the reference reaction (O_3 + oleic acid particles). Use of a smaller rate coefficient, k_2, for example, would proportionally decrease the minimum values of D_Y that would ensure adequate mixing for accurate use of the resistor model. However, this figure provides a useful indication of the conditions under which the diffusion of Y can be expected to affect the rate of uptake significantly.

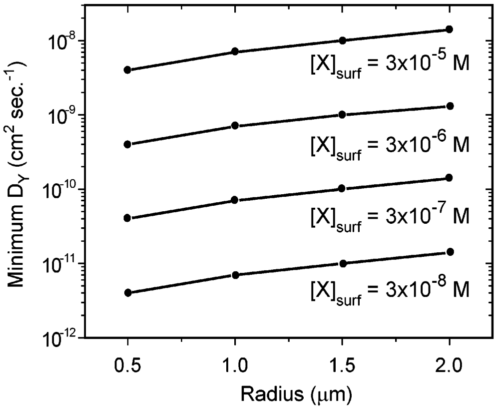

Figure 5. Minimum value of D_Y required to use the conventional resistor model to measure Γ_{rxn} from decays of [Y] with no more than 10% error. This value is a function of the particle size and the surface concentration of X. The other relevant parameters, k_2 and D_X, are the same as in Figure 1.

Resistor Model Including Diffusion within the Particle. *Modified Resistor Model.* The conventional resistor model used to describe reactive uptake is not valid for systems in which the diffusion of the condensed-phase species, Y, is slow. Inclusion of an additional conductance, recently proposed by Worsnop et al.,[16] extends the validity of the resistor model to smaller values of D_Y:

$$\Gamma^{Y}_{diff} = \frac{16RTD_Y}{P_X\bar{c}}\frac{[Y]}{a} \tag{7}$$

This expression was derived by considering the concentration gradient of Y within the particle and its effect on the diffusion of Y. This resistor ($1/\Gamma^{Y}_{diff}$) must be coupled with the reaction resistor ($1/\Gamma_{rxn}$), essentially representing a nonlinear differential equation which cannot be solved analytically. Therefore, part of the simplicity of the resistor model is lost and the solution for [Y] must now be obtained numerically.

Though eq 7 accounts for the gradient of Y, it neglects the effect on the diffusion of X. In the limit of small D_Y, Y is essentially stationary and the rate of reaction is determined by the rate at which X diffuses through Y. The concentration gradient of X within the particle is affected by the small D_Y, resulting in a faster rate of diffusion of X throughout the particle. Thus, an accurate description of this limit requires an additional conductance accounting for the increased rate of diffusion of X, which we introduce here:

$$\Gamma^{X}_{diff} = \frac{4RT}{\bar{c}}\frac{H_X D_X}{a[1 - ([Y]/[Y]_0)^{1/3}]} \tag{8}$$

This additional resistor ($1/\Gamma^{X}_{diff}$) is placed in parallel with the $1/\Gamma^{Y}_{diff}$ resistor of Worsnop et al., as shown in Figure 6. Thus, the conventional reactive uptake resistor, $1/\Gamma_{rxn}$, is modified by the two diffusion resistors, $1/\Gamma^{X}_{diff}$ and $1/\Gamma^{Y}_{diff}$. The conductance Γ^{Y}_{diff} represents diffusion of Y toward X, and Γ^{X}_{diff} represents diffusion of X toward Y in addition to that already included in Γ_{rxn}. When diffusion of Y is fast, uptake will be determined by Γ^{Y}_{diff} and Γ_{rxn}. However, as long as $\Gamma^{Y}_{diff} \gg \Gamma_{rxn}$, the rate of uptake will be determined by Γ_{rxn} alone. When diffusion of Y is slow, uptake is determined by both Γ^{X}_{diff} and Γ_{rxn}, and the relative weighting of these two resistors is governed by the magnitude of Γ^{Y}_{diff}.

Derivation of Modified Resistor Model. The expression in eq 8 was derived in the limit that Y does not diffuse at all and assuming that [X] decays linearly from the surface

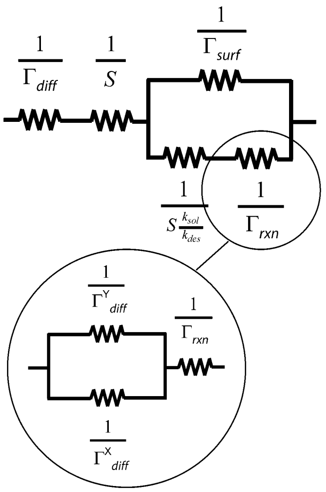

Figure 6. "Resistor" model for uptake of a gas-phase species by a particle. Each conductance is normalized to the gas-particle collision rate. Γ_{diff} represents the rate of diffusion of X to the particle, S is the sticking coefficient, $S^{k_{\mathrm{sol}}}/k_{\mathrm{des}}$ represents the rate of solvation into the bulk, and Γ_{surf} and Γ_{rxn} represent the rates of reaction at the surface and in the bulk, respectively. In the dual-diffusion model presented in this work, $1/\Gamma_{\mathrm{rxn}}$ is modified by resistors representing diffusion of Y, $1/\Gamma^{\mathrm{Y}}_{\mathrm{diff}}$,[16] and diffusion of X, $1/\Gamma^{\mathrm{X}}_{\mathrm{diff}}$, in the particle.

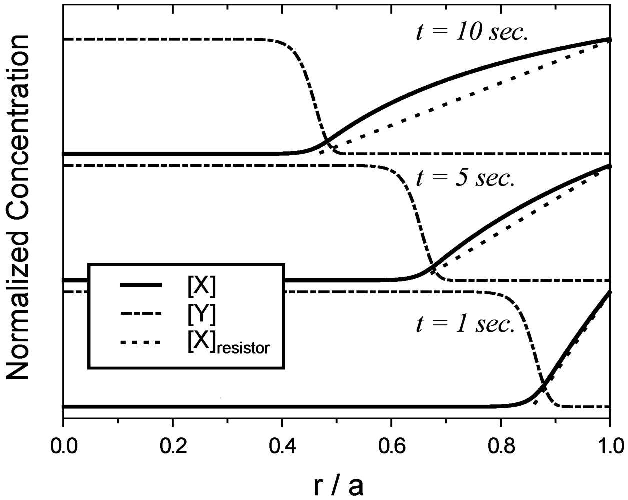

Figure 7. Concentration profiles of X (—) and Y (— -) calculated with the numerical PDE approach for $D_{\mathrm{Y}} = 0$ cm^2 s^{-1} at three different reaction times: $t = 1$ s, $t = 5$ s, and $t = 10$ s. The profile of [X] used to derive $\Gamma^{\mathrm{X}}_{\mathrm{diff}}$ is also shown for comparison (- - -). Note the close match between the slopes of the two [X] profiles at the surface ($r/a = 1$). All parameters are the same as in Figure 1.

(see Figure 7). A functional form for [X](r) can then be written, and from this an expression for the flux of X entering the particle can be derived:

$$[X](r) = H_{\mathrm{X}}P_{\mathrm{X}}\left(1 - \frac{a-r}{a-x}\right) \tag{9}$$

$$\mathrm{flux}_{\mathrm{X}} = D_{\mathrm{X}}\left(\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}r}\right)\Big|_{r=a} = D_{\mathrm{X}}\frac{H_{\mathrm{X}}P_{\mathrm{X}}}{a-x} \tag{10}$$

$$\Gamma^{\mathrm{X}}_{\mathrm{diff}} = \frac{\mathrm{flux}_{\mathrm{X}}}{P_{\mathrm{X}}\bar{c}/4RT} = \frac{4RT}{\bar{c}}\frac{D_{\mathrm{X}}H_{\mathrm{X}}}{a[1 - (\{[\mathrm{Y}]\}/\{[\mathrm{Y}]_0\})^{1/3}]} \tag{11}$$

where x is the point at which the two reactants meet. The value of x is rewritten as $a\cdot([Y]/[Y]_0)^{1/3}$ by assuming that the particle is completely reacted away outside of x but that it is not reacted at all inside of x (i.e., $[\mathrm{Y}] = [\mathrm{Y}]_0$ for $r < x$ and $[\mathrm{Y}] = 0$ for $r > x$). The validity of this assumption is borne out in Figure 7 which shows the concentration profiles of [X] at three different reaction times obtained with our coupled PDE approach (with $D_{\mathrm{Y}} = 0$ cm^2 s^{-1}) as well as that predicted by eq 9. For each time, the slope of [X] at the surface of the particle ($r/a = 1$) is approximated well by the slope of the line given by eq 9. The resulting expression for the flux, eq 10, therefore accurately represents the rate of uptake of X in the limit of no diffusion of Y.

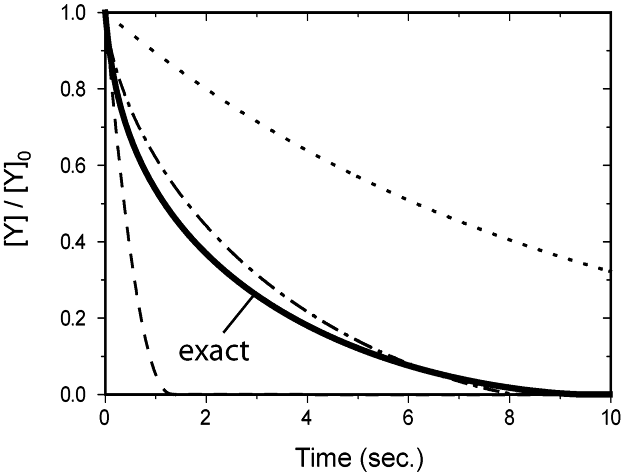

Figure 8. Calculated decay profiles of [Y] using the numerical PDE approach (—) and various resistor models where $D_{\mathrm{Y}} = 1 \times 10^{-10}$ cm^2 s^{-1} and all other parameters are the same as in Figure 1. The conventional resistor model with only Γ_{rxn} (- - -) overestimates the rate of reaction because the diffusion of Y is assumed to be fast. The resistor model of Worsnop et al.[16] (• • •), with both $\Gamma^{\mathrm{Y}}_{\mathrm{diff}}$ and Γ_{rxn}, underestimates the rate of reaction because the increase in the diffusion of X is not included. The dual diffusion model of this work (— •), including $\Gamma^{\mathrm{X}}_{\mathrm{diff}}$, $\Gamma^{\mathrm{Y}}_{\mathrm{diff}}$, and Γ_{rxn}, accurately accounts for diffusion of both X and Y within the particle.

Comparison of Resistor Models. The utility of our "dual-diffusion" modified resistor model is demonstrated in Figure 8 for the reference reaction with $D_{\mathrm{Y}} = 1 \times 10^{-10}$ cm^2 s^{-1} (all other parameters are the same as in Figure 1). The figure shows the decay curves calculated with the conventional resistor model, the Worsnop model (with the $1/\Gamma^{\mathrm{Y}}_{\mathrm{diff}}$ resistor) and our modified resistor model (with both $1/\Gamma^{\mathrm{X}}_{\mathrm{diff}}$ and $1/\Gamma^{\mathrm{Y}}_{\mathrm{diff}}$). The exact solution obtained with the numerical coupled PDE approach is also shown for comparison.

As with the Worsnop model, our modified resistor system must be solved numerically. Nevertheless, the numerical calculation of this resistor model is much less computationally intensive than the full numerical solution of the coupled set of PDEs. For example, the solution from the dual-diffusion resistor model required about 8000 times less CPU time than the corresponding solution obtained with the PDE approach (0.06 s vs 500 s on a Pentium V, 1.8 GHz computer with 512 MB RAM).

It is clear that the most complete and accurate treatment of the simultaneous diffusion and reaction of both X and Y is obtained by solving the coupled PDEs. However, our dual-diffusion resistor model offers a computationally simple alternative to this full solution with improved accuracy over both the conventional and Worsnop resistor models.

Conclusion

The usefulness of numerically solving the coupled partial differential equations describing simultaneous diffusion and reaction within a particle has been demonstrated. The solutions to these equations provide a concentration profile of each reactant as a function of both time and position within the particle. These solutions prove to be more accurate than those obtained with current resistor models in cases where diffusion within the particle limits uptake. The magnitude of this effect depends on both the size of the particle and the surface concentration of the species that is initially in the gas phase. Under typical atmospheric conditions the rate of uptake will not be limited by diffusion within the particle unless the particle is extremely viscous or solid. However, it is clear that for some laboratory experiments, in which larger particles and larger concentrations of gas-phase species are used, the diffusion of the condensed-phase species may represent a significant limitation to the rate of uptake and should be included in the analysis. The numerical solutions have also been used to improve the conventional resistor model to describe more accurately the rate of uptake when diffusion within the particle is limiting.

The numerical PDE approach offers a general method for treating both diffusion and reaction within the particle and can be used to solve systems more complicated than those presented here. For example, it is possible to include surface and bulk reactions occurring at different rates, secondary reactions of the initial reaction products, heterogeneous concentration domains within the particle, and time-varying rates of diffusion. This approach should prove to be a useful tool for investigating reactive uptake by authentic atmospheric particles as well as those used in laboratory studies under a wide range of conditions.

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