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Technical note

Analytical solution for transient partitioning and reaction of a condensing vapor species in a droplet

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ABSTRACT

We present the exact analytical solution of the transient equation of gas-phase diffusion of a condensing vapor to, and diffusion and reaction in, an aqueous droplet. Droplet-phase reaction is represented by first-order chemistry. The solution facilitates study of the dynamic nature of the vapor uptake process as a function of droplet size, Henry's law coefficient, and first-order reaction rate constant for conversion in the droplet phase.

1. Introduction

The general overall atmospheric gas-to-droplet conversion process comprises: (1) gas-phase diffusion from the bulk gas to the surface of a droplet; (2) absorption into the droplet; and (3) simultaneous diffusion and reaction inside the droplet. Step (1) is controlled by the steady-state gas-phase diffusion flux to the droplet surface and interfacial accommodation. (The time scale to establish a steady state molecular diffusion profile in the gas phase around a droplet of atmospheric size is of order 10^{-6} s (Seinfeld and Pandis, 2006), so that the gas-phase concentration of the condensing species around the droplet can be considered, at all times, to be in steady-state.) The overall rate at which the process of transfer of a species to the droplet phase occurs depends on its solubility, its droplet-phase diffusivity, and the rate of its droplet-phase chemical reaction. Coupled diffusion–reaction problems of this type have been simulated numerically (Shiraiwa et al., 2012) and both analytically and numerically (Vesala et al., 2001; Zaveri et al., 2013).

We present in this note the exact analytical solution to the diffusion-reaction problem for first-order reaction in the droplet phase. First-order reaction of the species in the droplet is not overly restrictive, as the time scale for more complex chemistry can be approximated by the inverse of the first-order rate constant. The solution is first obtained for a bulk gas-phase concentration that is maintained constant. We then derive the analytical solution for the case in which the bulk gas-phase concentration decreases with time owing to depletion by reaction in the droplet.

2. Formulation of the problem

The mathematical formulation of the problem described above is given by Shi and Seinfeld (1991) in the context of a solute dissolving and reacting in an atmospheric droplet. Let $G(r,t)$ and $A(r,t)$ be the gas-phase and droplet-phase concentrations, respectively, of the condensing species. The diffusive flux of the species into the droplet (of radius a) is

$$D_a\left(\frac{\partial A}{\partial r}\right)_{r=a} = \frac{1}{4}\alpha\bar{v}\left(G(a,t) - \frac{A(a,t)}{HRT}\right) \tag{1}$$

where α is the accommodation coefficient, the fraction of molecules striking the interface that are incorporated into the droplet, $\bar{v}$ is the mean molecular speed of the species in the gas phase, H is the Henry's Law coefficient for the species, R is the gas law constant, T is the temperature, and D_a is the diffusion coefficient of the species in the droplet phase. In this formulation, the gas–droplet equilibrium is represented in terms of a Henry's law coefficient, as is appropriate for a relatively dilute droplet. The gas-phase concentration profile $G(r,t)$ around the droplet at all times can be taken to be the steady state profile (Seinfeld and Pandis, 2006).

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$$G(r,t) = G_\infty(t) - \frac{a}{r}[G_\infty(t) - G(a,t)] \tag{2}$$

where $G_\infty(t)$ is the concentration of the condensing species in the bulk gas phase. Equality of fluxes across the air-droplet interface gives

$$D_a\left(\frac{\partial A}{\partial r}\right)_{r=a} = D_g\left(\frac{\partial G}{\partial r}\right)_{r=a} \tag{3}$$

Combining Equations (1)–(3), we get

$$D_a\left(\frac{\partial A}{\partial r}\right)_{r=a} + \frac{\upsilon_s}{HRT}A(a,t) = \upsilon_s G_\infty(t) \tag{4}$$

where

$$\upsilon_s = \frac{\frac{\alpha\bar{\upsilon}}{4}\frac{D_g}{a}}{\frac{\alpha\bar{\upsilon}}{4}+\frac{D_g}{a}} \tag{5}$$

Initially we consider the case in which $G_\infty(t)$ is a constant, G_∞; that is, the concentration of the condensing species in the bulk gas phase is maintained at a constant value.

The transient diffusion–reaction problem in the droplet phase obeys,

$$\frac{\partial A(r,t)}{\partial t} = D_a\left(\frac{\partial^2 A(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial A(r,t)}{\partial r}\right) - kA(r,t) \tag{6}$$

$$A(r,0) = A_1 \tag{7}$$

$$\left(\frac{\partial A}{\partial r}\right)_{r=0} = 0 \quad \text{(symmetry at droplet center)} \tag{8}$$

$$-D_a\left(\frac{\partial A}{\partial r}\right)_{r=a} = \gamma(A(a,t) - A_0) \tag{9}$$

where A_1 is an arbitrary initial concentration in the droplet and

$$\gamma = \frac{\upsilon_s}{HRT} \tag{10}$$

$$A_0 = HRTG_\infty \tag{11}$$

Using a transformation due to Danckwerts (See Supplementary Material), the solution to equations (6)–(9) can be obtained from that for the identical problem in the absence of reaction ($k = 0$). Calling the droplet-phase solution to the pure diffusion problem $C(r,t)$, the two solutions are related by

$$A(r,t) = k\int_0^t C(r,t')e^{-kt'}dt' + C(r,t)e^{-kt} \tag{12}$$

3. Solution of the transient diffusion–reaction problem

The solution of the pure diffusion problem, $C(r,t)$, governed by (6)–(9) with $k = 0$ is (Crank, 1956; equation (6.40)),

$$C(r,t) = -\frac{2A_0La}{r}\sum_{n=1}^{\infty}\frac{e^{-\frac{D_a\beta_n^2 t}{a^2}}\sin\left(\beta_n\frac{r}{a}\right)}{\left\{\beta_n^2 + L(L-1)\right\}\sin(\beta_n)} \tag{13}$$

where β_n are the roots of

$$\beta_n\cot(\beta_n) + L - 1 = 0, \quad L = \frac{a\gamma}{D_a} \tag{14}$$

We show in the Supplementary Material the step-by-step derivation of this solution.

Using equation (12), the full solution for $A(r,t)$ in which $G_\infty(t)$ is a constant, G_∞, is:

$$\begin{aligned} A(r,t) = {} & k\int_0^t\left[HRTG_\infty - \frac{2HRTG_\infty La}{r}\sum_{n=1}^{\infty}\frac{e^{-\frac{D_a\beta_n^2 t'}{a^2}}\sin\left(\beta_n\frac{r}{a}\right)}{\left\{\beta_n^2+L(L-1)\right\}\sin(\beta_n)}\right]e^{-kt'}dt' \\ & + \left[HRTG_\infty - \frac{2HRTG_\infty La}{r}\sum_{n=1}^{\infty}\frac{e^{-\frac{D_a\beta_n^2 t'}{a^2}}\sin\left(\beta_n\frac{r}{a}\right)}{\left\{\beta_n^2+L(L-1)\right\}\sin(\beta_n)}\right]e^{-kt}\,\beta_n\cot(\beta_n) + L - 1 = 0, \quad L = \frac{a\gamma}{D_a} \end{aligned} \tag{15}$$

The above solution for the coupled diffusion-reaction problem holds for a constant G_∞. We now wish to extend that solution to the case in which $G_\infty = G_o$ at $t = 0$ but can decrease as a function of time owing to uptake and conversion in the droplet phase. As G_∞ changes with time, the entire solution itself changes with time. The fully time-dependent problem, in which G_∞ is changing on the

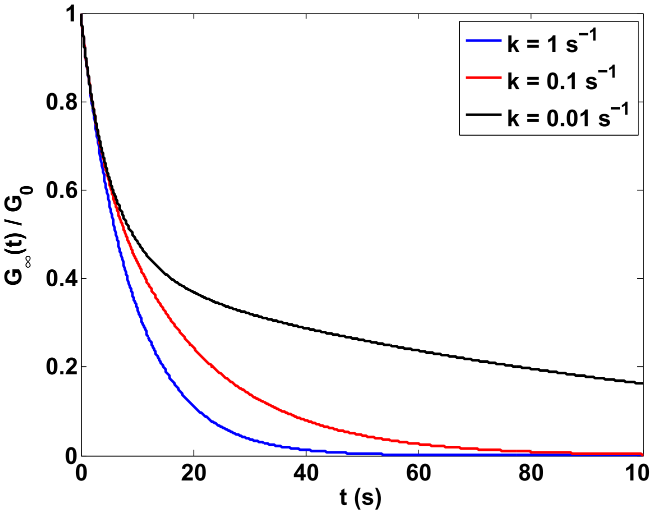

Fig. 1. Dimensionless bulk gas-phase concentration of the condensing species as a function of time for a range of first-order reaction rate constant values.