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Impact of the Knudsen number and mass-transfer expression on multi-phase kinetic modeling

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ABSTRACT

Three different mass-transfer expressions are employed within the Model of Aerosol, Gas, and Interfacial Chemistry (MAGIC) to study gas-phase molecular chlorine and bromine production from NaCl and NaBr aerosols, respectively. Simulations of chamber experiments are performed in which NaCl aerosols react with gas-phase ozone in the presence of UV light, in order to identify the importance of the Knudsen number and mass-transfer expression in systems with varying contributions from gas-phase, aqueous-phase, and interfacial chemistry. In the case of NaBr aerosols, simulations are performed of both dark and photolytic conditions. A range of Knudsen numbers spanning the continuum, transition and free-molecular regimes is studied. Particle size is varied over three orders of magnitude, and particle concentration is changed to keep either (a) total aerosol volume or (b) total aerosol surface area constant. When total aerosol volume is constant, the total amount of surface area available for interfacial reaction increases linearly with Knudsen number. Consequently peak gas-phase Cl_2 and Br_2 concentrations increase by two orders of magnitude from the continuum regime to the free-molecular regime. When total aerosol surface area is constant, total aerosol volume is inversely proportional to Knudsen number, with lesser volume being available at higher Knudsen numbers. Consequently Cl^- depletion in the kinetic regime leads to most gas-phase Cl_2 being produced in the transition regime. Gas-phase Br_2 concentration trends are determined by aqueous-phase reaction mechanisms, leading to a monotonic decrease in production with Knudsen number. At all Knudsen numbers, more gas-phase bromine is produced in the photolytic case than in the dark case, the difference being significant in the transition regime. Results of this study suggest that halogen production is insensitive to the mass-transfer expression used in the simulations.

1. Introduction

Detailed models of atmospheric systems include non-equilibrium kinetics, with interactions between gaseous and aqueous-phases. Although such detailed models are intractable when used in large three-dimensional simulations, valuable insight is gleaned into important processes of atmospheric relevance. For example, Knipping et al. (2000) obtained evidence for interfacial reactions occurring on the surface of aerosol particles using the MAGIC model (Model of Aerosol, Gaseous, and Interfacial Chemistry). Knipping et al. (2000) and subsequent studies (Hunt et al., 2004; Thomas et al., 2006, 2007) have shown that far greater amounts of gaseous Cl_2 and Br_2 are released into the gas-phase due to interfacial reactions than is possible from reactions in the gas-phase or aqueous-phase when considering deliquesced NaCl and NaBr particles respectively. Chlorine chemistry is important in ozone production via photochemical reactions involving VOCs and NO_x in coastal regions since VOCs, NO_x, and sea-salt particles are all present in significant concentrations here (Knipping and Dabdub, 2003). Over the open ocean, in the remote marine boundary layer, and in polar regions, halogen chemistry plays an important role in ozone destruction (Foster et al., 2001; Piot and von Glasow, 2008; Read et al., 2008). In all these regions, sea-salt aerosol is present in the marine boundary layer at relative humidities well over the deliquescence point. The interfacial reactions examined in the above studies are the following:

$$OH_{(g)} + Cl^-_{surface} \rightarrow 0.5Cl_{2(g)} + OH^-_{(aq)} \quad (1)$$

$$OH_{(g)} + Br^-_{surface} \rightarrow 0.5Br_{2(g)} + OH^-_{(aq)} \quad (2)$$

$$O_{3(g)} + Br^-_{surface} \rightarrow 0.5Br_{2(g)} + O^-_{3(aq)}. \quad (3)$$

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The hydroxyl radical in the first two reactions is generated by the photolysis of ozone (Finlayson-Pitts and Pitts, 2000),

$$O_{3(g)} + h\nu \rightarrow O(^1D)_{(g)} + O_{2(g)} \quad (4)$$

$$O(^1D)_{(g)} + H_2O_{(g)} \rightarrow 2OH_{(g)}. \quad (5)$$

Reactions (4) and (5) occur only during photolytic conditions, i.e., when ozone is exposed to a UV light source. Reaction with ozone on the surface of NaBr particles presents an alternate route for $Br_{2(g)}$ to be released from aerosols and may be a significant source of bromine in the dark when $OH_{(g)}$ is not available. The interface reactions, as represented above, constitute the net outcome of a process that most likely involves one or more intermediates.

Any multi-phase kinetics model in general, and MAGIC in particular, consists of numerous gaseous and aqueous reaction rate constants representing chemistry in the respective phases, Henry's law constants and mass accommodation coefficients used in determining mass-transfer rates between the phases, and parameters to calculate interfacial reaction rates. In situations that are of atmospheric relevance, it is likely that the gaseous and aqueous-phases are not in equilibrium. As a result, non-equilibrium expressions are used to define the rate of mass transfer between the phases. In many atmospheric models, such as those described in Jacob (2000) and von Glasow et al. (2002), the mass-transfer expression due to Schwartz (1986) is used due to its simplicity, both conceptually and computationally. There have been limited studies that use other mass-transfer expressions, for example Pandis and Seinfeld (1989), but none of them compare results using different mass-transfer expressions. The studies that compare mass-transfer expressions often are limited in scope. For instance, Sander (1999) compared values of the mass-transfer coefficient, k_{mt}, obtained using two different expressions, but did not include them in an atmospherically relevant model.

The present work is aimed at implementing different mass-transfer expressions in a detailed chemical kinetics model of atmospheric relevance. For this purpose, three expressions for the mass-transfer coefficient, developed by Fuchs (1964), Fuchs and Sutugin (1971), and Schwartz (1986), are implemented in MAGIC and are used to study the production of gas-phase molecular chlorine and bromine from deliquesced NaCl and NaBr particles respectively. Since exact rate expressions for the interfacial reactions (1)–(3) are not known, the interfacial reaction rates are calculated based on rates of mass-transfer to the interface. This approach also is adopted by Jacob (2000) and Thomas et al. (2006, 2007). Since interfacial reaction rates depend on the mass-transfer rate using this approach, the importance of using a detailed, physically sound model to represent inter-phase mass transfer is enhanced greatly.

This paper is organized as follows. In the next section, a description of the problem is provided by introducing and explaining the three mass-transfer expressions. The various situations considered to compare the three mass expressions are discussed in Section 3. Results are presented and discussed in Section 4. Finally, conclusions and atmospheric implications are provided in Section 5.

2. Problem description

In general, a non-equilibrium, multi-phase kinetics model should account for the following physical and chemical processes: (i) gas-phase diffusion and chemical reactions; (ii) aqueous-phase diffusion and chemical reactions; (iii) interfacial mass transport; and (iv) interfacial reactions, if any. MAGIC includes detailed sub-models for each of the above processes. The model was developed to simulate time evolution of chemical species in the gas- and aqueous-phases for reactions of NaCl and NaBr particles in the presence of ozone in an enclosed chamber. The chamber design, experiments, and MAGIC are described in detail elsewhere (Oum et al., 1998; DeHaan et al., 1999; Knipping et al., 2000; Knipping and Dabdub, 2002; Hunt et al., 2004). The model includes a total of 24 gas-phase and 44 aqueous-phase species, whose concentrations are governed by the following equations (Thomas et al., 2006, 2007):

$$\frac{\partial C_g}{\partial t} = R_g \pm \omega R_{int} - \omega k_{mt}\left(C_g - \frac{C_{aq}}{HRT}\right) \quad (6)$$

$$\frac{\partial C_{aq}}{\partial t} = R_{aq} \mp R_{int} + k_{mt}\left(C_g - \frac{C_{aq}}{HRT}\right), \quad (7)$$

where C_g (molecules cm^{-3}) and C_{aq} (mol L^{-1}) represent species concentration in the gas- and aqueous-phases respectively, t denotes time, R_g, R_{aq}, and R_{int} (concentration s^{-1}) denote chemical reaction rates in the gas-phase, aqueous-phase and at the interface respectively, k_{mt} (s^{-1}) is the mass-transfer coefficient, H (M atm^{-1}) is the effective Henry's law constant, R is the universal gas constant, T is the absolute temperature (298 K), and ω is a dimensionless ratio representing the volumetric aqueous aerosol liquid water mixing ratio. Species concentrations, as a function of time, are obtained by solving the coupled system of differential equations simultaneously for each of the gas-phase and aqueous-phase species involved.

2.1. *Mass transport between the phases*

In MAGIC, 15 species are transported between the gas- and aqueous-phases across the aerosol surface. For these species, interfacial mass transport is described by the use of a mass-transfer coefficient, k_{mt}. The mass-transfer coefficient is a first-order rate coefficient that combines first-order rates of gas-phase diffusion to the aerosol surface and kinetic, or 'free-molecular', transport across the aerosol surface.

Gas-phase diffusion far away from aerosol particles is governed by continuum transport. Closer to the particles, however, a continuum assumption is no longer universally valid and size of the particles relative to the mean free path of the gas-phase molecules must be considered. When the particle radius (r) is of the same order as the mean free path (λ) of the gas-phase molecules, the transition regime is in effect. In this regime, species concentration distributions are governed rigorously by the Boltzmann equation for which a general solution does not exist. To avoid solving the Boltzmann equation directly, an approach based on flux-matching is used. Non-continuum effects are assumed to be limited to a small spherical region of thickness Δ around the particle. This thickness (Δ) is of the order of the mean free path and the kinetic theory of gases is assumed to apply in this region. Three mass-transfer expressions based on different flux-matching schemes, which use the same definition of the mean free path, $\lambda = 3D_g/\overline{v}$, are employed in this study.

Schwartz (1986) derived an expression for the mass transport coefficient by assuming that at the droplet surface, transport suddenly switches from the continuum regime to the kinetic regime, implementing a flux-matching at the droplet surface ($\Delta = 0$). In this scenario, the mass-transfer coefficient is,

$$k_{mt}^{Sch} = \left(\frac{r^2}{3D_g} + \frac{4r}{3\overline{v}\alpha}\right)^{-1}, \quad (8)$$

where D_g (cm^2 s^{-1}) is the gas-phase diffusivity, $\overline{v}$ (cm s^{-1}) is the mean molecular speed, and α (dimensionless) is the mass accommodation coefficient.