

# Modeling kinetic partitioning of secondary organic aerosol and size distribution dynamics: representing effects of volatility, phase state, and particle-phase reaction

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## Abstract

This paper describes and evaluates a new framework for modeling kinetic gas-particle partitioning of secondary organic aerosol (SOA) that takes into account diffusion and chemical reaction within the particle phase. The new framework uses a combination of: (a) an analytical quasi-steady-state treatment for the diffusion-reaction process within the particle phase for fast-reacting organic solutes, and (b) a two-film theory approach for slow- and non-reacting solutes. The framework is amenable for use in regional and global atmospheric models, although it currently awaits specification of the various gas- and particle-phase chemical reactions and the related physicochemical properties that are important for SOA formation. Here, the framework is implemented in the computationally efficient Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) to investigate the competitive growth dynamics of the Aitken and accumulation mode particles. Results show that the timescale of SOA partitioning and the associated size distribution dynamics depend on the complex interplay between organic solute volatility, particle-phase bulk diffusivity, and particle-phase reactivity (as exemplified by a pseudo-first-order reaction rate constant), each of which can vary over several orders of magnitude. In general, the timescale of SOA partitioning increases with increase in volatility and decrease in bulk diffusivity and rate constant. At the same time, the shape of the aerosol size distribution displays appreciable

1 narrowing with decrease in volatility and bulk diffusivity and increase in rate constant. A  
2 proper representation of these physicochemical processes and parameters are needed in the  
3 next generation models to reliably predict not only the total SOA mass, but also its  
4 composition and number size distribution, all of which together determine its overall optical  
5 and cloud-nucleating properties.

6

## 7 **1 Introduction**

8 Submicron sized atmospheric aerosol particles are typically composed of ammonium, sulfate,  
9 nitrate, black carbon, organics, sea salt, mineral dust, and water that are often internally mixed  
10 with each other in varying proportions. Depending on their dry state composition and overall  
11 hygroscopicity, aerosol particles in the size range 0.03-0.1  $\mu\text{m}$  (dry diameter) and larger may  
12 act as cloud condensation nuclei (CCN) (Dusek et al., 2006; Gunthe et al., 2009, 2011) while  
13 those larger than 0.1  $\mu\text{m}$  (wet diameter) efficiently scatter solar radiation. Aerosol number and  
14 composition size distributions, therefore, together hold the key to determining its overall  
15 climate-relevant properties.

16 Organic compounds constitute 20-90% of the submicron aerosol mass and are thought to play  
17 a vital role in both the direct and indirect aerosol radiative forcing of climate (Kanakidou et  
18 al., 2005). While primary organic aerosols (POA) from fossil fuel combustion and biomass  
19 burning are directly emitted into the submicron size range, the dominant source of organic  
20 aerosols is secondary, which involves gas-to-particle conversion of many different volatile  
21 organic compounds (VOCs) of both anthropogenic and biogenic origin (Zhang et al., 2007).  
22 Furthermore, biogenic VOCs are estimated to be the dominant source of secondary organic  
23 aerosol (SOA), but their formation appears to be strongly influenced by anthropogenic  
24 emissions (Weber et al., 2007; Hoyle et al., 2011; Shilling et al., 2013). Organic vapors are  
25 also implicated in facilitating new particle formation initiated by sulfuric acid (Kulmala et al.,  
26 2004; Paasonen et al., 2010; Kuang et al., 2012) and are found to play a crucial role in the  
27 subsequent growth of the nanoparticles (Smith et al., 2008; Pierce et al., 2011, 2012; Riipinen  
28 et al., 2011; Winkler et al., 2012). Thus, the majority of the optically- and CCN-active  
29 particles are produced through the growth of smaller particles by condensation of SOA  
30 species (Riipinen et al., 2012). It is therefore necessary that climate models be able to

1 accurately simulate not just the total organic mass loading, but also the evolution of aerosol  
2 number and composition size distributions resulting from SOA formation.

3 It is broadly understood that, in cloud-free air, SOA forms via three possible mechanisms: 1)  
4 effectively irreversible condensation of very low volatility organic vapors produced by gas-  
5 phase oxidation (Donahue et al., 2011; Pierce et al., 2011); 2) volume-controlled reversible  
6 absorption of semi-volatile organic vapors into pre-existing particle organic phase according  
7 to Raoult's law (Pankow, 1994) or into preexisting particle aqueous phase according to  
8 Henry's law (Carlton and Turpin, 2013); and 3) absorption of semi-volatile and volatile  
9 organic vapors into pre-existing aerosol followed by particle-phase reactions to form  
10 effectively non-volatile products such as organic salts (Smith et al., 2010 ), oligomers, organic  
11 acids, and other high molecular weight oxidation products (Gao et al., 2004; Kalberer et al.,  
12 2004; Heaton et al., 2007; Nozière et al., 2007; Ervens et al., 2010; Wang et al., 2010; Hall  
13 and Johnston, 2011; Liu et al., 2012), hemiacetals (Kroll et al., 2008; Ziemann et al., 2012;  
14 Shiraiwa et al., 2013), and organosulfates (Surratt et al., 2007; Zaveri et al., 2010). Recently,  
15 Liu et al. (2014) presented an exact analytical solution to the diffusion-reaction problem in the  
16 aqueous phase. While aqueous-phase chemistry in cloud droplets is also a potential source of  
17 SOA (Carlton et al., 2008; Ervens et al., 2008; Mouchel-Vallon et al., 2013), this route is not  
18 considered in the present study. Several recent studies also indicate that the phase state of  
19 SOA may be viscous semi-solids under dry and moderate relative humidity conditions  
20 (Virtanen et al., 2010; Vaden et al., 2011; Saukko et al., 2012), with very low particle-phase  
21 bulk diffusivities (Abramson et al., 2013; Renbaum-Wolff et al., 2013). The timescales of  
22 SOA partitioning (Shiraiwa and Seinfeld, 2012b) and the resulting aerosol size distributions  
23 from these three mechanisms can be quite different, and the particle phase state is expected to  
24 modulate the growth dynamics as well.

25 Riipinen et al. (2011) analyzed the evolution of ambient aerosol size distributions with a  
26 simplified model consisting of mechanisms #1 and #2 for liquid particles and concluded that  
27 both mechanisms were roughly equally needed to explain the observed aerosol growth.  
28 Perraud et al. (2012) studied the gas-particle partitioning of organic nitrate vapors formed  
29 from simultaneous oxidation of  $\alpha$ -pinene by  $O_3$  and  $NO_3$  in a flow tube reactor. Their model  
30 analysis suggested that, despite being semi-volatile, the organic nitrate species had effectively  
31 irreversibly condensed (mechanism #1) as their adsorbed layers were continuously "buried"  
32 in presumably semi-solid particles by other incoming organic vapors. In a theoretical study,

1 Zhang et al. (2012) contrasted the aerosol size distributions produced by mechanisms #1 and  
2 #2 for liquid particles and illustrated the roles of solute volatility and vapor source rate in  
3 shaping the size distribution via mechanism #2. In another theoretical study, Shiraiwa and  
4 Seinfeld (2012b) used the detailed multilayer kinetic flux model KM-GAP (Shiraiwa et al.,  
5 2012a; based on the PRA model framework of Pöschl-Rudich-Ammann, 2007) to investigate  
6 the effect of phase state on SOA partitioning. They showed that the timescale for gas-particle  
7 equilibration via mechanism #2 increases from hours to days for organic aerosol associated  
8 with semi-solid particles, low volatility, large particle size, and low mass loadings. More  
9 recently, Shiraiwa et al. (2013a) studied SOA formation from photooxidation of dodecane in  
10 the presence of dry ammonium sulfate seed particles in an environmental chamber. Their  
11 analysis of the observed aerosol size distribution evolution with the KM-GAP model revealed  
12 the presence of particle-phase reactions (i.e., mechanism #3), which contributed more than  
13 half of the SOA mass, with the rest formed via mechanism #2. Furthermore, the physical state  
14 of the SOA was assumed to be semi-solid with an average bulk diffusivity of  $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ ,  
15 and the particle-phase reactions were predicted to occur mainly on the surface.

16 While valuable insights into the effect of phase state on SOA formation have emerged from  
17 several recent studies, a comprehensive, quantitative analysis of the effects of organic solute  
18 volatility, phase state, and particle-phase reaction on aerosol growth dynamics has not yet  
19 been performed. Additionally, there is a lack of a kinetic SOA partitioning treatment for semi-  
20 solids (with particle-phase chemical reactions) that is amenable for use in regional and global  
21 atmospheric models. The present work addresses both these topics. The paper is structured as  
22 follows. In Sect. 2, we examine the dynamics of diffusion and reaction in a spherical particle  
23 with an analytical solution to the problem. In Sect. 3, we extend the MOSAIC (Model for  
24 Simulating Aerosol Interactions and Chemistry) aerosol model (Zaveri et al., 2008) to include  
25 a new framework for kinetic gas-particle partitioning of SOA and evaluate it against a  
26 rigorous model based on the finite difference approach. The new framework uses a  
27 combination of: (a) an analytical quasi-steady-state treatment for the diffusion-reaction  
28 process within the particle phase for fast-reacting species, and (b) a two-film theory approach  
29 for slow- and non-reacting organic solutes. The framework is amenable for eventual use in  
30 regional and global climate models, although it currently awaits specification of the actual  
31 particle-phase reactions that are important for SOA formation. In Sect. 4, we apply the model  
32 to evaluate the timescale of SOA partitioning and the associated evolution of the number and

1 composition size distributions for a range of solute volatilities, bulk diffusivities, and particle-  
2 phase reaction rates. We close with a summary of our findings and their implications.

## 3 **2 Dynamics of Diffusion and Reaction within a Particle**

4 Consider an organic solute  $i$  that diffuses from the gas phase to a single spherical organic  
5 aerosol particle and reacts irreversibly with a pseudo-first-order rate constant  $k_c$  ( $s^{-1}$ ) as it  
6 diffuses inside the particle. This process is illustrated in Fig. 1 using three species ( $P_1$ ,  $P_2$ , and  
7  $P_3$ ) for simplicity. The organic solute  $P_1$  diffuses and reacts to form a non-volatile species  $P_2$   
8 inside an organic particle (of radius  $R_p$ ) that is initially composed of a non-volatile organic  
9 species  $P_3$ . The solute's gas-phase concentrations far away from the particle (i.e., in the bulk  
10 gas-phase) and just above the particle surface are  $\bar{C}_g$  and  $\bar{C}_g^s$  ( $\text{mol cm}^{-3}(\text{air})$ ), respectively.  
11 The solute's particle-phase concentration just inside the particle surface and at any location in  
12 the bulk of the particle are denoted as  $A^s$  and  $A$  ( $\text{mol cm}^{-3}(\text{particle})$ ), respectively. The gas-  
13 and particle-phase diffusivities of the solute are  $D_g$  and  $D_b$  ( $\text{cm}^2 \text{s}^{-1}$ ), respectively.

14 In this section we shall focus on the dynamics of diffusion and reaction *inside* the particle. In  
15 order to derive the timescales relevant to this problem, the particle, initially free of the organic  
16 solute (i.e., at time  $t = 0$ ), is assumed to be exposed to a constant concentration just inside the  
17 particle surface,  $A_i^s$ , at all times  $t > 0$  (this assumption will be relaxed in Sect. 3 where we  
18 will relate the temporally changing gas-phase concentration of the solute to its particle-phase  
19 concentration). Assuming that the diffusive flux of the solute into the particle follows Fick's  
20 law, the transient partial differential equation describing the particle-phase concentration  
21  $A_i(r, t)$  as a function of radius  $r$  and time  $t$  can be written as:

$$22 \quad \frac{\partial A_i(r, t)}{\partial t} = D_{b,i} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial A_i(r, t)}{\partial r} \right) - k_{c,i} A_i(r, t). \quad (1)$$

23 The particle is assumed to be spherically symmetrical with respect to the concentration  
24 profiles of the organic solute in the particle at any given time, so the concentration gradient at  
25 the center of the particle (i.e.,  $r = 0$ ) is always zero. These assumptions give rise to the  
26 following initial and boundary conditions:

$$27 \quad \text{I.C.: } A_i(r, 0) = 0, \quad (2a)$$

$$28 \quad \text{B.C. 1: } A_i(R_p, t) = A_i^s, \quad (2b)$$

1 B.C. 2:  $\frac{\partial A_i(0,t)}{\partial r} = 0$ . (2c)

2 Equation (1) with conditions (2) can be analytically solved by first solving the pure diffusion  
 3 problem in the absence of reaction (Carslaw and Jaeger, 1959; Crank, 1975) and then  
 4 extending the solution to the case of first-order chemical reaction using the method of  
 5 Danckwerts (1951) to yield the solution:

6 
$$\frac{A_i(r,t)}{A_i^s} = \frac{R_p}{r} \frac{\sinh(q_i r / R_p)}{\sinh(q_i)} + \frac{2R_p}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n n \sin(n\pi r / R_p)}{(q_i / \pi)^2 + n^2} \exp\left\{-\left(k_{c,i} + \frac{n^2 \pi^2 D_{b,i}}{R_p^2}\right)t\right\}$$
 (3)

7 where  $q_i$  is a dimensionless diffusion-reaction parameter defined as the ratio of the particle  
 8 radius  $R_p$  to the so-called reacto-diffusive length  $\sqrt{D_{b,i} / k_{c,i}}$  (Pöschl et al., 2007):

9 
$$q_i = R_p \sqrt{\frac{k_{c,i}}{D_{b,i}}}$$
 (4)

10 It should be noted that this solution assumes that  $R_p$  remains constant with time, so diffusion  
 11 of additional material into the particle is relatively small (this assumption will also be relaxed  
 12 in Sect. 3). It is also worth noting here that in glassy particles, the diffusion fronts of  
 13 plasticizing agents (such as water) may move linearly inward, leading to a linear dependence  
 14 on  $R_p$  instead of  $R_p^2$  in Fickian diffusion (Zobrist et al. 2011).

15 Now, the timescale for Fickian diffusion of the dissolved solute  $i$  in the particle,  $\tau_{da}$ , and the  
 16 timescale for chemical reaction,  $\tau_c$  (Seinfeld and Pandis, 2006) are defined as:

17 
$$\tau_{da,i} = \frac{R_p^2}{\pi^2 D_{b,i}}$$
 (5)

18 
$$\tau_{c,i} = \frac{1}{k_{c,i}}$$
 (6)

19 The model described by these equations has been applied to investigate mass transfer  
 20 limitation to the rate of SO<sub>2</sub> oxidation in cloud droplets (Schwartz and Freiberg, 1981; Shi and  
 21 Seinfeld, 1991), for which the droplets typically exceed 10 μm diameter, with the aqueous-

1 phase diffusivity about  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . Here we apply this model to analyze the effects of  
2 particle-phase reactions in organic particles of sizes ranging from  $\sim 10^{-3}$  to  $1 \text{ }\mu\text{m}$  diameter,  
3 with  $D_b$  values ranging from  $<10^{-18}$  to  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (Renbaum-Wolff et al., 2013). Since the  
4 actual particle-phase reactions of various organic species and the associated rate constants are  
5 still not well defined, we use a pseudo-first-order reaction as a proxy and vary its rate constant  
6  $k_c$  over several orders of magnitude ( $10^{-5}$  to  $10^{-1} \text{ s}^{-1}$ ) to examine its effect on the dynamics of  
7 particle growth.

8 The right-hand-side of Eq. (3) comprises two terms. The first term is the concentration profile  
9 at steady state with the surface concentration, while the second term describes the temporal  
10 evolution of the concentration profile. At steady state, the transient term disappears for  
11  $t \gg \tau_{da}$  and  $\tau_c$ . Fig. 2 illustrates the relative effects of bulk diffusivity and reaction rate  
12 constant on the temporal evolution of the diffusing solute concentration profiles within a  
13 particle of diameter  $D_p = 0.1 \text{ }\mu\text{m}$ . The top row represents a liquid organic particle with a  
14 rather high bulk diffusivity,  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , with (a) no reaction ( $k_c = 0$ ), and (b) a modest  
15 reaction rate constant,  $k_c = 5 \times 10^{-4} \text{ s}^{-1}$ . In case (a),  $\tau_{da} = 2.5 \text{ }\mu\text{s}$ , and the solute attains a  
16 uniform steady-state concentration profile across the particle radius in a little over  $8 \text{ }\mu\text{s}$  (i.e.,  
17 about  $4\tau_{da}$ ). The temporal evolution of the concentration profiles in case (b) appears to be  
18 identical to case (a) despite the presence of a chemical reaction, because  $\tau_{da}$  is  $2.5 \text{ }\mu\text{s}$  but  $\tau_c =$   
19  $2000 \text{ s}$ , i.e., diffusion occurs much more rapidly than reaction. In contrast, the bottom row  
20 represents a semi-solid organic particle,  $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ , with (c) no reaction, and (d)  $k_c =$   
21  $5 \times 10^{-4} \text{ s}^{-1}$ . In case (c),  $\tau_{da} = 2533 \text{ s}$  (i.e., 42 min) and  $\sim 160 \text{ min}$  is required for the solute to  
22 attain a uniform steady state profile. In case (d),  $\tau_{da}$  and  $\tau_c$  are comparable, and as a result the  
23 solute not only reaches the steady state sooner (in about 60 min) than in the no-reaction case,  
24 but also the steady state concentration profile is visibly non-uniform. This is a result of the  
25 fact that there is sufficient time for appreciable amounts of the solute to be consumed by the  
26 reaction as it diffuses towards the center of the particle.

27 Fig. 3 illustrates the steady state concentration profiles for a range of  $k_c$  values (from  $10^{-5}$  to  
28  $0.1 \text{ s}^{-1}$ ) in a particle of diameter  $D_p = 0.1 \text{ }\mu\text{m}$  with four different  $D_b$  values: (a)  $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  
29 (b)  $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ , (c)  $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ , and (d)  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$ . All together, these cases represent

1 twenty different combinations of  $\tau_{da}$  and  $\tau_c$ . In case (a),  $\tau_{da} \ll \tau_c$  for all the  $k_c$  values  
 2 considered here, and as a result the steady state concentration profiles are essentially uniform  
 3 across the entire particle, with the consumption of the solute by chemical reaction occurring  
 4 uniformly across the entire volume of the particle. In case (b), even though the particle is  
 5 considered to be a semi-solid with  $D_b = 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ ,  $\tau_{da}$  and  $\tau_c$  become comparable only  
 6 when  $k_c = 0.1 \text{ s}^{-1}$  (and higher). However, slower reactions produce non-uniform steady state  
 7 concentration profiles in cases (c) and (d) for  $D_b$  values  $10^{-13} \text{ cm}^2 \text{ s}^{-1}$  and lower. In these  
 8 cases, most of the solute is consumed near the surface of the particle, with a concentration that  
 9 becomes progressively depleted towards the center of the particle as  $k_c$  increases. Thus, the  
 10 particle growth is volume reaction-controlled when the concentration profile is uniform and  
 11 tends to be surface reaction-controlled at the other extreme.

12 Since the timescale for diffusion varies as  $R_p^2$ , the diffusion limitation to reaction also  
 13 depends strongly on particle size. As shown in Fig. 4, the relative effects of particle size, bulk  
 14 diffusivity, and reaction rate on the shape of the steady state concentration profiles are  
 15 concisely captured in terms of the dimensionless parameter  $q$ , which is a function of  $R_p$ ,  $k_c$ ,  
 16 and  $D_b$  (Eq. (4)). At low values of  $q$  ( $< 0.5$ ), the steady state concentration profile is nearly  
 17 uniform, but becomes increasingly non-uniform for  $q$  values of the order of unity and greater.

18 While the temporal evolution of the radial concentration profile is highly informative, the  
 19 timescale to reach steady state, as well as the shape of the steady state profile, can be  
 20 conveniently quantified in terms of the average particle-phase concentration  $\bar{A}(t)$ . We  
 21 integrate the concentration profile given by Eq. (3) over the volume of the particle to obtain:

$$22 \quad \frac{\bar{A}_i(t)}{A_i^s} = \frac{\int_0^{R_p} 4\pi r^2 \frac{A_i(r,t)}{A_i^s} dr}{\frac{4}{3}\pi R_p^3} = Q_i - U_i(t), \quad (7)$$

23 where

$$24 \quad Q_i = 3 \left( \frac{q_i \coth q_i - 1}{q_i^2} \right), \quad (8)$$



$$U_i(t) = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp\left\{-\left(k_{c,i} + \frac{n^2 \pi^2 D_{b,i}}{R_p^2}\right)t\right\}}{(q_i / \pi)^2 + n^2}. \quad (9)$$

Here,  $Q_i$  is the ratio of the average particle-phase concentration to the surface concentration at steady-state, while  $U_i(t)$  is the transient term, the value of which is always equal to  $Q_i$  at  $t=0$  and decreases exponentially to zero as  $t \rightarrow \infty$ . As noted earlier, the surface concentration  $A_i^s$  is assumed to be constant in the analytical solution of Eq. (1). However, since  $A_i^s$  can gradually change over time due to changes in the gas-phase concentration and particle composition, it is more appropriate to refer to the steady state as quasi-steady state. The timescale to reach a quasi-steady state ( $\tau_{QSS}$ ) within the particle can then be defined as the e-folding time for the exponential decay of the unsteady state term  $U_i$  relative to the quasi-steady state term  $Q_i$ . Thus, setting  $U_i(\tau_{QSS}) = Q_i / e$ , we get:

$$\sum_{n=1}^{\infty} \frac{\exp\left\{-\left(k_{c,i} + \frac{n^2 \pi^2 D_{b,i}}{R_p^2}\right)\tau_{QSS}\right\}}{(q_i / \pi)^2 + n^2} = \frac{1}{e} \times \frac{\pi^2}{2} \left( \frac{q_i \coth q_i - 1}{q_i^2} \right). \quad (10)$$

For a given set of values for  $D_p$ ,  $D_b$ , and  $k_c$ , Eq. (10) can be numerically solved for  $\tau_{QSS}$  with the bisection method.

We first examine the dependence of  $\tau_{QSS}$  and  $Q$  on  $D_b$  and  $k_c$  for a particle of  $D_p = 0.1 \mu\text{m}$  (Fig. 5). The values of  $D_b$  are varied over fourteen orders of magnitude from  $10^{-19} \text{cm}^2 \text{s}^{-1}$  (almost solid) to  $10^{-5} \text{cm}^2 \text{s}^{-1}$  (liquid water) to cover the full range of semi-solid and liquid organic particles, and  $k_c$  values are varied over six orders of magnitude from  $10^{-6} \text{s}^{-1}$  (very slow reaction) to  $1 \text{s}^{-1}$  (practically instantaneous reaction). As seen in Fig. 5a, the contours of  $\tau_{QSS}$  range from 1  $\mu\text{s}$  for liquid particles to 1 day for highly viscous semi-solid particles. For the semi-solid particles, there are two regions in the semi-solid zone as depicted by the gray dotted line. In the region above the dotted line,  $\tau_{QSS}$  is sensitive only to the value of  $k_c$  and decreases rapidly with increase in  $k_c$ . For instance, at  $D_b = 10^{-19} \text{cm}^2 \text{s}^{-1}$ ,  $\tau_{SS} = \sim 1$  day for  $k_c = 5 \times 10^{-6} \text{s}^{-1}$  but decreases to  $< 1$  min for  $k_c = 10^{-2} \text{s}^{-1}$ . In the region below the dotted line,  $\tau_{QSS}$  is sensitive only to the value of  $D_b$  for both semi-solid and liquid particles. For example,

1 at  $D_b = \sim 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ ,  $\tau_{QSS}$  remains constant at  $\sim 1$  min for  $k_c$  values from  $10^{-6}$  up to about  
 2  $10^{-2} \text{ s}^{-1}$  (i.e., up to the dotted line) and only then becomes sensitive to reaction at higher values  
 3 of  $k_c$ .  $\tau_{QSS}$  is sensitive to both  $k_c$  and  $D_b$  only in the relatively narrow envelope along the  
 4 dotted line itself. As seen in Fig. 5b, the values of  $Q$  are  $< 0.001$  for highly viscous semi-solid  
 5 particles and high  $k_c$  values, while they approach unity as  $D_b$  increases and  $k_c$  decreases.  
 6 Note that the dotted line in Fig. 5a roughly corresponds to the contour for  $Q = 0.6$  in Fig. 5b.

7 Next, we examine the dependence of  $\tau_{QSS}$  and  $Q$  on particle size. Fig. 6 shows  $\tau_{QSS}$  vs.  $D_p$   
 8 for  $D_b$  values ranging from  $10^{-18}$  to  $10^{-10} \text{ cm}^2 \text{ s}^{-1}$  for (a)  $k_c = 0 \text{ s}^{-1}$ , (b)  $k_c = 10^{-3} \text{ s}^{-1}$ , (c)  $k_c =$   
 9  $0.01 \text{ s}^{-1}$ , and (d)  $k_c = 0.1 \text{ s}^{-1}$ . As seen in Fig. 6a, for any given  $D_b$ ,  $\tau_{QSS}$  increases by five  
 10 orders of magnitude as  $D_p$  increases from  $0.003$  to  $1 \text{ }\mu\text{m}$ . At the upper end, particles with  $D_b$   
 11  $< 10^{-18} \text{ cm}^2 \text{ s}^{-1}$  have  $\tau_{QSS}$  about 10 min at  $D_p = 0.003 \text{ }\mu\text{m}$  and increase to more than  $10^4$  min  
 12 at  $D_p = 0.1 \text{ }\mu\text{m}$ . In contrast, particles with  $D_b > 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  have  $\tau_{QSS}$  below 1 min  
 13 (indicated by the dotted gray line) for sizes up to  $0.7 \text{ }\mu\text{m}$ . From a practical standpoint, since  
 14 most ambient SOA particles are smaller than  $\sim 0.7 \text{ }\mu\text{m}$ , concentration profiles of non-reacting  
 15 solutes inside particles with  $D_b > 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  may be assumed to be at steady-state.  
 16 However, significant diffusion limitation can exist for non-reacting solutes in particles with  
 17  $D_b < 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  depending on their size. In stark contrast, for reacting solutes,  $\tau_{QSS}$   
 18 asymptotically approaches a common maximum value for all values of  $D_b$  as the particle size  
 19 increases as shown in Fig. 6b,c,d. This maximum value of  $\tau_{QSS}$  is about 7, 0.7, and 0.07 min  
 20 for  $k_c = 10^{-3}$ ,  $10^{-2}$ , and  $0.1 \text{ s}^{-1}$ , respectively. The typical timescale for changes in the bulk gas-  
 21 phase concentrations due to transport and chemical reaction is of the order 10 min or more.  
 22 Thus, from a practical standpoint, the particle-phase concentration profiles of solutes reacting  
 23 with  $k_c > 10^{-2} \text{ s}^{-1}$  (for which  $\tau_{QSS} \leq 0.7$  min) may be assumed to be at quasi-steady state in  
 24 particles of any size and any  $D_b$  value.

25 Fig. 7 illustrates variation of  $Q$  with  $D_p$  for the four cases shown in Fig. 6. At quasi-steady  
 26 state, the particle-phase concentration profile for non-reacting solutes is always uniform (i.e.,  
 27  $Q = 1$ ) even though  $\tau_{QSS}$  can differ significantly depending on the particle size and  $D_b$  value  
 28 (Fig. 7a). For reacting solutes with  $k_c$  up to  $0.1 \text{ s}^{-1}$ ,  $Q$  remains nearly equal to unity in

1 particles with  $D_b > 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  and  $D_p$  up to  $1 \text{ }\mu\text{m}$ . For  $D_b < 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ ,  $Q$  decreases as  
2  $D_p$  increases for a given  $D_b$ , while it increases as  $D_b$  increases for a given  $D_p$ .

3 In general, the above analysis indicates that: a) for a given  $D_p$ , a more reactive solute will  
4 reach quasi-steady state sooner and exhibit a more non-uniform concentration profile than a  
5 less reactive one, especially in particles with lower  $D_b$  than higher, and b) for a given set of  
6 values for  $k_c$  and  $D_b$ , a solute in smaller particles will reach quasi-steady state sooner and  
7 exhibit a more uniform quasi-steady state concentration profile than in larger particles.

8

### 9 **3 Kinetic Gas-Particle Partitioning Model**

10 We shall now describe the development of a new framework for modeling kinetic partitioning  
11 of SOA based on the insights gained from timescale analysis of the diffusion-reaction process  
12 within the particle phase. The framework takes into account solute volatility, gas-phase  
13 diffusion, interfacial mass accommodation, particle-phase diffusion, and particle-phase  
14 reaction. However, instead of numerically resolving the concentration gradient inside the  
15 particle (Shiraiwa et al., 2012a), which is computationally expensive and therefore impractical  
16 for inclusion in 3-D Eulerian models, we use the analytical expressions of the quasi-steady  
17 state and transient behavior of the solute diffusing and reacting within the particle.

#### 18 **3.1 Model Framework**

##### 19 **3.1.1 Single Particle Equations**

20 We begin by relating the average particle-phase concentration of the solute  $\bar{A}_i$  ( $\text{mol cm}^{-3}$   
21  $_{(\text{particle})}$ ) to its average bulk gas-phase concentration  $\bar{C}_{g,i}$  ( $\text{mol cm}^{-3}(\text{air})$ ) over a single  
22 particle. Similar to the timescale for diffusion in the particle-phase (Eq. (5)), the timescale for  
23 the gas-phase concentration gradient outside the particle to reach a quasi-steady state ( $\tau_{dg}$ ) is  
24 given by (Seinfeld and Pandis, 2006):

$$25 \tau_{dg,i} = \frac{R_p^2}{\pi^2 D_{g,i}}, \quad (11)$$

1 where  $D_{g,i}$  ( $\text{cm}^2 \text{s}^{-1}$ ) is the gas-phase diffusivity. For a typical  $D_{g,i}$  of  $0.05 \text{ cm}^2 \text{ s}^{-1}$ , the value  
 2 of  $\tau_{dg}$  is of the order  $10^{-8}$  s or less for submicron size aerosols, which is much smaller than  
 3 the typical timescale for changes in the bulk gas-phase concentration in the ambient  
 4 atmosphere. We can therefore safely assume that the gas-phase concentration profile of the  
 5 solute around the particle is at quasi-steady state at any instant.

6 An ordinary differential equation describing the rate of change of  $\bar{A}_i$  due to mass transfer  
 7 between gas and a single particle with particle-phase reaction can then be written as:

$$8 \quad \frac{d\bar{A}_i}{dt} = \frac{3}{R_p} k_{g,i} (\bar{C}_{g,i} - C_{g,i}^s) - k_{c,i} \bar{A}_i, \quad (12)$$

9 where  $C_{g,i}^s$  ( $\text{mol cm}^{-3}(\text{air})$ ) is the gas-phase concentration of the solute just outside the surface  
 10 of the particle, and  $k_{g,i}$  ( $\text{cm s}^{-1}$ ) is the gas-side mass transfer coefficient given as:

$$11 \quad k_{g,i} = \frac{D_{g,i}}{R_p} f(Kn_i, \alpha_i). \quad (13)$$

12 Here  $f(Kn_i, \alpha_i)$  is the transition regime correction factor (Fuchs and Sutugin, 1971) to the  
 13 Maxwellian flux as a function of the Knudsen number  $Kn_i = \lambda_i / R_p$  (where  $\lambda_i$  is the mean  
 14 free path) and the so-called mass accommodation coefficient,  $\alpha_i$ , which is defined as the  
 15 fraction ( $0 \leq \alpha_i \leq 1$ ) of the incoming molecules that is incorporated into the particle surface:

$$16 \quad f(Kn_i, \alpha_i) = \frac{0.75\alpha_i(1 + Kn_i)}{Kn_i(1 + Kn_i) + 0.283\alpha_i Kn_i + 0.75\alpha_i}. \quad (14)$$

17 While the above correction factor was derived from a numerical solution of the Boltzmann  
 18 diffusion equation for neutron transfer to a black sphere (i.e., representative of light molecules  
 19 in a heavy background gas), its applicability for higher molecular weight trace gases in air has  
 20 been experimentally confirmed (Seinfeld and Pandis, 2006, and references therein).

21 The timescale to achieve interfacial phase equilibrium between  $C_{g,i}^s$  and the particle-phase  
 22 concentration of  $i$  just inside the surface,  $A_i^s$  ( $\text{mol cm}^{-3}(\text{particle})$ ) is at least (Seinfeld and  
 23 Pandis, 2006):

$$\tau_{p,i} = D_{b,i} \left( \frac{4}{\alpha_i \bar{v}_i} \right)^2, \quad (15)$$

where  $\bar{v}_i$  is the average speed of solute molecules in the gas phase. From kinetic theory of gases  $\bar{v}_i = (8\mathfrak{R}T / \pi M_i)^{1/2}$  where  $\mathfrak{R}$  is the universal gas constant ( $8.314 \times 10^7$  erg K<sup>-1</sup> mol<sup>-1</sup>),  $T$  (K) is temperature, and  $M_i$  is the molecular weight of the solute. For representative values of  $D_{b,i} \leq 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>,  $M_i = 100$  g mol<sup>-1</sup>,  $T = 298$  K, and  $\alpha_i$  ranging from 0.1 to 0.001, the value of  $\tau_{p,i}$  is of the order  $10^{-6}$  s or less, which means it can be safely assumed that the interfacial phase equilibrium is achieved virtually instantaneously. We thus relate  $C_{g,i}^s$  and  $A_i^s$  according to Raoult's law as:

$$C_{g,i}^s = \frac{A_i^s}{\sum_j A_j^s} C_{g,i}^* \quad (16)$$

where  $C_{g,i}^*$  is the effective saturation vapor concentration (mol cm<sup>-3</sup>(air)), and  $\sum_j A_j^s$  is the total particle-phase concentration of all the organic species at the surface. However, since the surface concentrations of all the species are not always known, we use the total average particle-phase concentration  $\sum_j \bar{A}_j$  as an approximation for  $\sum_j A_j^s$ . Thus Eq. (12) is rewritten in terms of  $A_i^s$  as:

$$\frac{d\bar{A}_i}{dt} = \frac{3}{R_p} k_{g,i} \left( \bar{C}_{g,i} - \frac{A_i^s}{\sum_j \bar{A}_j} C_{g,i}^* \right) - k_{c,i} \bar{A}_i. \quad (17)$$

$A_i^s$  can be assumed to be equal to  $\bar{A}_i$  in liquid particles for a non-reactive or slowly reacting solute that quickly attains a uniform concentration profile (as was previously shown in Fig. 2a,b). But, as discussed in the previous section, this equality may not hold for reactive and non-reactive solutes in semi-solid particles. In such cases, Eq. (7) can be used to express  $A_i^s$  in terms of  $\bar{A}_i$  as long as  $A_i^s$  does not change with time, because the analytical solution to Eq. (1) assumes a constant  $A_i^s$  according to the boundary condition (2b). In practice, however, Eq.

1 (7) can be used if the timescale for changes in  $A_i^s$  is much greater than the timescale for the  
 2 solute to relax to its quasi-steady state profile inside the particle. With this caveat, we get:

$$3 \quad \frac{d\bar{A}_i}{dt} = \frac{3}{R_p} k_{g,i} \left\{ \bar{C}_{g,i} - \frac{\bar{A}_i}{\sum_j \bar{A}_j} \frac{C_{g,i}^*}{(Q_i - U_i(t))} \right\} - k_{c,i} \bar{A}_i. \quad (18)$$

4 Note that Eq. (18) describes kinetic mass transfer of species  $i$  between bulk gas-phase and a  
 5 single particle, with chemical reaction within the particle phase, and includes mass-transfer  
 6 limitations due to gas-phase diffusion, interfacial mass accommodation, and particle-phase  
 7 diffusion. Previously, the mass accommodation coefficient ( $\alpha$ ) has been often used as a  
 8 tunable parameter to fit the observed kinetic limitation to mass-transfer during SOA  
 9 partitioning (Bowman et al., 1997; Saathoff et al., 2009; Parikh et al., 2011). However,  $\alpha$   
 10 does not correctly capture the mass transfer limitations due to diffusion and chemical  
 11 reaction occurring within the bulk of the particle. In the present framework, the interfacial  
 12 and bulk particle phase limitations to mass transfer are represented separately, with the  
 13 appropriate dependence for the latter on particle size.

14 In Eq. (18), the term  $U_i(t)$  is to be evaluated at the “time since start.” Equation (18) can  
 15 therefore only be used in a Lagrangian box model framework for a “closed system” where we  
 16 can specify an initial concentration of the solute vapor (at time  $t = 0$ ), which then partitions to  
 17 the particle-phase as a function of time. The solute vapor in the closed system is not subjected  
 18 to emissions, dilution, and loss due to gas-phase oxidation. In the case of no particle-phase  
 19 reaction, the solute vapor will eventually reach equilibrium with the particles. In the presence  
 20 of particle-phase reaction, the solute vapor concentration will eventually decay to zero. This is  
 21 in stark contrast with the “general system” such as the ambient atmosphere and 3-D  
 22 atmospheric chemistry transport models where the solute vapor at a given location may  
 23 continuously change due to emissions, dilution, and gas-phase chemistry in addition to gas-  
 24 particle partitioning. As a result, it is not possible to evaluate  $U_i(t)$  in the general system,  
 25 because we cannot keep track of the “time since start” in the same sense as used in the  
 26 transient analytical solution to Eq. (1). Therefore, based on the value of  $k_c$  and the associated  
 27 timescale for the particle-phase concentration profile to reach quasi steady state ( $\tau_{QSS}$ ), the  
 28 following two approximations to Eq. (18) are made for it to be applicable to the general  
 29 system.

## 1 **Approximation 1: For Fast Reactions** ( $k_{c,i} \geq 0.01 \text{ s}^{-1}$ )

2 As discussed in the previous section (Fig. 6c),  $\tau_{QSS}$  for a solute reacting with  $k_{c,i} \geq 0.01 \text{ s}^{-1}$  is  
3 less than 1 min in particles with any  $D_b$  and of any size. Compared to the typical time step  
4 values of 5 min or greater in 3-D Eulerian models, the particle-phase concentration profile for  
5 solutes with  $\tau_{QSS} \leq 1$  min may be assumed to be at quasi-steady-state, and the term  $U_i(t)$  can  
6 be safely neglected in Eq. (18) to yield:

$$7 \quad \frac{d\bar{A}_i}{dt} = \frac{3}{R_p} k_{g,i} \left\{ \bar{C}_{g,i} - \frac{\bar{A}_i}{\sum_j \bar{A}_j} \frac{C_{g,i}^*}{Q_i} \right\} - k_{c,i} \bar{A}_i \quad \text{for } k_{c,i} \geq 0.01 \text{ s}^{-1}. \quad (19)$$

8 A similar equation was derived by Shi and Seinfeld (1991) for reactive mass transport of  $\text{SO}_2$   
9 (with Henry's law for absorption) in cloud droplets assuming quasi-steady state within the  
10 droplet phase. Now, as  $k_c \rightarrow 0$ ,  $Q \rightarrow 1$ , and mass transfer is governed entirely by gas-phase  
11 diffusion and interfacial mass accommodation in Eq. (19). As a result, Eq. (19) tends to lose  
12 its ability to capture the resistance to mass transfer due to slow diffusion in the particle phase  
13 as  $k_c \rightarrow 0$ . Therefore, an alternate treatment for mass transfer is needed for slow reactions.

## 14 **Approximation 2: For Slow Reactions** ( $k_{c,i} < 0.01 \text{ s}^{-1}$ )

15 For  $k_{c,i} < 0.01 \text{ s}^{-1}$  (or  $\tau_{QSS} > 1$  min), we use the classical two-film theory of mass transfer  
16 between the gas and particle phases. The two-film theory was originally introduced by Lewis  
17 and Whitman (1924) and has been widely used to model mass transfer in two phase systems,  
18 with and without chemical reactions (Astarita, 1967; Doraiswamy and Sharma, 1984; Bird et  
19 al., 2007). Fig. 8 shows the schematic of the two-film model which assumes that the  
20 concentration gradients in the gas and particle phases are confined in the respective  
21 hypothetical "films" adjacent to the interface. The gas- and particle-side film thicknesses are  
22 denoted by  $\delta_g$  and  $\delta_p$  (cm), respectively, and the respective mass transfer coefficients ( $\text{cm s}^{-1}$ )  
23 are defined as  $k_g = D_g / \delta_g$  and  $k_p = D_b / \delta_p$ . The overall gas-side mass transfer coefficient  
24  $K_g$  ( $\text{cm s}^{-1}$ ) is then given by (see Appendix A for the derivation):

$$25 \quad \frac{1}{K_{g,i}} = \frac{1}{k_{g,i}} + \frac{1}{k_{p,i}} \left( \frac{C_{g,i}^*}{\sum_j \bar{A}_j} \right). \quad (20)$$

1 The ordinary differential equation describing the rate of change of  $\bar{A}_i$  due to gas-particle mass  
 2 transfer and particle-phase reaction can then be written in terms of the overall driving force  
 3 as:

$$4 \quad \frac{d\bar{A}_i}{dt} = \frac{3}{R_p} K_{g,i} \left\{ \bar{C}_{g,i} - \frac{\bar{A}_i}{\sum_j \bar{A}_j} C_{g,i}^* \right\} - k_{c,i} \bar{A}_i \quad \text{for } k_{c,i} < 0.01 \text{ s}^{-1}. \quad (21)$$

5 A similar equation was derived by Zaveri (1997) for reactive mass transport of SO<sub>2</sub> (with  
 6 Henry's law for absorption) in cloud droplets assuming quasi-steady state within the droplet  
 7 phase. The advantage of the two-film model formulation is that the diffusion limitations from  
 8 both the gas and particle sides are represented in the overall mass transfer coefficient, and can  
 9 therefore be used to model mass transfer of slow-reacting solutes. The gas-side mass transfer  
 10 coefficient ( $k_g$ ) is already known from Eq. (13) where  $\delta_g = R_p$ . However, the particle-side  
 11 film thickness,  $\delta_p$ , and therefore  $k_p$ , are not readily known. In a general system, the bulk gas-  
 12 and particle-phase concentrations of a reactive semi-volatile solute tend to reach a quasi-  
 13 steady state when the net source rate of the solute in the gas phase is relatively steady. Since  
 14 both Eqs. (19) and (21) describe the same process, they should predict identical gas- and  
 15 particle-phase concentrations at quasi-steady-state. Thus, setting  $d\bar{A}_i / dt = 0$  in both Eqs. (19)  
 16 and (21) and equating the expressions for  $(\bar{A}_i / \bar{C}_{g,i})$  resulting from each of them yields the  
 17 general expressions for  $\delta_p$  and  $k_p$  in terms of  $D_b$ ,  $k_c$ , and  $R_p$  (see Appendix B for the  
 18 derivation):

$$19 \quad \delta_{p,i} = R_p \left( \frac{1 - Q_i}{q_i \coth q_i - 1} \right), \quad (22)$$

$$20 \quad k_{p,i} = \frac{D_{b,i}}{R_p} \left( \frac{q_i \coth q_i - 1}{1 - Q_i} \right). \quad (23)$$

21 For the limiting case of a non-reactive solute,  $k_c \rightarrow 0$ ,  $q \rightarrow 0$ ,  $Q \rightarrow 1$  and Eq. (23) reduces to:

$$22 \quad k_{p,i} = 5 \frac{D_{b,i}}{R_p}. \quad (24)$$



### 1 3.1.2 Polydisperse Aerosol Equations

2 We now extend the closed system box model Eq. (18) for a single particle to a polydisperse  
 3 aerosol in a sectional framework. For a given size section  $m$ , with number concentration  $N_m$   
 4 ( $\text{cm}^{-3}(\text{air})$ ) and particle radius  $R_{p,m}$  (cm), we define  $\bar{C}_{a,i,m}$  ( $\text{mol cm}^{-3}(\text{air})$ ) as the total average  
 5 concentration of solute  $i$  in size section  $m$ :

$$6 \quad \bar{C}_{a,i,m} = \frac{4}{3} \pi R_{p,m}^3 N_m \bar{A}_{i,m}. \quad (25)$$

7 Multiplying Eq. (18) by  $(4\pi R_{p,m}^3 N_m / 3)$  gives:

$$8 \quad \frac{d\bar{C}_{a,i,m}}{dt} = 4\pi R_{p,m}^2 N_m k_{g,i,m} \left\{ \bar{C}_{g,i} - \bar{C}_{a,i,m} \frac{S_{i,m}}{(Q_i - U_i(t))} \right\} - k_{c,i} \bar{C}_{a,i,m}, \quad (26)$$

9 where  $S_{i,m}$  is the saturation ratio:

$$10 \quad S_{i,m} = \frac{C_{g,i}^*}{\sum_j \bar{C}_{a,j,m}}. \quad (27)$$

11 The corresponding equation governing the gas-phase concentration of solute  $i$  is:

$$12 \quad \frac{d\bar{C}_{g,i}}{dt} = - \sum_m \left[ 4\pi R_{p,m}^2 N_m k_{g,i,m} \left\{ \bar{C}_{g,i} - \bar{C}_{a,i,m} \frac{S_{i,m}}{(Q_i - U_i(t))} \right\} \right]. \quad (28)$$

13 Similarly, the particle-phase and gas-phase equations for polydisperse aerosols in the general  
 14 system are as follows.

15 **Approximation 1: For  $k_{c,i} \geq 0.01 \text{ s}^{-1}$**

$$16 \quad \frac{d\bar{C}_{a,i,m}}{dt} = 4\pi R_{p,m}^2 N_m k_{g,i,m} \left( \bar{C}_{g,i} - \bar{C}_{a,i,m} \frac{S_{i,m}}{Q_i} \right) - k_{c,i} \bar{C}_{a,i,m}, \quad (29)$$

$$17 \quad \frac{d\bar{C}_{g,i}}{dt} = - \sum_m \left[ 4\pi R_{p,m}^2 N_m k_{g,i,m} \left( \bar{C}_{g,i} - \bar{C}_{a,i,m} \frac{S_{i,m}}{Q_i} \right) \right]. \quad (30)$$

18 **Approximation 2: For  $k_{c,i} < 0.01 \text{ s}^{-1}$**

$$19 \quad \frac{d\bar{C}_{a,i,m}}{dt} = 4\pi R_{p,m}^2 N_m K_{g,i,m} \left( \bar{C}_{g,i} - \bar{C}_{a,i,m} S_{i,m} \right) - k_{c,i} \bar{C}_{a,i,m}, \quad (31)$$

$$1 \quad \frac{d\bar{C}_{g,i}}{dt} = -\sum_m \left[ 4\pi R_{p,m}^2 N_m K_{g,i,m} (\bar{C}_{g,i} - \bar{C}_{a,i,m} S_{i,m}) \right]. \quad (32)$$

2 The proposed framework, described by Eqs. (29) through (32), is relatively simple and  
 3 amenable for use in regional and global aerosol models, although it presently awaits  
 4 specification of the actual particle-phase chemical reactions that are important for SOA  
 5 formation.

6 We have implemented both the closed system and general system frameworks in the  
 7 computationally efficient, multicomponent aerosol box-model MOSAIC and adapted the  
 8 existing semi-implicit Euler method solver to numerically integrate the set of coupled  
 9 ordinary differential equations for any number of solutes  $i$  over any number of size bins  $m$   
 10 (Zaveri et al., 2008). Sectional growth in MOSAIC is calculated using the two-moment  
 11 approach of Simmel and Wurzler (2006). The closed system framework is to be used in the  
 12 box-model version only while the general system framework can be used in both box- and 3-  
 13 D Eulerian models. The complete solution to these equations may be labeled as “semi-  
 14 numerical,” because the particle-phase diffusion-reaction process is represented analytically  
 15 while the set of ordinary differential equations themselves are integrated numerically.

16 MOSAIC already performs kinetic partitioning of inorganic gases ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ , and  
 17  $\text{NH}_3$ ) to size-distributed particles and predicts liquid water associated with inorganic species  
 18 as a function of relative humidity. While the focus of the present work is on kinetic  
 19 partitioning of organic gases to particulate organic phase, the new framework can be readily  
 20 adapted to kinetically partition water soluble organic gases into the particulate aqueous phase  
 21 if that is the only liquid phase in the particle. However, additional research is needed to  
 22 extend the present framework to mixed inorganic-organic particles that experience liquid-  
 23 liquid phase separation (i.e., coexistence of separate aqueous and organic phases; You et al.,  
 24 2012).

## 25 **3.2 Model Validation**

26 We shall now validate the new framework in MOSAIC against a “fully numerical” finite-  
 27 difference solution to Eq. (1) with a flux type boundary condition that includes mass transfer  
 28 of the solute between the gas phase and the particle surface. The volume of the spherical  
 29 particle is resolved with multiple layers, and diffusion and reaction of the solute species  
 30 through these layers are integrated numerically. We used 300 uniformly-spaced layers in the

1 present exercise. The finite difference model is conceptually similar to the KM-GAP model  
 2 (Shiraiwa et al., 2012a), but does not include reversible adsorption at the surface and heat  
 3 transfer processes. The finite-difference solution is used as a benchmark here because it  
 4 rigorously solves Eq. (1) and does not assume the surface concentration to remain constant  
 5 with time.

6 For validation purposes, we consider a monodisperse semi-solid aerosol composed of non-  
 7 volatile organic species  $P_3$  (molecular weight  $100 \text{ g mol}^{-1}$  and density  $1 \text{ g cm}^{-3}$ ), with initial  
 8 particle diameter  $D_p = 0.2 \text{ }\mu\text{m}$ , particle number concentration  $N = 5000 \text{ cm}^{-3}$ , and bulk  
 9 diffusivity  $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ . For simplicity, the molecular weight and density of the  
 10 condensing solute ( $P_1$ ) and its reaction product species ( $P_2$ ) are also assumed to be  $100 \text{ g mol}^{-1}$   
 11 and  $1 \text{ g cm}^{-3}$ , respectively. The three species ( $P_1$ ,  $P_2$ , and  $P_3$ ) are assumed to form an ideal  
 12 solution that participates in the absorption of  $P_1$  according to Raoult's law. Model validation  
 13 is demonstrated below for both closed and general systems.

### 14 3.2.1 Closed System

15 In three separate closed system cases, the initial monodisperse aerosol was exposed to the  
 16 solute ( $P_1$ ) gas concentration of  $2 \text{ }\mu\text{g m}^{-3}$  with volatility  $C_g^* = 10, 100, \text{ and } 1000 \text{ }\mu\text{g m}^{-3}$ . Fig. 9  
 17 compares the solution given by MOSAIC (Eqs. (26) and (28)) with the finite-difference  
 18 model solution for gas-phase concentration decay due to kinetic gas-particle partitioning for  
 19 particle-phase reaction rate constants  $k_c$  ranging from 0 to  $0.1 \text{ s}^{-1}$ . When  $k_c = 0$ , the gas-phase  
 20 concentration reaches an equilibrium value that depends on the solute volatility, while in other  
 21 cases it decays to zero at different rates as governed by the particle-phase reaction rate  
 22 constant and diffusion limitation. MOSAIC is able to reproduce the finite difference results  
 23 quite well, although small deviations can be seen during the initial portions of the gas decay  
 24 for  $k_c \leq 10^{-4} \text{ s}^{-1}$  and  $C_g^* = 10 \text{ and } 100 \text{ }\mu\text{g m}^{-3}$ . The following metrics were used to quantify the  
 25 accuracy of MOSAIC relative to the finite difference (FD) model:

$$26 \text{ Mean Normalized Bias, } \text{MNB} = \frac{\overline{(C_{g,1}^{\text{MOSAIC}} - C_{g,1}^{\text{FD}})}}{C_{g,1}^{\text{FD}}}, \quad (33)$$

$$27 \text{ Mean Normalized Gross Error, } \text{MNGE} = \frac{\overline{|C_{g,1}^{\text{MOSAIC}} - C_{g,1}^{\text{FD}}|}}{C_{g,1}^{\text{FD}}}, \quad (34)$$

$$28 \text{ Maximum Normalized Gross Error, } \text{maxNGE} = \max(|C_{g,1}^{\text{MOSAIC}} - C_{g,1}^{\text{FD}}|/C_{g,1}^{\text{FD}}). \quad (35)$$

1 These metrics were calculated using the model outputs at 5 min intervals for the 10 h long  
2 simulations. However, negligibly small gas-phase concentrations ( $< 0.05 \mu\text{g m}^{-3}$ ) towards the  
3 latter part of the simulations (where applicable) were excluded in the calculations of the  
4 metrics. The results are displayed in Table 1. The MNB and MNGE are comparable in  
5 magnitude and range from  $\sim 0.1\%$  to  $\sim 10\%$ , with values greater than  $\sim 5\%$  seen only for  $C_g^* =$   
6  $10 \mu\text{g m}^{-3}$ . The large maxNGE values ( $> 20\%$ ) seen for  $C_g^* = 10 \mu\text{g m}^{-3}$  occur as the gas-phase  
7 concentrations approach zero. Overall, the agreement between the two models is quite good  
8 for the closed system.

### 9 **3.2.2 General System**

10 In three separate general system cases, the initial monodisperse aerosol was exposed to solute  
11  $P_1$  with  $C_g^* = 10, 100,$  and  $1000 \mu\text{g m}^{-3}$  at a constant gas-phase source rate of  $\gamma = 0.1 \mu\text{g m}^{-3}$   
12  $\text{h}^{-1}$  in each case. The initial gas-phase concentration of  $P_1$  was zero in each case. Fig. 10  
13 compares the evolution of the gas-phase concentration of  $P_1$  predicted by MOSAIC (Eqs.  
14 (29)-(32)) and the finite-difference model. The particle-phase reaction rate constant  $k_c$  ranged  
15 from 0 to  $0.1 \text{ s}^{-1}$ . When  $k_c = 0$ , the gas-phase concentration of  $P_1$  increases almost linearly  
16 with time upon reaching quasi-equilibrium with the particle phase. For  $k_c > 0$ , the gas-phase  
17 concentration of  $P_1$  remains constant after the initial build up as the source rate is balanced by  
18 the loss rate due to particle-phase diffusion and reaction. This quasi-steady state gas-phase  
19 concentration level depends on the combination of  $C_g^*$ ,  $D_b$ , and  $k_c$ . For  $C_g^* = 10 \mu\text{g m}^{-3}$ , the  
20 time required to establish quasi-steady state between gas and particle phases ranges from less  
21 than 1 h at  $k_c = 0.1 \text{ s}^{-1}$  to more than 20 h at  $k_c = 10^{-4} \text{ s}^{-1}$ . The time to reach quasi-equilibrium  
22 (for non-reactive solutes) and quasi-steady state (for reactive solutes) increases as the value of  
23  $C_g^*$  increases. Approximations 1 and 2 in MOSAIC are able to capture both the initial “spin-  
24 up” phase, when the gas-phase concentration builds up, as well as the later phase where the  
25 concentration remains in quasi-equilibrium or quasi-steady state. Furthermore, for  $k_c = 10^{-3} \text{ s}^{-1}$ ,  
26 Approximation 1 (black dotted line in Fig. 10) gives nearly identical results as  
27 Approximation 2 for all three  $C_g^*$  values, indicating that the transition from one to the other  
28 does not cause a sudden change in the behavior of the solution. Approximation 1 predicts  
29 faster gas uptake than the finite difference model for slow reactions while Approximation 2

1 predicts slower gas uptake than the finite difference model for fast reactions (not shown),  
2 especially for low volatility solutes ( $C_g^* = \sim 10 \mu\text{g m}^{-3}$ ). A combination of Approximations 1  
3 and 2 is thus needed to cover the full range of possible  $k_c$  values.

4 The normalized gross errors in MOSAIC are relatively large during the spin-up phase where  
5 the gas-phase concentrations are very small. In a 3-D Eulerian model application, the spin-up  
6 phase occurs at the beginning of the simulation and is usually discarded. Here, we discard the  
7 first two hours of spin-up in each simulation to avoid small gas-phase concentrations when  
8 calculating the bias and error metrics, shown in Table 2. Both MNB and MNGE are generally  
9 less than  $\sim 3\%$ . The maxNGE values ranged between 0.3 and 8.5%. The overall performance  
10 of MOSAIC for the general system is excellent.

### 11 **3.3 Future Considerations**

12 While the general system framework is amenable for eventual use in regional and global  
13 climate models, it currently awaits specification of the various gas and particle-phase  
14 chemistries important for SOA formation. The following issues must be must be taken into  
15 consideration when specifying the various physical and chemical details in the model and  
16 evaluating it using laboratory and field observations.

17 First, the present framework uses a pseudo-first order (PFO) reaction for a condensing solute  
18 as a proxy for second order chemical reactions that may occur within a particle. The  
19 assumption of PFO reaction for the condensing solute is valid when the pre-existing bulk  
20 reactant species is uniformly distributed with the depth of the particle, e.g., when the reaction  
21 timescale for the reactant species is much longer than that for diffusion. The issue arises when  
22 the reaction time scale is much shorter than that for diffusion such that the bulk reactant  
23 species is not homogeneously distributed depth-wise (Berkemeier et al., 2013). In such cases,  
24 it may be possible to parameterize the PFO reaction rate constant for the condensing solute in  
25 terms of its second order rate constant multiplied by the volume average concentration of the  
26 pre-existing reactant solutes in the particle phase. The detailed finite difference model using  
27 second order reactions can be used to provide guidance for improving and validating the  
28 parameterized reactions in the semi-numerical framework.

29 Second, while the present framework allows particles of different sizes and composition to  
30 have different bulk diffusivities, it cannot explicitly treat the potential variation of diffusivity

1 within a given particle of complex morphology. Examples include black carbon or solid  
2 ammonium sulfate particles coated with organics as well as particles with non-ideal internal  
3 mixtures of hydrophobic and hydrophilic organics. The diffusion-reaction process inside such  
4 complex and potentially non-spherical particles will again have to be parameterized based on  
5 the average bulk properties, with possible guidance from more detailed finite difference  
6 models where applicable.

7 Third, as mentioned earlier, the new framework can be readily adapted to kinetically partition  
8 water soluble organic gases into the particulate aqueous phase if that is the only liquid phase  
9 in the particle. However, additional work is needed to extend the present framework to mixed  
10 inorganic-organic particles in which water and organics may form separate liquid phases (You  
11 et al., 2012).

12

#### 13 **4 Results and Discussion**

14 We now apply the updated MOSAIC model to a series of polydisperse aerosol scenarios to  
15 investigate the influence of particle-phase reactions, phase state, and solute volatility on SOA  
16 partitioning timescale and the evolution of aerosol size distribution. While the exact  
17 mechanism(s) responsible for the growth of newly formed particles (1 to 10 nm range) is still  
18 unknown, it is suspected to occur via effectively irreversible condensation of very low  
19 volatility organic species which can overcome the strong Kelvin effect (Pierce et al., 2011) .  
20 In the present study, we focus on the competitive growth dynamics of the Aitken and  
21 accumulation mode particles, as might result after the newly formed particles have grown up  
22 to Aitken mode sizes. The Kelvin effect and coagulation are neglected for simplicity. Fig. 11  
23 shows the initial aerosol number and volume size distributions used for this exercise. Again,  
24 this pre-existing aerosol is assumed to be composed of non-volatile organic species ( $P_3$ ) of  
25 molecular weight  $100 \text{ g mol}^{-1}$  and density  $1 \text{ g cm}^{-3}$ . The entire size distribution, consisting of  
26 an Aitken mode and an accumulation mode, is discretized over 1000 logarithmically-spaced  
27 size bins (lower boundary of the smallest bin =  $0.008 \text{ }\mu\text{m}$  and the upper boundary of the  
28 largest bin =  $1 \text{ }\mu\text{m}$ ). The total number concentration of particles in the Aitken mode is  $6223$   
29  $\text{cm}^{-3}$  while that in the accumulation mode is  $1139 \text{ cm}^{-3}$ ; the total aerosol mass concentration is  
30  $2 \text{ }\mu\text{g m}^{-3}$ . Fig. 11 also shows the condensational sink  $k_{CS,i,m} = 4\pi R_{p,m}^2 N_m k_{g,i,m}$  for each size bin  
31  $m$  as a function of  $D_p$ . For this particular size distribution, the sum of  $k_{CS}$  over all the size

1 bins in the Aitken mode is equal to that in the accumulation mode, so that there is no initial  
2 bias in the condensation rate of the solute species towards either mode merely due to  
3 differences in the initial condensational sink rates for the two modes. Both closed and general  
4 systems scenarios are examined.

#### 5 **4.1 Closed System**

6 A set of closed system simulations was performed in which the initial organic aerosol was  
7 separately exposed to the solute gas ( $P_1$ ) with three different  $C_g^*$  values: 10, 100, and 1000  $\mu\text{g}$   
8  $\text{m}^{-3}$  (molecular weight = 100  $\text{g mol}^{-1}$ ), with an initial gas-phase concentration of 6  $\mu\text{g m}^{-3}$  in  
9 each case. For each solute volatility case, the effect of aerosol phase state was examined using  
10 four different  $D_b$  values:  $10^{-6}$ ,  $10^{-12}$ ,  $10^{-13}$ , and  $10^{-15}$   $\text{cm}^2 \text{s}^{-1}$ . In all cases,  $k_c$  was set at  $0.01 \text{ s}^{-1}$   
11 so that  $\tau_{SS}$  was always less than  $\sim 0.7$  min across the entire size distribution. In each case, the  
12 simulation was run until the gas-phase solute was completely absorbed and reacted to form a  
13 non-volatile product in the particle phase. Again, the molecular weight and density of the  
14 product species ( $P_2$ ) were assumed to be 100  $\text{g mol}^{-1}$  and 1  $\text{g cm}^{-3}$ , respectively, and all three  
15 species ( $P_1$ ,  $P_2$ , and  $P_3$ ) were assumed to form an ideal solution that participated in the  
16 absorption of  $P_1$  according to Raoult's law. An additional set of reference simulations were  
17 performed for two extreme scenarios: 1) instantaneous particle-phase reaction (i.e.,  $k_c \rightarrow \infty$ ),  
18 which is equivalent to solving the non-volatile solute condensation case (i.e., mechanism #1),  
19 and 2) no particle-phase reaction ( $k_c = 0$ ), which is referred to as Raoult's law partitioning  
20 (i.e., mechanism #2). In the latter case, the initial gas-phase concentrations for the different  
21  $C_g^*$  subcases were increased such that 6  $\mu\text{g m}^{-3}$  of solute was partitioned into the particle  
22 phase at steady state (i.e., at equilibrium) in each case.

##### 23 **4.1.1 Reference Cases**

24 We shall first discuss the results of the closed system reference cases. Fig. 12 shows the gas-  
25 phase decay and the corresponding temporal evolution of aerosol size distribution and mass  
26 fraction of newly formed SOA for the instantaneous particle-phase reaction case. Here, gas-  
27 particle partitioning is independent of the particle phase state and is governed entirely by gas-  
28 phase diffusion limitation. Vapor concentration is completely depleted in about 1 h, and  
29 aerosol size distribution evolution displays the well-known narrowing characteristics as the

1 small particles grow faster (more precisely, have greater  $d \ln D_p / dt$ ) than the large ones  
2 (Zhang et al., 2012). Consequently, the mass fraction of the newly formed SOA in smaller  
3 particles is much higher than in the larger ones. Note that in the SOA mass fraction panel, the  
4 left-most point on each line with mass fraction  $\approx 1$  corresponds to the smallest initial particles  
5 ( $D_p = 0.008 \mu\text{m}$  at  $t = 0$ ).

6 In contrast, aerosol evolution due to Raoult's law partitioning depends on both solute  
7 volatility and particle phase state. Fig. 13 shows the gas-phase concentration decay and the  
8 corresponding aerosol size distribution and SOA mass fraction evolution for the less volatile  
9 solute with  $C_g^* = 10 \mu\text{g m}^{-3}$ . The effect of phase state is illustrated with two bulk diffusivities:  
10  $D_b = 10^{-6}$  and  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$ . In the case with liquid particles ( $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ), there is  
11 negligible resistance to mass transfer within the particle (refer to Fig. 6a), and as a result the  
12 vapor concentration rapidly decreases during the first 1 h and reaches a steady state in about  
13 7.5 h. In the first  $\sim 20$  min, the size distribution exhibits the narrowing of the Aitken mode  
14 similar to that seen in gas-phase diffusion-limited growth, although not as intense. The SOA  
15 mass fraction reaches up to 0.97 in small particles while it is only about 0.25 in the large  
16 particles. However, as the vapor concentration decreases further, the peak of the size  
17 distribution begins to decrease and the width broadens due to evaporation from small particles  
18 while the large particles continue to grow (Zhang et al., 2012). The SOA mass fraction in  
19 small particles decreases to 0.75, while it gradually increases to 0.75 in the large particles.  
20 The vapor concentration remains steady while this inter-particle mass transfer (via the gas  
21 phase) occurs over a relatively longer period ( $\sim 480$  h) until the entire aerosol size distribution  
22 reaches equilibrium.

23 Similar behavior is seen in the case with semi-solid particles ( $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ ), although  
24 the timescale over which it occurs is relatively longer due to much higher particle-phase  
25 diffusion limitation. While the vapor concentration declines rapidly in the beginning (e-  
26 folding timescale of 16.5 h), it takes about 175 h to reach the steady state and more than 400 h  
27 for the aerosol size distribution to reach equilibrium. Also, because the particle-phase  
28 diffusion limitation is much less in small particles than the large ones (refer to Fig. 6a), the  
29 Aitken mode exhibits more intense narrowing and a higher peak (at about 1 h) than seen in  
30 liquid particles. Then, again, as the vapor concentration decreases further, the width broadens  
31 and the peak decreases due to evaporation of small particles while the large ones continue to



1 grow more slowly. The final aerosol size distribution and SOA mass fraction across the size  
2 spectrum are identical (within numerical errors) to those obtained in the liquid particle case.

3 Fig. 14 shows the results for the more volatile solute with  $C_g^* = 1000 \mu\text{g m}^{-3}$ . In the case with  
4 liquid particles ( $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ), the vapor concentration reaches the steady state in just 20  
5 min (vs. 7.5 h for  $C_g^* = 10 \mu\text{g m}^{-3}$ ) while it takes nearly 400 h (vs. 175 h for  $C_g^* = 10 \mu\text{g m}^{-3}$ )  
6 in the case with semi-solid particles ( $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ ). Again, the final aerosol size  
7 distribution and SOA mass fraction solutions at equilibrium are identical to those obtained for  
8 the  $C_g^* = 10 \mu\text{g m}^{-3}$  cases, but their temporal evolutions are quite different. In the case with  
9 liquid particles, the width of the aerosol size distribution does not narrow and the peak height  
10 remains the same as the particles grow. This is because the small particles quickly attain a  
11 quasi-equilibrium state with the more volatile solute. Consequently, the SOA mass fraction in  
12 the small particles quickly reaches the equilibrium value of 0.75 (instead of overshooting as  
13 seen for  $C_g^* = 10 \mu\text{g m}^{-3}$ ) while the larger particles catch up just a bit more slowly. The entire  
14 size distribution reaches equilibrium within 1 h.

15 In the case with semi-solid particles, the Aitken mode size distribution narrows (similar to  
16 that seen in Fig. 13a) in the first few minutes, but broadens back within 30 min. Again, the  
17 SOA mass fraction in small particles quickly reaches the equilibrium value of 0.75, while it  
18 still takes  $\sim 480$  h for the large particles in the spectrum to reach equilibrium due to the  
19 significant diffusion limitation in the particle phase.

#### 20 **4.1.2 Reactive Partitioning Cases**

21 We now present results for the closed-system reactive partitioning cases with  $k_c = 0.01 \text{ s}^{-1}$ .  
22 Fig. 15 shows vapor concentration decay for each of the three solute volatility cases ( $C_g^* = 10$ ,  
23  $100$ , and  $1000 \mu\text{g m}^{-3}$ ) for  $D_b$  values ranging from  $10^{-6}$  to  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$ . It also shows a plot of  
24 the e-folding timescale ( $\tau_g$ ) for the decay as a function of  $D_b$  for the different volatilities.  
25 Each plot includes the reference case of instantaneous reaction for comparison. Unlike in  
26 Raoult's law partitioning, the vapor concentration always decays to zero in reactive  
27 partitioning and the decay rate slows down with increase in  $C_g^*$ . The vapor decay rate also  
28 slows down with decrease in  $D_b$  and it is especially sensitive to  $D_b$  in semi-solid particles.

1 Fig. 16 illustrates the effects of the different  $C_g^*$  and  $D_b$  values on the final aerosol size  
2 distribution. The final results for the reference cases of instantaneous reaction and Raoult's  
3 law partitioning are also shown for easy comparison. In the case of  $C_g^* = 10 \mu\text{g m}^{-3}$ , the  
4 Aitken mode exhibits significant narrowing for all values of  $D_b$ . The narrowing becomes  
5 more pronounced for  $D_b < 10^{-13} \text{ cm}^2 \text{ s}^{-1}$  with the shape of the entire size distribution for  $D_b =$   
6  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$  being nearly identical to that for the instantaneous reaction reference case.  
7 Further decrease in  $D_b$  will produce even more narrowing. Since there is negligible particle-  
8 phase diffusion limitation for  $D_b > 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  ( $Q \approx 1$ ; Fig. 7c), the size distribution of liquid  
9 aerosol narrows because its initial evolution (in the case of low volatility solutes) resembles  
10 that of gas-phase diffusion-limited growth, and the particle-phase reaction rate is fast enough  
11 to transform the absorbed solute to a non-volatile product before it can evaporate. For  $D_b <$   
12  $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ , the steep gradient in  $Q$  across the size distribution results in significantly lower  
13 surface concentrations over small semi-solid particles compared to the large ones. The small  
14 semi-solid particles therefore grow even faster than the large ones compared to the  
15 corresponding liquid aerosol case, producing relatively more intense narrowing of the size  
16 distribution.

17 As the solute  $C_g^*$  increases to 100 and 1000  $\mu\text{g m}^{-3}$ , liquid particles tend to attain quasi-  
18 equilibrium with the gas phase relatively faster than the solute reacts within the particle. As a  
19 result, the final size distributions for  $D_b \leq 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  progressively resemble that of the  
20 Raoult's law partitioning case. However, significant narrowing is still seen for  $D_b = 10^{-15} \text{ cm}^2$   
21  $\text{s}^{-1}$  due to the steep gradient in  $Q$  across the size distribution, which causes the small semi-  
22 solid particles to grow much faster than the large semi-solid ones when compared to the  
23 corresponding liquid aerosol case where  $Q \approx 1$  across the entire size distribution. In general,  
24 the final size distribution shape tends to be closer to that for instantaneous reaction case for  
25 lower  $C_g^*$  and  $D_b$  values and higher  $k_c$  values, while it tends to be closer to that for Raoult's  
26 law partitioning for higher  $C_g^*$  and  $D_b$  and lower  $k_c$ .

27 Fig. 17 illustrates the influence of  $C_g^*$  and  $D_b$  values on the final SOA mass fraction size  
28 distribution. Curves for the two reference cases are also included for comparison. In the case  
29 of  $C_g^* = 10 \mu\text{g m}^{-3}$ , the curves for all  $D_b$  values are similar to that of the instantaneous

1 reference case due to appreciable narrowing of the size distribution. But as  $C_g^*$  increases, the  
2 SOA mass fraction curves progressively become more uniform for  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  while  
3 they remain non-uniform for  $D_b < 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  for particles with  $D_p > 0.2 \text{ }\mu\text{m}$ . In all  $C_g^*$   
4 cases, the SOA mass fraction curves for  $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$  closely resemble the instantaneous  
5 reaction case.

## 6 **4.2 General System**

7 A set of general system simulations was performed in which the initial organic aerosol was  
8 separately exposed to solutes with  $C_g^* = 10, 100, \text{ and } 1000 \text{ }\mu\text{g m}^{-3}$  at a moderate but constant  
9 gas-phase source rate of  $\gamma = 0.6 \text{ }\mu\text{g m}^{-3} \text{ h}^{-1}$  in each case. The effect of aerosol phase state was  
10 examined using two different  $D_b$  values:  $10^{-6}$  and  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$ . For each combination of  $C_g^*$   
11 and  $D_b$  values, the effect of particle-phase reaction was examined for  $k_c = 0.01, 0.1, 1, \text{ and}$   
12  $\infty \text{ s}^{-1}$ . Each simulation was 12 h long.

13 Fig. 18 shows the time evolutions of total SOA mass concentration for liquid particles ( $D_b =$   
14  $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) with different solute  $C_g^*$  values and the corresponding final aerosol size  
15 distributions at  $t = 12 \text{ h}$ . In the case with  $C_g^* = 10 \text{ }\mu\text{g m}^{-3}$ , the SOA formation rate is  
16 essentially the same for  $k_c \geq 0.01 \text{ s}^{-1}$ , with a total of about  $7 \text{ }\mu\text{g m}^{-3}$  SOA formed at the end of  
17 12 h. Appreciable narrowing of the Aitken mode size distribution occurs for  $k_c = 0.01 \text{ s}^{-1}$ ,  
18 which is qualitatively similar to the closed system results for  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  shown  
19 previously in Fig. 16a. Higher  $k_c$  values produce even more intense narrowing of the Aitken  
20 mode and the shapes are practically indistinguishable from that for instantaneous reaction. As  
21  $C_g^*$  increases, the solute vapor tends towards quasi-equilibrium with the particle phase for low  
22  $k_c$  values. As a result, the SOA formation rate slows down and the Aitken mode shapes for  
23  $k_c = 0.01 \text{ s}^{-1}$  qualitatively tend to resemble that of Raoult's law partitioning in the closed  
24 system shown previously in Fig. 16b,c. But as  $k_c$  increases, the mass transfer becomes  
25 progressively more gas-phase diffusion limited, which results in faster growth of the smaller  
26 particles and, therefore, increasing narrowing of the Aitken mode.

1 Fig. 19 shows the results for semi-solid particles ( $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ ). It is seen that the  
2 presence of significant particle-phase diffusion limitation slows down the SOA formation  
3 rates, especially with increasing  $C_g^*$  and decreasing  $k_c$ . The marked size-dependence of the  
4 diffusion limitation also gives rise to more intense narrowing of the size distribution than seen  
5 in the corresponding liquid particle cases.

6 In the absence of particle-phase reaction (i.e.,  $k_c = 0$ , not shown in the figures) only  $\sim 1.2 \mu\text{g}$   
7  $\text{m}^{-3}$  SOA is formed in both the liquid and semi-solid aerosol cases after 12 h when  $C_g^* = 10$   
8  $\mu\text{g m}^{-3}$  while negligibly small amounts of SOA are formed for higher  $C_g^*$  values. Overall, the  
9 growth characteristics seen in the general system cases considered here are qualitatively  
10 similar to the closed system results, although significant differences between them can occur  
11 if the vapor source rate is appreciably different than the one used in the present study. For  
12 instance, if the vapor source rate is very small, then the growth characteristics will tend  
13 towards Raoult's law partitioning. In contrast, if the vapor source rate is very high, then the  
14 growth will tend to become gas-phase diffusion limited.

15

## 16 **5 Summary and Implications**

17 We have extended the computationally efficient MOSAIC aerosol model (Zaveri et al., 2008)  
18 to include a new framework for kinetic SOA partitioning that takes into account solute  
19 volatility, gas-phase diffusion, interfacial mass accommodation, particle-phase diffusion, and  
20 particle-phase reaction. The framework uses a combination of: (a) an analytical quasi-steady-  
21 state treatment for the diffusion-reaction process within the particle phase for fast-reacting  
22 organic solutes such that the timescales ( $\tau_{QSS}$ ) for their particle-phase concentrations to reach  
23 quasi-steady state are shorter than 1 min, and (b) a two-film theory approach for slow- and  
24 non-reacting organic solutes. The updated MOSAIC model was successfully validated against  
25 a benchmark finite-difference solution of the diffusion-reaction problem. MOSAIC already  
26 predicts liquid water associated with inorganic species, and the new framework can be readily  
27 adapted to kinetically partition water soluble organic gases into the particulate aqueous phase  
28 if that is the only liquid phase in the particle. Additional work is needed to treat mass transfer  
29 of gas-phase species to mixed inorganic-organic particles that experience liquid-liquid phase  
30 separation (You et al., 2012). The proposed framework is amenable for use in regional and

1 global atmospheric models, although it currently awaits specification of the various gas- and  
2 particle-phase chemistries and the related physicochemical properties that are important for  
3 SOA formation.

4 In the present study, we have applied the model to evaluate the effects of solute volatility  
5 ( $C_g^*$ ), particle-phase bulk diffusivity ( $D_b$ ), and particle-phase chemical reaction, as  
6 exemplified by the pseudo-first-order rate constant ( $k_c$ ), on kinetic SOA partitioning. We  
7 focus on the competitive growth dynamics of the Aitken and accumulation mode particles due  
8 to condensation while the Kelvin effect and coagulation are neglected for simplicity. Our  
9 analysis shows that the timescale of SOA partitioning and the associated evolution of aerosol  
10 number and composition size distributions depend on the complex interplay between  $C_g^*$ ,  $D_b$ ,  
11 and  $k_c$ , each of which can vary over several orders of magnitude. The key findings and their  
12 implications are summarized below.

13 a) In the case of instantaneous particle-phase reaction ( $k_c \rightarrow \infty$ ), SOA partitioning is  
14 mathematically equivalent to irreversible condensation of non-volatile organic vapors ( $C_g^*$   
15 = 0; mechanism #1). Mass transfer is gas-phase diffusion limited, which produces the  
16 well-known narrowing of the aerosol size distribution as small particles grow faster than  
17 the large ones (Zhang et al., 2012).

18 b) In the case of non-reactive reversible absorption of semi-volatile and volatile organic  
19 vapors by Raoult's law ( $k_c = 0$ ; mechanism #2), the final partitioning across the size  
20 distribution is volume-controlled (Zhang et al., 2012) and the partitioning timescale  
21 increases with decrease in  $C_g^*$  and  $D_b$  (Shiraiwa and Seinfeld, 2012b). In the absence of  
22 the Kelvin effect and coagulation, the mole fraction of SOA across the final size  
23 distribution at equilibrium is identical. As a result, the size distribution simply shifts along  
24 the diameter axis while its shape (mode widths and peak heights) remains unchanged.  
25 However, in a closed system, this mechanism may produce temporary narrowing of the  
26 size distribution as small particles reach quasi-equilibrium faster than the large ones  
27 (Zhang et al., 2012). The narrowing is especially pronounced if the pre-existing particles  
28 are highly viscous semi-solids ( $D_b < 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ ) and the initial gas-phase concentration  
29 is appreciably higher than the solute vapor volatility. Also, while the vapor concentration  
30 may reach a steady-state relatively quickly, the timescale for the "narrowed" aerosol size

- 1 distribution to relax back to its final (equilibrium) shape can be of the order few minutes  
2 to days, depending on the values of  $D_b$  and  $C_g^*$ .
- 3 c) In the case of reactive partitioning (finite  $k_c$ ; mechanism #3), the size distribution  
4 experiences permanent narrowing (Shiraiwa et al., 2013a), which can be especially  
5 pronounced for low values of  $C_g^*$  ( $\sim 10 \mu\text{g m}^{-3}$  and less) and  $D_b$  ( $< 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ ) and high  
6 values of  $k_c$  ( $\sim 0.01 \text{ s}^{-1}$  and higher). As  $C_g^*$  and  $D_b$  increase and  $k_c$  decreases, the  
7 narrowing reduces and the final size distribution tends to resemble that produced by  
8 mechanism #2. But unlike in mechanism #2, the gas-phase concentration of the solute  
9 eventually decays to zero and the partitioning timescale increases with increase in  $C_g^*$  and  
10 decrease in  $D_b$  and  $k_c$ . The partitioning timescale and the shape of the size distribution  
11 are especially sensitive to the phase state when  $D_b$  is about  $10^{-13} \text{ cm}^2 \text{ s}^{-1}$  or less. At  $D_b =$   
12  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$  and  $k_c = 0.01 \text{ s}^{-1}$ , the decay timescale ranges from 1 h for  $C_g^* = 10 \mu\text{g m}^{-3}$  to  
13 about 3 days for  $C_g^* = 1000 \mu\text{g m}^{-3}$ . Consequently, for intermediate volatility solutes ( $C_g^*$   
14  $> 1000 \mu\text{g m}^{-3}$ ) to partition in appreciable amounts to semi-solid SOA via particle-phase  
15 reactions, their  $k_c$  values need to be  $> 0.1 \text{ s}^{-1}$ .
- 16 d) From a practical standpoint, the particle-phase concentration profiles of a solute (with any  
17  $C_g^*$ ) reacting with  $k_c > 0.01 \text{ s}^{-1}$  may be assumed to be at steady-state in particles of any  
18 size and any phase state. Furthermore, for  $k_c \leq 0.1 \text{ s}^{-1}$  and  $D_b \geq 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ , the  
19 particle-phase reaction occurs uniformly through the entire volume of submicron particles.  
20 At higher  $k_c$  or lower  $D_b$  values, the particle-phase concentration profile becomes  
21 increasingly non-uniform (i.e., depleted towards the center of the particle) as the particle  
22 size increases. As a result, particle-phase reactions in large semi-solid particles occur  
23 primarily near the surface while in smaller particles the same reactions may still occur  
24 through the entire volume. These differences in the diffusion-reaction dynamics across the  
25 size distribution, and its dependence on the particle phase state, together control the SOA  
26 partitioning timescale and the size distribution evolution.
- 27 e) Observations of the evolution of the size distribution can provide valuable clues about the  
28 underlying mechanisms of SOA formation (Riipinen et al., 2011; Shiraiwa et al., 2013a).

1 However, all three mechanisms, under certain combinations of  $C_g^*$ ,  $D_b$ , and  $k_c$  values,  
 2 can produce similar looking aerosol number size distributions. A concerted experimental  
 3 strategy is therefore necessary to properly constrain these and other key model parameters  
 4 and effectively evaluate the next generation of SOA models that treat phase state  
 5 thermodynamics, particle-phase diffusion and particle-phase reactions.

- 6 f) A proper representation of these physicochemical processes and parameters are needed to  
 7 reliably predict not only the total SOA mass, but also its composition and number size  
 8 distributions, which together determine its overall optical and cloud-nucleating properties.

9 Future model development work entails implementation of comprehensive gas-phase VOC  
 10 oxidation mechanisms and the key particle-phase reactions that form organic salts, oligomers,  
 11 hemiacetals, organosulfates, and other high molecular weight oxidation products, which  
 12 constitute a significant fraction of SOA. At the same time, a computationally efficient  
 13 treatment for phase transition thermodynamics (including liquid-liquid phase separation) is  
 14 needed to provide the combined feedbacks of ambient temperature, relative humidity, and  
 15 particle composition on the bulk diffusivity and reactivity of the absorbed organic solutes.

## 17 **Appendix A: Overall Gas-side Mass Transfer Coefficient $K_g$**

18 Flux  $F$  ( $\text{mol cm}^{-2} \text{s}^{-1}$ ) of species  $i$  across the gas-particle interface can be written in multiple  
 19 ways depending on the choice of the mass transfer coefficient:

20 Gas-side mass transfer coefficient:  $F_i = k_{g,i}(\bar{C}_{g,i} - C_{g,i}^s)$ , (A1)

21 Particle-side mass transfer coefficient:  $F_i = k_{p,i}(A_i^s - \bar{A}_i)$ , (A2)

22 Overall gas-side mass transfer coefficient:  $F_i = K_{g,i}(\bar{C}_{g,i} - S'_i \bar{A}_i)$ . (A3)

23 In Eq. (A3) the term  $(\bar{C}_{g,i} - S'_i \bar{A}_i)$  is the overall driving force for mass transfer between the  
 24 bulk gas-phase and the average bulk particle phase, where

25 
$$S'_i = \frac{C_{g,i}^*}{\sum_j \bar{A}_j}. \quad (\text{A4})$$

1 In the above equations,  $k_g$  ( $\text{cm s}^{-1}$ ) is the gas-side mass transfer coefficient,  $k_p$  ( $\text{cm s}^{-1}$ ) is the  
 2 particle-side mass transfer coefficient, and  $K_g$  ( $\text{cm s}^{-1}$ ) is the overall gas-side mass transfer  
 3 coefficient.

4 We can rewrite Eq. (A3) as:

$$5 \frac{1}{K_{g,i}} = \frac{\bar{C}_{g,i} - S'_i \bar{A}_i}{F_i} = \frac{(\bar{C}_{g,i} - C_{g,i}^s) + (C_{g,i}^s - S'_i \bar{A}_i)}{F_i}. \quad (\text{A5})$$

6 Applying Raoult's law at the interface, we get:

$$7 C_{g,i}^s = S'_i A_i^s. \quad (\text{A6})$$

8 Combining Eqs. (A5) and (A6), we get:

$$9 \frac{1}{K_{g,i}} = \frac{(\bar{C}_{g,i} - C_{g,i}^s)}{F_i} + \frac{S'_i (A_i^s - \bar{A}_i)}{F_i}. \quad (\text{A7})$$

10 Combining Eqs. (A1), (A2), and (A7), we can relate the overall gas-side mass transfer  
 11 coefficient to gas-side and particle-side mass transfer coefficients as:

$$12 \frac{1}{K_{g,i}} = \frac{1}{k_{g,i}} + \frac{S'_i}{k_{p,i}}. \quad (\text{A8})$$

13 Finally, replacing the flux term in Eq. (19) with Eq. (A3) gives

$$14 \frac{d\bar{A}_i}{dt} = \frac{3}{R_p} K_{g,i} \left\{ \bar{C}_{g,i} - \frac{\bar{A}_i}{\sum_j \bar{A}_j} C_i^* \right\} - k_{c,i} \bar{A}_i. \quad (\text{A9})$$

15

## 16 **Appendix B: Particle-side Mass Transfer Coefficient $k_p$**

17 As noted in the main paper, the particle-side film thickness  $\delta_p$ , and therefore  $k_p$  and  $K_g$ , are  
 18 not readily known. We estimate these parameters by assuming that under quasi-steady state  
 19 conditions, the analytical solution (Eq. (19)) and the two-film theory (Eq. (21)) give the same  
 20 results. Under quasi-steady state conditions, Eq. (19) becomes:

$$21 \frac{d\bar{A}_i}{dt} = \frac{3}{R_p} k_{g,i} \left\{ \bar{C}_{g,i} - \frac{S'_i \bar{A}_i}{Q_i} \right\} - k_{c,i} \bar{A}_i = 0. \quad (\text{B1})$$



1 Rearranging Eq. (B1), we have:

$$2 \quad \frac{\bar{A}_i}{\bar{C}_{g,i}} = \left( \frac{S'_i}{Q_i} + \frac{k_{c,i}R_p}{3k_{g,i}} \right)^{-1}. \quad (\text{B2})$$

3 Similarly, assuming quasi-steady-state for Eq. (21), we get:

$$4 \quad \frac{d\bar{A}_i}{dt} = \frac{3}{R_p} K_{g,i} \{ \bar{C}_{g,i} - S'_i \bar{A}_i \} - k_{c,i} \bar{A}_i = 0. \quad (\text{B3})$$

5 Rearranging Eq. (B3), we have:

$$6 \quad \frac{\bar{A}_i}{\bar{C}_{g,i}} = \left( S'_i + \frac{k_{c,i}R_p}{3K_{g,i}} \right)^{-1}. \quad (\text{B4})$$

7 With our assumption that the two approaches produce the same quasi-steady state solutions,  
8 the left-hand-sides of Eqs. (B2) and (B4) are equal, so equating their right-hand-sides gives:

$$9 \quad \frac{S'_i}{Q_i} + \frac{k_{c,i}R_p}{3k_{g,i}} = S'_i + \frac{k_{c,i}R_p}{3K_{g,i}}. \quad (\text{B5})$$

10 Substituting the expression for  $K_{g,i}$  from Eq. (A8) in Eq. (B5), and simplifying the resulting  
11 equation for  $k_{p,i}$  yields:

$$12 \quad k_{p,i} = \frac{k_{c,i}R_p}{3} \left( \frac{Q_i}{1-Q_i} \right). \quad (\text{B6})$$

13 Substituting the expression for  $Q_i$  from Eq. (8) in Eq. (B6), we get:

$$14 \quad k_{p,i} = \frac{k_{c,i}R_p}{q_i^2} \left( \frac{q_i \coth q_i - 1}{1-Q_i} \right). \quad (\text{B7})$$

15 Using  $q_i^2 = R_p^2 k_{c,i} / D_{b,i}$  in Eq. (B7) gives:

$$16 \quad k_{p,i} = \frac{D_{b,i}}{R_p} \left( \frac{q_i \coth q_i - 1}{1-Q_i} \right). \quad (\text{B8})$$

17 The particle-side film thickness is then expressed as:

$$18 \quad \delta_{p,i} = R_p \left( \frac{1-Q_i}{q_i \coth q_i - 1} \right). \quad (\text{B9})$$

1 Note that as  $k_{c,i} \rightarrow 0$ ,  $q_i \rightarrow 0$ , and  $Q_i \rightarrow 1$ . Taylor's series expansion of Eq. (B8) yields:

$$2 \quad k_{p,i} = \frac{D_{b,i} \left( \frac{1}{3} - \frac{q^2}{45} + \frac{2q^4}{945} - \dots \right)}{R_p \left( \frac{1}{15} - \frac{2q^2}{315} + \dots \right)}. \quad (\text{B10})$$

3 Thus, in the limiting case of non-reacting solute ( $k_{c,i} = 0$ ), Eq. (B10) reduces to:

$$4 \quad k_{p,i} = 5 \frac{D_{b,i}}{R_p}. \quad (\text{B11})$$

5

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1 Table 1. Bias and Error Statistics for MOSAIC Predictions for the Closed System  
 2 Simulations.

$k_c$ ( $s^{-1}$ )	$C_g^* = 10 \mu\text{g m}^{-3}$			$C_g^* = 100 \mu\text{g m}^{-3}$			$C_g^* = 1000 \mu\text{g m}^{-3}$		
	MNB (%)	MNGE (%)	maxNGE (%)	MNB (%)	MNGE (%)	maxNGE (%)	MNB (%)	MNGE (%)	maxNGE (%)
0	4.5	4.5	7.7	0.3	0.3	0.4	0.03	0.03	0.1
$10^{-4}$	8.5	11.3	19.4	-1.7	1.7	3.1	-0.3	0.3	0.4
$10^{-3}$	10.0	11.3	25.7	-1.3	1.3	3.2	-0.1	0.1	0.2
$10^{-2}$	-1.3	1.3	3.4	3.4	3.4	4.2	-0.3	0.3	1.0
$10^{-1}$	-4.3	4.3	10.7	-2.2	2.6	7.7	0.5	0.7	1.1

3

4

1 Table 2. Bias and Error Statistics for MOSAIC Predictions for the General System  
 2 Simulations.

$k_c$ ( $s^{-1}$ )	$C_g^* = 10 \mu\text{g m}^{-3}$			$C_g^* = 100 \mu\text{g m}^{-3}$			$C_g^* = 1000 \mu\text{g m}^{-3}$		
	MNB (%)	MNGE (%)	maxNGE (%)	MNB (%)	MNGE (%)	maxNGE (%)	MNB (%)	MNGE (%)	maxNGE (%)
0	0.8	0.8	8.5	0.3	0.3	2.0	0.03	0.03	0.3
$10^{-4}$	-1.0	2.2	6.4	0.6	0.6	1.8	0.1	0.1	0.2
$10^{-3}$	-3.0	3.1	5.8	-0.7	1.2	3.1	0.1	0.1	0.2
$10^{-2}$	-3.2	3.2	5.8	-2.3	2.3	4.8	-0.2	0.2	0.8
$10^{-1}$	-2.4	2.4	5.0	-0.2	1.4	2.8	1.0	1.0	1.6

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4

## 1 **Figure Captions**

2

3 Figure 1. Schematic of the gas-particle mass transfer process, with both diffusion and reaction  
4 occurring inside the particle phase.

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6 Figure 2. Normalized transient concentration  $(A(r,t)/A^s)$  profiles as a function of  
7 normalized radius  $(r/R_p)$  for a particle of diameter  $R_p = 0.05 \mu\text{m}$  for different values of bulk  
8 phase diffusivity and first-order reaction rate constants: (a)  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $k_c = 0 \text{ s}^{-1}$ ; (b)  
9  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $k_c = 5 \times 10^{-4} \text{ s}^{-1}$ ; (c)  $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ ,  $k_c = 0 \text{ s}^{-1}$ ; and (d)  $D_b = 10^{-15} \text{ cm}^2$   
10  $\text{ s}^{-1}$ ,  $k_c = 5 \times 10^{-4} \text{ s}^{-1}$ .

11

12 Figure 3. Normalized steady-state concentration  $(A(r)/A^s)_{SS}$  profiles as a function of  
13 normalized radius  $(r/R_p)$  for a particle of diameter  $R_p = 0.05 \mu\text{m}$  and a range of  $k_c$  values  
14 for (a)  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  (b)  $D_b = 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  (c)  $D_b = 10^{-13} \text{ cm}^2 \text{ s}^{-1}$  (d)  $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ .

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16 Figure 4. Normalized steady state concentration  $(A(r)/A^s)_{SS}$  profiles as a function of  
17 normalized radius  $(r/R_p)$  for different values of dimensionless diffuso-reactive parameter  $q$ .

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19 Figure 5. (a) Contour plots of: (a) particle-phase quasi-steady state timescale  $(\tau_{QSS})$ , and (b)  
20 quasi-steady state parameter  $Q = (\bar{A}/A^s)_{QSS}$  as functions of first-order rate constant  $(k_c)$  and  
21 bulk diffusion coefficient  $(D_b)$  for a species diffusing and reacting within semi-solid and  
22 liquid particles of diameter  $D_p = 0.1 \mu\text{m}$ .

23

24 Figure 6. Dependence of  $\tau_{QSS}$  on particle diameter  $D_p$  for  $D_b$  values ranging from  $10^{-10}$  to  $10^{-18}$   
25  $\text{ cm}^2 \text{ s}^{-1}$ : (a)  $k_c = 0 \text{ s}^{-1}$ ; (b)  $k_c = 10^{-3} \text{ s}^{-1}$ ; (c)  $k_c = 10^{-2} \text{ s}^{-1}$ ; and (d)  $k_c = 10^{-1} \text{ s}^{-1}$ .

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4 Figure 8. Schematic of the two-film theory.

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6 Figure 9. Comparison of MOSAIC (lines) and finite difference model (filled circles) solutions  
7 for gas-phase concentration decay in a closed system due to kinetic gas-particle partitioning to  
8 particles with initial  $D_p = 0.2 \mu\text{m}$ ,  $N = 5000 \text{ cm}^{-3}$ ,  $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$  and  $k_c$  ranging from 0  
9 to  $0.1 \text{ s}^{-1}$  for three solute volatilities: (a)  $C_g^* = 10 \mu\text{g m}^{-3}$ , (b)  $C_g^* = 100 \mu\text{g m}^{-3}$ , and (c)  $C_g^* =$   
10  $1000 \mu\text{g m}^{-3}$ .

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12 Figure 10. Comparison of MOSAIC (lines) and finite difference model (filled circles)  
13 solutions for gas-phase concentration evolution in a general system due to kinetic gas-particle  
14 partitioning to particles with initial  $D_p = 0.2 \mu\text{m}$ ,  $N = 5000 \text{ cm}^{-3}$ ,  $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ ,  $\gamma = 0.1$   
15  $\mu\text{g m}^{-3} \text{ h}^{-1}$ , and  $k_c$  ranging from 0 to  $0.1 \text{ s}^{-1}$  for three solute volatilities: (a)  $C_g^* = 10 \mu\text{g m}^{-3}$ ,  
16 (b)  $C_g^* = 100 \mu\text{g m}^{-3}$ , and (c)  $C_g^* = 1000 \mu\text{g m}^{-3}$ .

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18 Figure 11. Initial aerosol number and volume size distributions along with the condensational  
19 sink  $k_{CS}$ . The dashed line demarcates the Aitken mode from the accumulation mode and the  
20 initial condensation sink is such that the sum of  $k_{CS}$  over all the size bins in the Aitken mode  
21 is equal to that in the accumulation mode.

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23 Figure 12. Results for the instantaneous reaction reference case ( $k_c \rightarrow \infty$ ; equivalent to non-  
24 volatile solute condensation): (a) Gas-phase concentration decay; (b) temporal evolution of  
25 aerosol size distribution; and (c) temporal evolution of the mass fraction of newly formed  
26 SOA.

27

1 Figure 13. Results for kinetic SOA partitioning due to Raoult's law ( $k_c = 0 \text{ s}^{-1}$ ) for  $C_g^* = 10$   
2  $\mu\text{g m}^{-3}$ : (a) Gas-phase concentration decay for  $D_b = 10^{-6}$  and  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$ , (b) aerosol  
3 evolution for  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ; (c) SOA mass fraction evolution for  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ; (d)  
4 aerosol evolution for  $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ ; and (e) SOA mass fraction evolution for  $D_b = 10^{-15}$   
5  $\text{cm}^2 \text{ s}^{-1}$ . In both cases, the final (i.e., equilibrium) concentration of the newly formed SOA is 6  
6  $\mu\text{g m}^{-3}$ .

7  
8 Figure 14. Same as Fig. 13, except  $C_g^* = 1000 \mu\text{g m}^{-3}$ .

9  
10 Figure 15. Gas-phase concentration decay due to kinetic SOA partitioning with particle-phase  
11 reaction ( $k_c = 0.01 \text{ s}^{-1}$ ) for bulk diffusivities ranging from  $10^{-6}$  to  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$  and three gas  
12 volatilities: (a)  $C_g^* = 10 \mu\text{g m}^{-3}$ ; (b)  $C_g^* = 100 \mu\text{g m}^{-3}$ ; and (c)  $C_g^* = 1000 \mu\text{g m}^{-3}$ . Each plot  
13 also shows gas-phase concentration decay for the reference case of instantaneous reaction  
14 (black line,  $k_c \rightarrow \infty$ ). In each case, the final concentration of the newly formed SOA is  $6 \mu\text{g}$   
15  $\text{m}^{-3}$ . Panel (d) shows the plot of gas-phase concentration decay timescale ( $\tau_g$ ) as a function of  
16  $D_b$  for the different gas volatilities.

17  
18 Figure 16. Initial (dashed line) and final (solid lines) aerosol number size distribution due to  
19 Raoult's law gas-particle partitioning coupled with particle-phase reaction ( $k_c = 0.01 \text{ s}^{-1}$ ) for  
20 bulk diffusivities ranging from  $10^{-6}$  to  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$  and three gas volatilities: (a)  $C_g^* = 10 \mu\text{g}$   
21  $\text{m}^{-3}$ ; (b)  $C_g^* = 100 \mu\text{g m}^{-3}$ ; and (c)  $C_g^* = 1000 \mu\text{g m}^{-3}$ . Panel (d) shows the final size  
22 distributions for the two reference cases: instantaneous reaction (black line;  $k_c \rightarrow \infty$ ) and  
23 Raoult's law partitioning (gray line;  $k_c = 0$ ) for any  $D_b$  and  $C_g^* > 0$ . As illustrated in Fig. 15,  
24 the time required to reach the final state differs significantly for different cases, but the final  
25 SOA formed in each case is  $6 \mu\text{g m}^{-3}$ .

26

1 Figure 17. Final size distributions of the newly formed SOA mass fraction for different  $D_b$   
2 values and: (a)  $C_g^* = 10 \mu\text{g m}^{-3}$ ; (b)  $C_g^* = 100 \mu\text{g m}^{-3}$ ; and (c)  $C_g^* = 1000 \mu\text{g m}^{-3}$ . Each panel  
3 also shows the reference plots for instantaneous reaction (black line;  $k_c \rightarrow \infty$ ) and for  
4 Raoult's law partitioning (gray line;  $k_c = 0 \text{ s}^{-1}$ ) for any  $D_b$  and  $C_g^* > 0$ .

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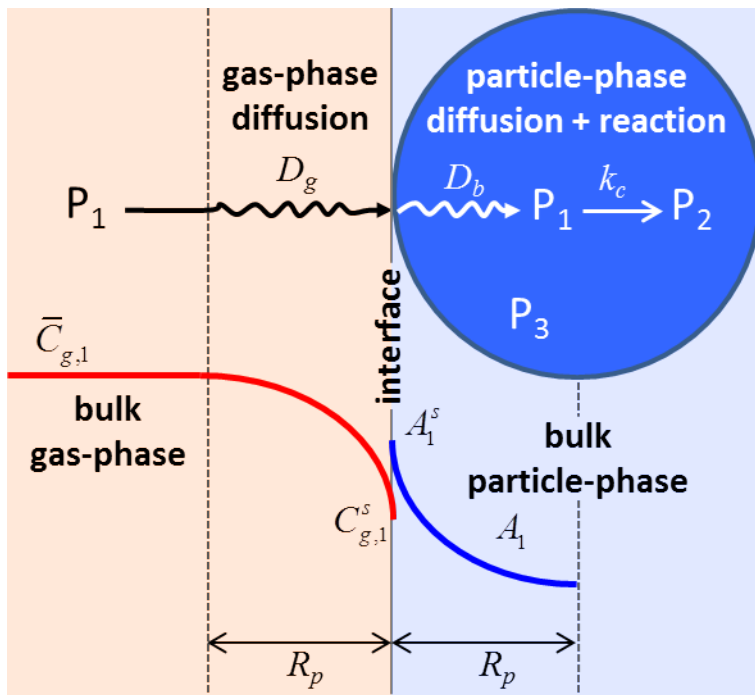
6 Figure 18. Temporal evolution of total SOA mass concentration (left column) and aerosol size  
7 distribution (right column) at  $t = 12 \text{ h}$  for  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $\gamma = 0.6 \mu\text{g m}^{-3} \text{ h}^{-1}$ ,  $k_c = 0.01$  to  $\infty$   
8  $\text{s}^{-1}$ , and three different solute volatilities: (a, b)  $C_g^* = 10 \mu\text{g m}^{-3}$ ; (c, d)  $C_g^* = 100 \mu\text{g m}^{-3}$ ; and (e,  
9 f)  $C_g^* = 1000 \mu\text{g m}^{-3}$ .

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11 Figure 19. Same as Fig. 18, except  $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ .

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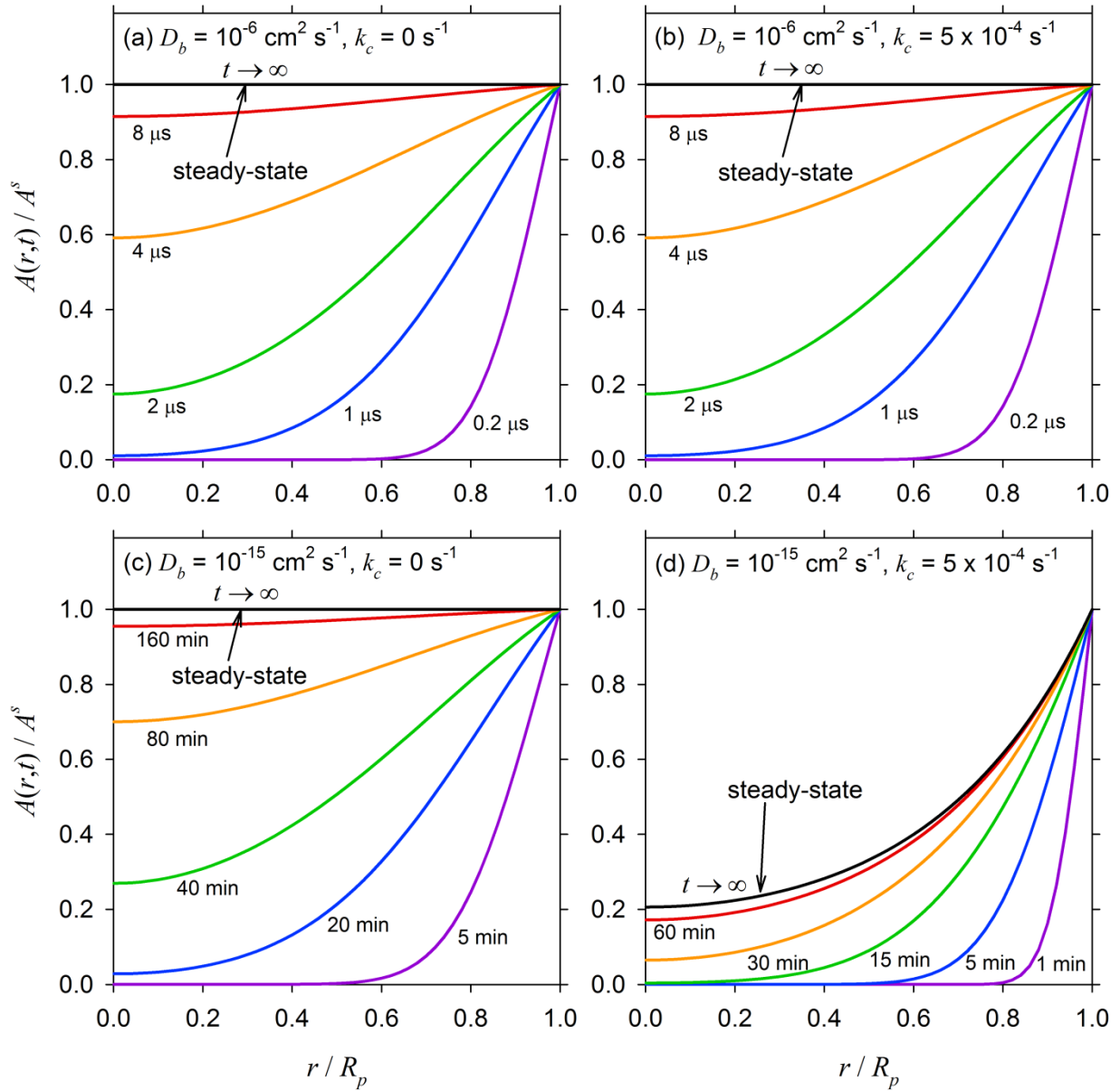


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3 Figure 1. Schematic of the gas-particle mass transfer process, with both diffusion and reaction

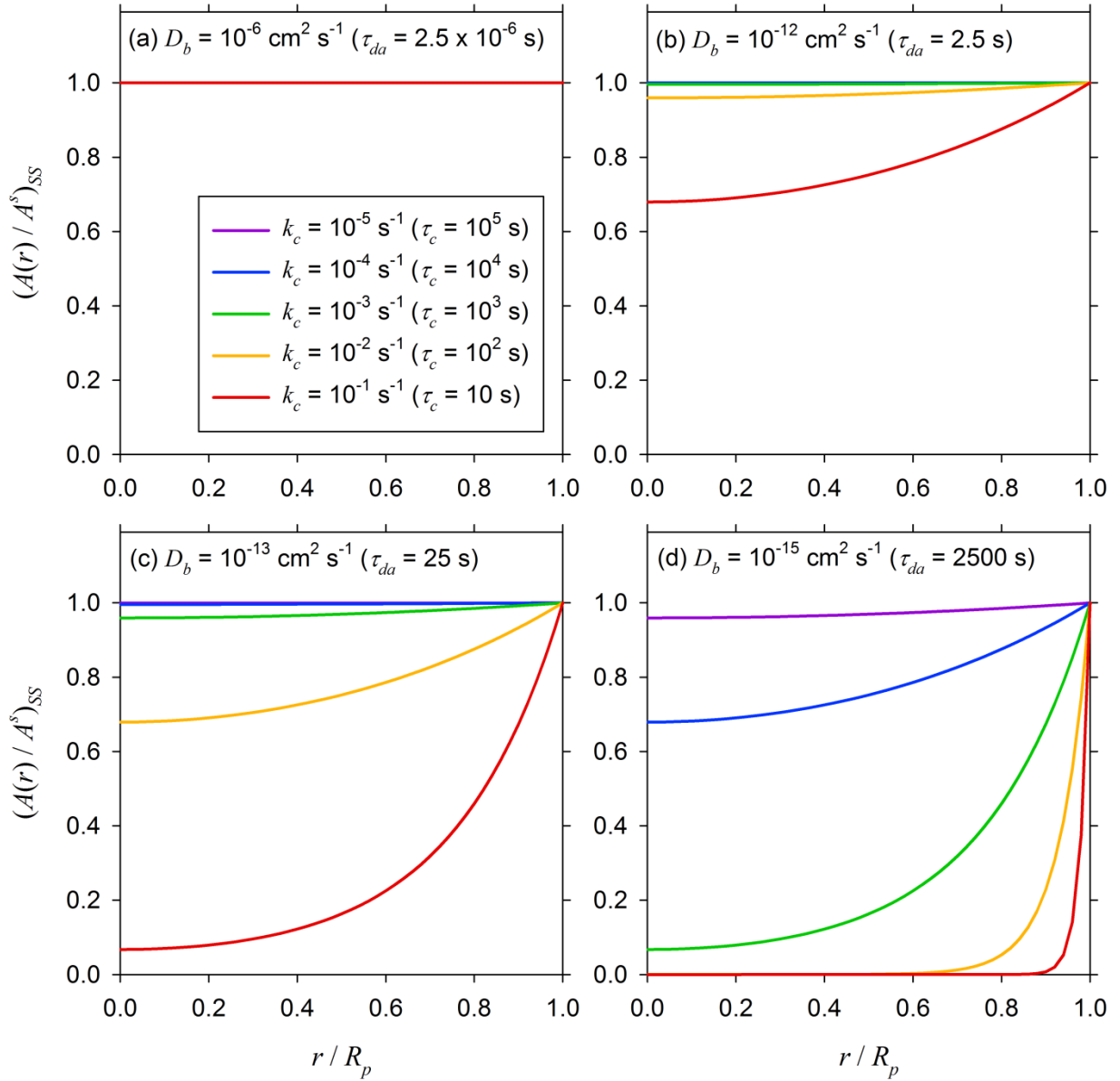
4 occurring inside the particle phase.



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3 Figure 2. Normalized transient concentration ( $A(r,t)/A^s$ ) profiles as a function of  
 4 normalized radius ( $r/R_p$ ) for a particle of diameter  $R_p = 0.05 \mu\text{m}$  for different values of bulk  
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 6  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $k_c = 5 \times 10^{-4} \text{ s}^{-1}$ ; (c)  $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ ,  $k_c = 0 \text{ s}^{-1}$ ; and (d)  $D_b = 10^{-15} \text{ cm}^2$   
 7  $\text{ s}^{-1}$ ,  $k_c = 5 \times 10^{-4} \text{ s}^{-1}$ .

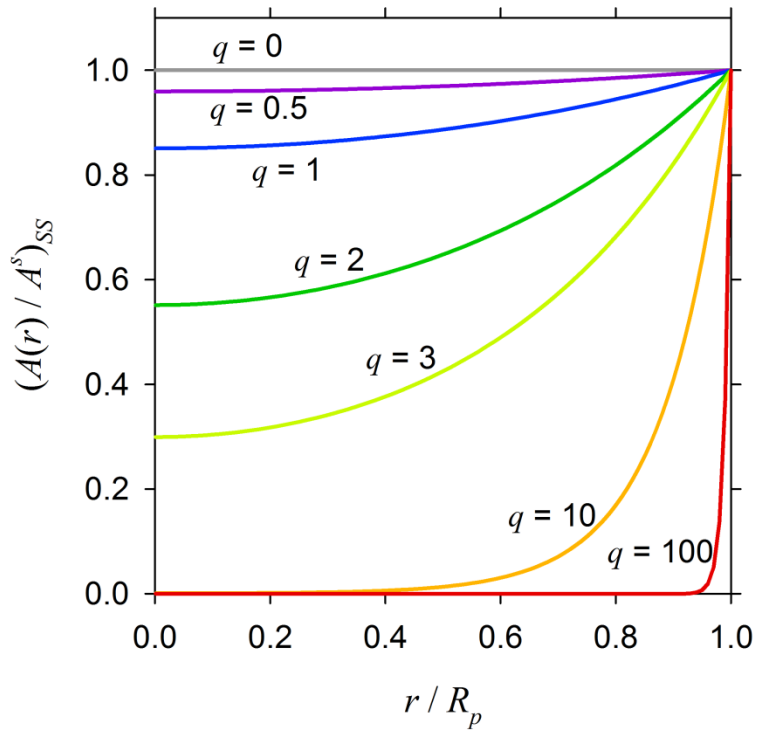


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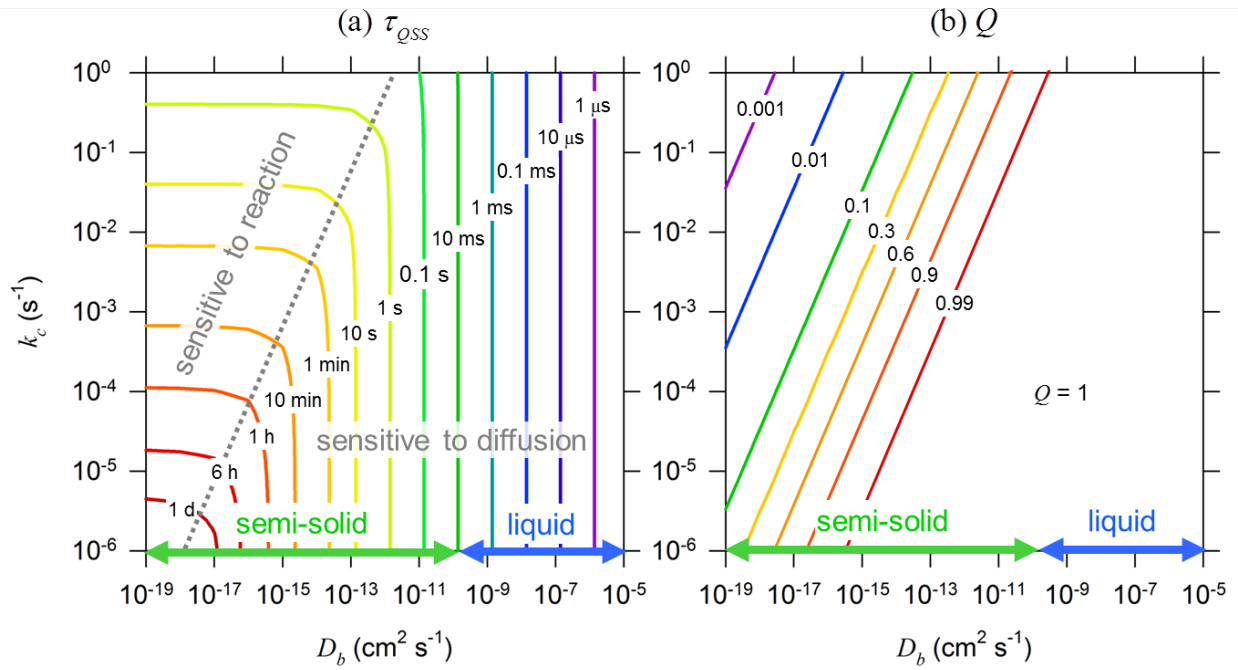
3 Figure 3. Normalized steady-state concentration  $(A(r)/A^s)_{SS}$  profiles as a function of  
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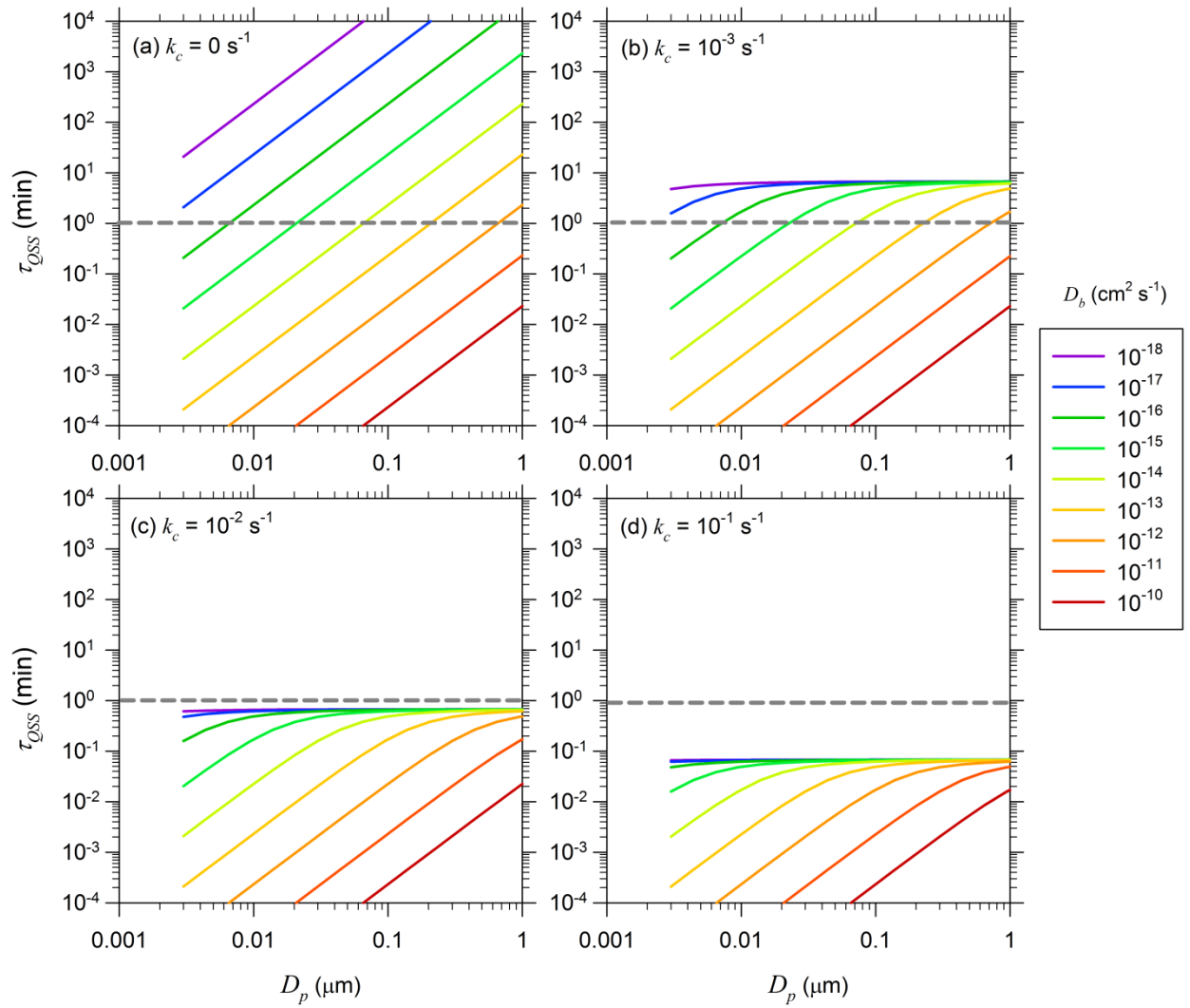
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Figure 4. Normalized steady state concentration  $(A(r) / A^s)_{SS}$  profiles as a function of normalized radius  $(r / R_p)$  for different values of dimensionless diffuso-reactive parameter  $q$ .



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Figure 5. (a) Contour plots of: (a) particle-phase quasi-steady state timescale ( $\tau_{QSS}$ ), and (b) quasi-steady state parameter  $Q = (\bar{A} / A^s)_{QSS}$  as functions of first-order rate constant ( $k_c$ ) and bulk diffusion coefficient ( $D_b$ ) for a species diffusing and reacting within semi-solid and liquid particles of diameter  $D_p = 0.1 \mu m$ .

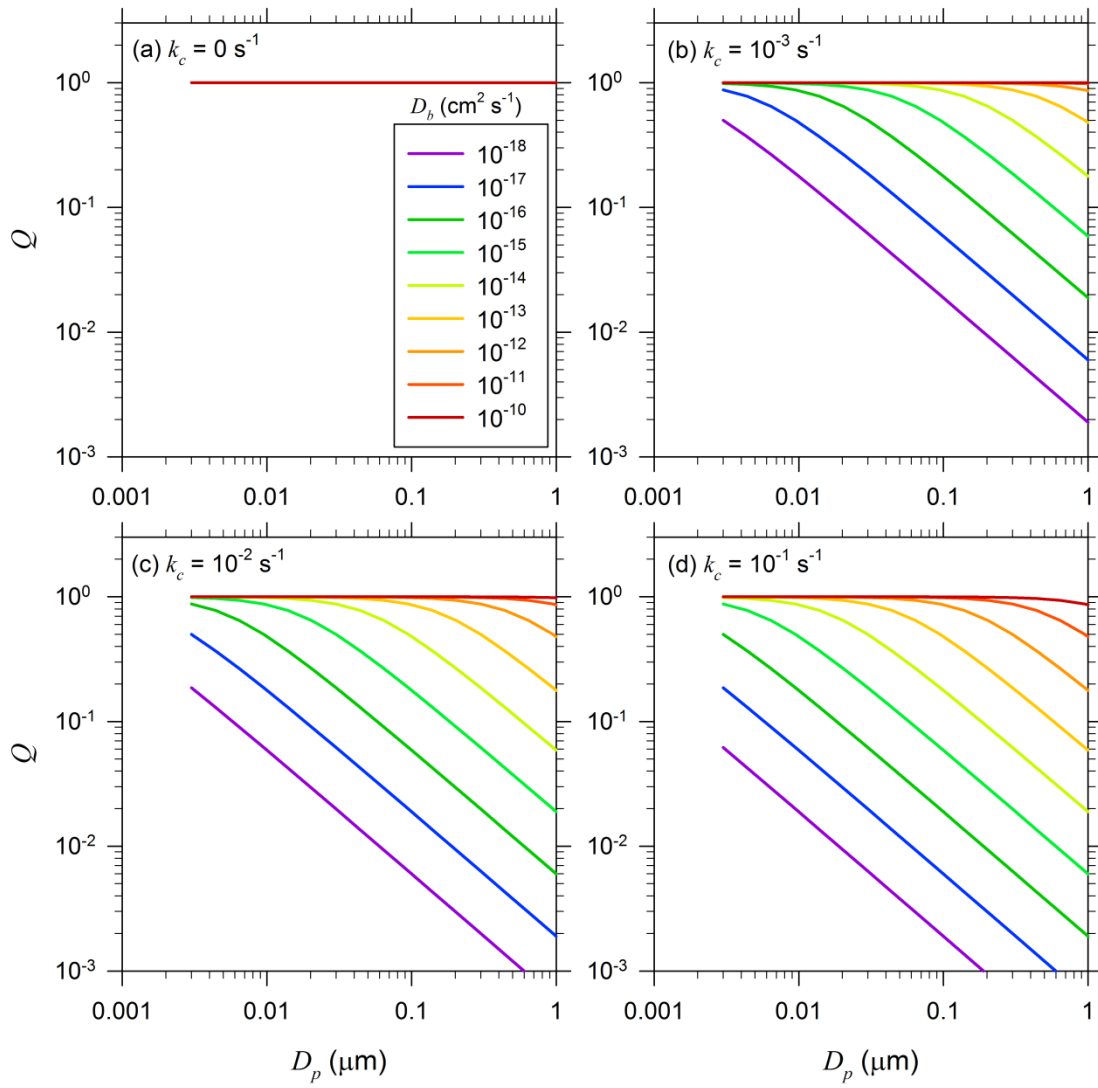


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3 Figure 6. Dependence of  $\tau_{QSS}$  on particle diameter  $D_p$  for  $D_b$  values ranging from  $10^{-10}$  to  $10^{-18}$

4  $\text{cm}^2 \text{ s}^{-1}$ : (a)  $k_c = 0 \text{ s}^{-1}$ ; (b)  $k_c = 10^{-3} \text{ s}^{-1}$ ; (c)  $k_c = 10^{-2} \text{ s}^{-1}$ ; and (d)  $k_c = 10^{-1} \text{ s}^{-1}$ .

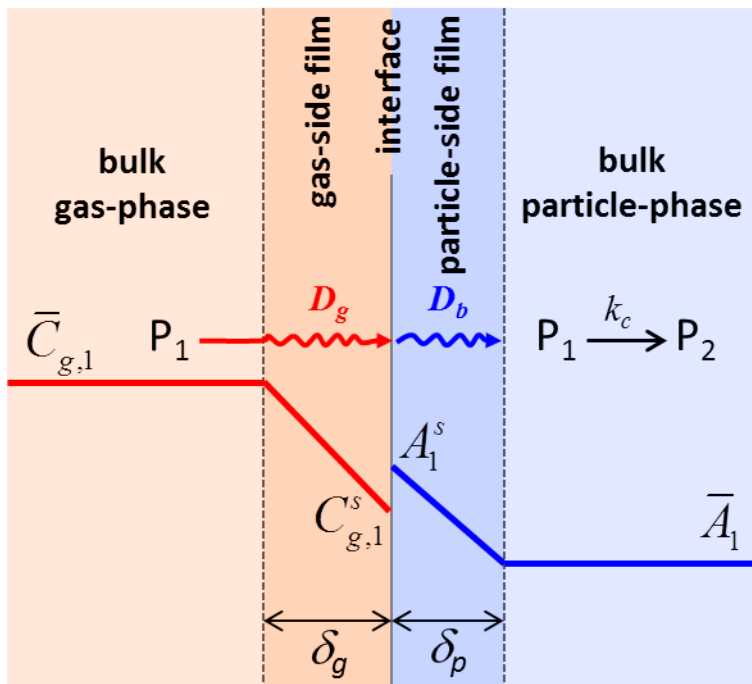


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3 Figure 7. Dependence of  $Q$  on particle diameter  $D_p$  for  $D_b$  values ranging from  $10^{-10}$  to  $10^{-18}$

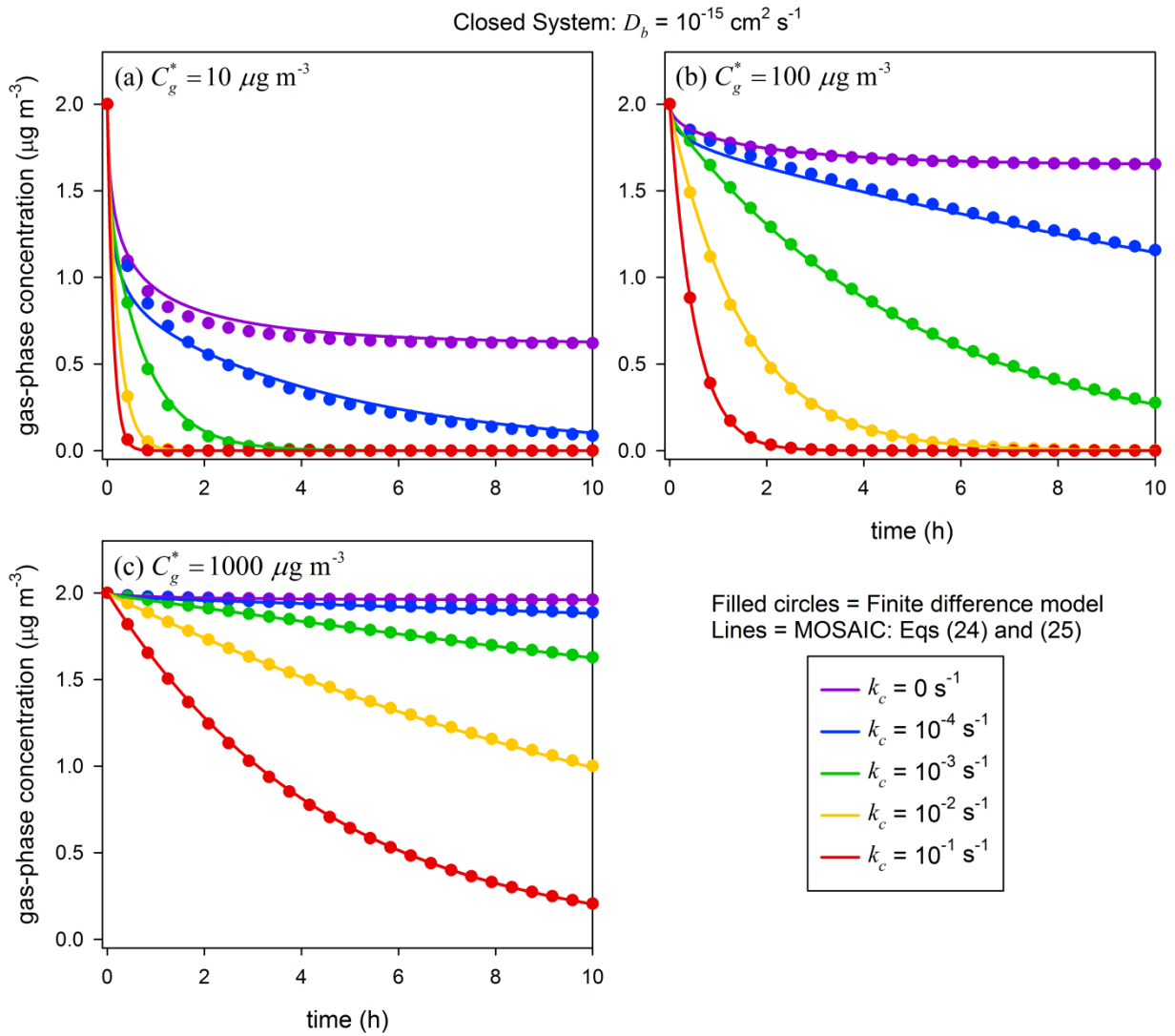
4  $\text{cm}^2 \text{s}^{-1}$ : (a)  $k_c = 0 \text{ s}^{-1}$ ; (b)  $k_c = 10^{-3} \text{ s}^{-1}$ ; (c)  $k_c = 10^{-2} \text{ s}^{-1}$ ; and (d)  $k_c = 10^{-1} \text{ s}^{-1}$ .



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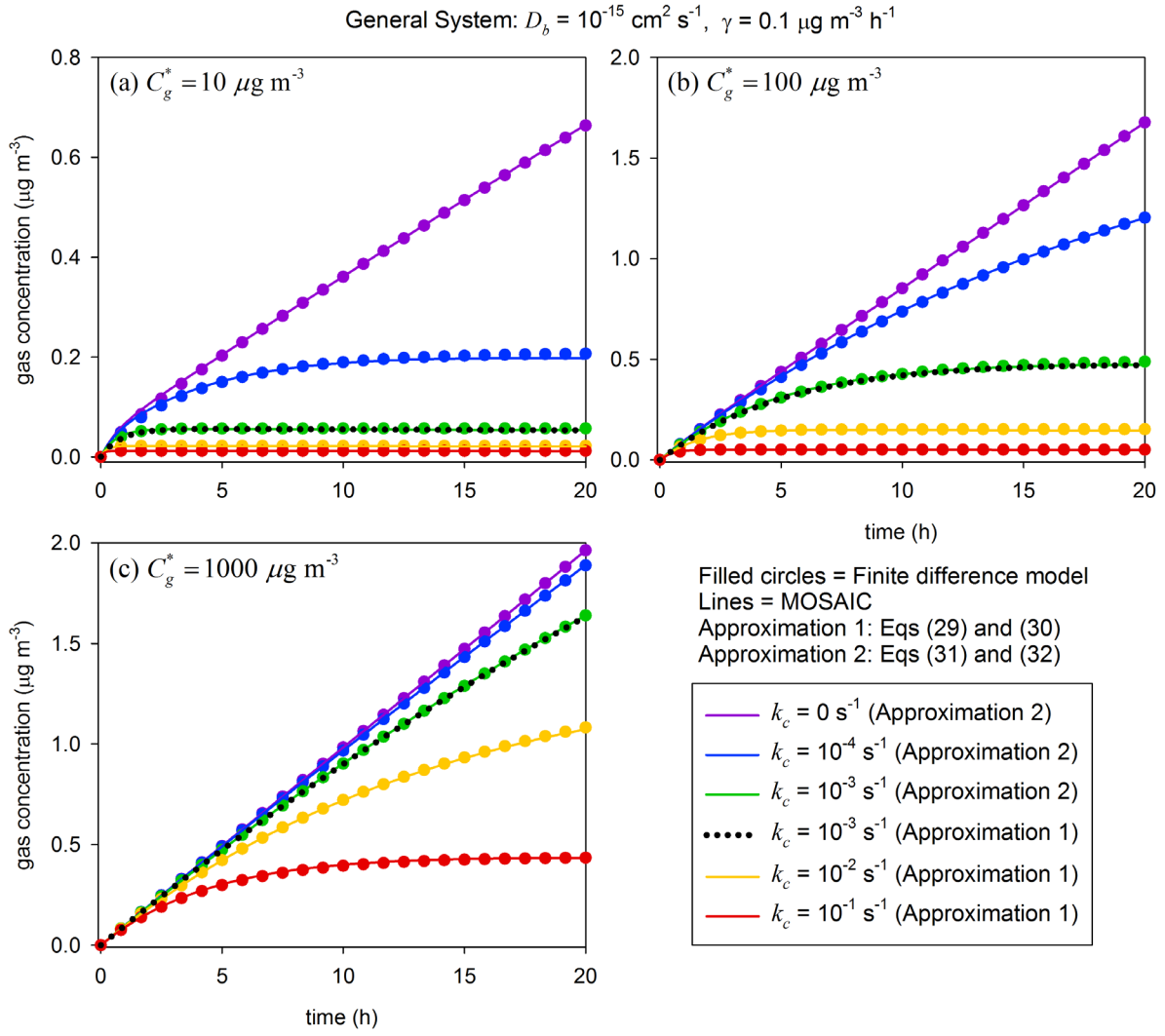
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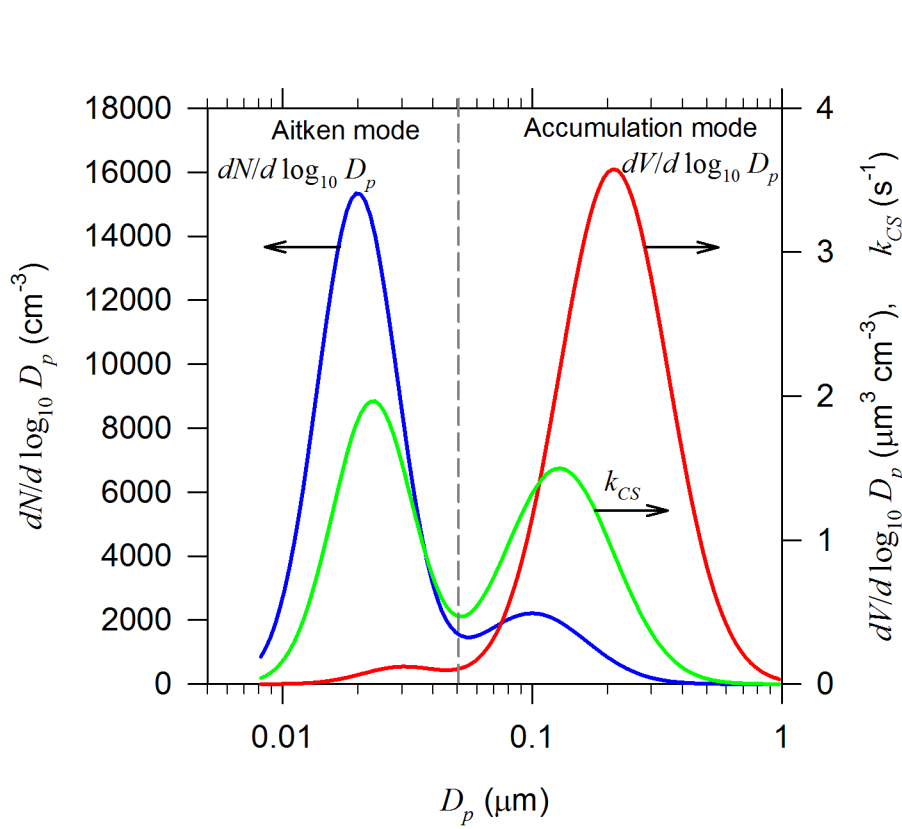
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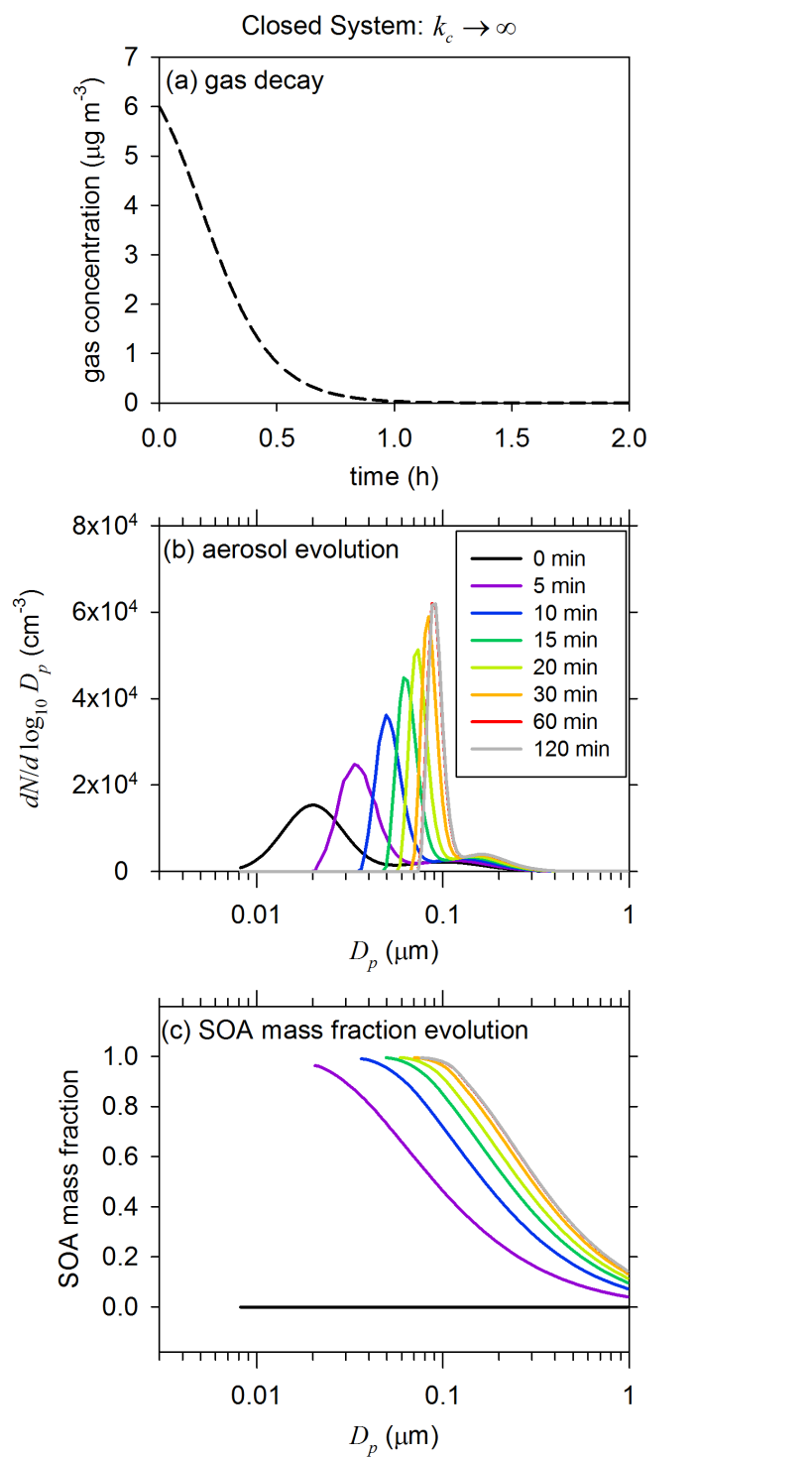
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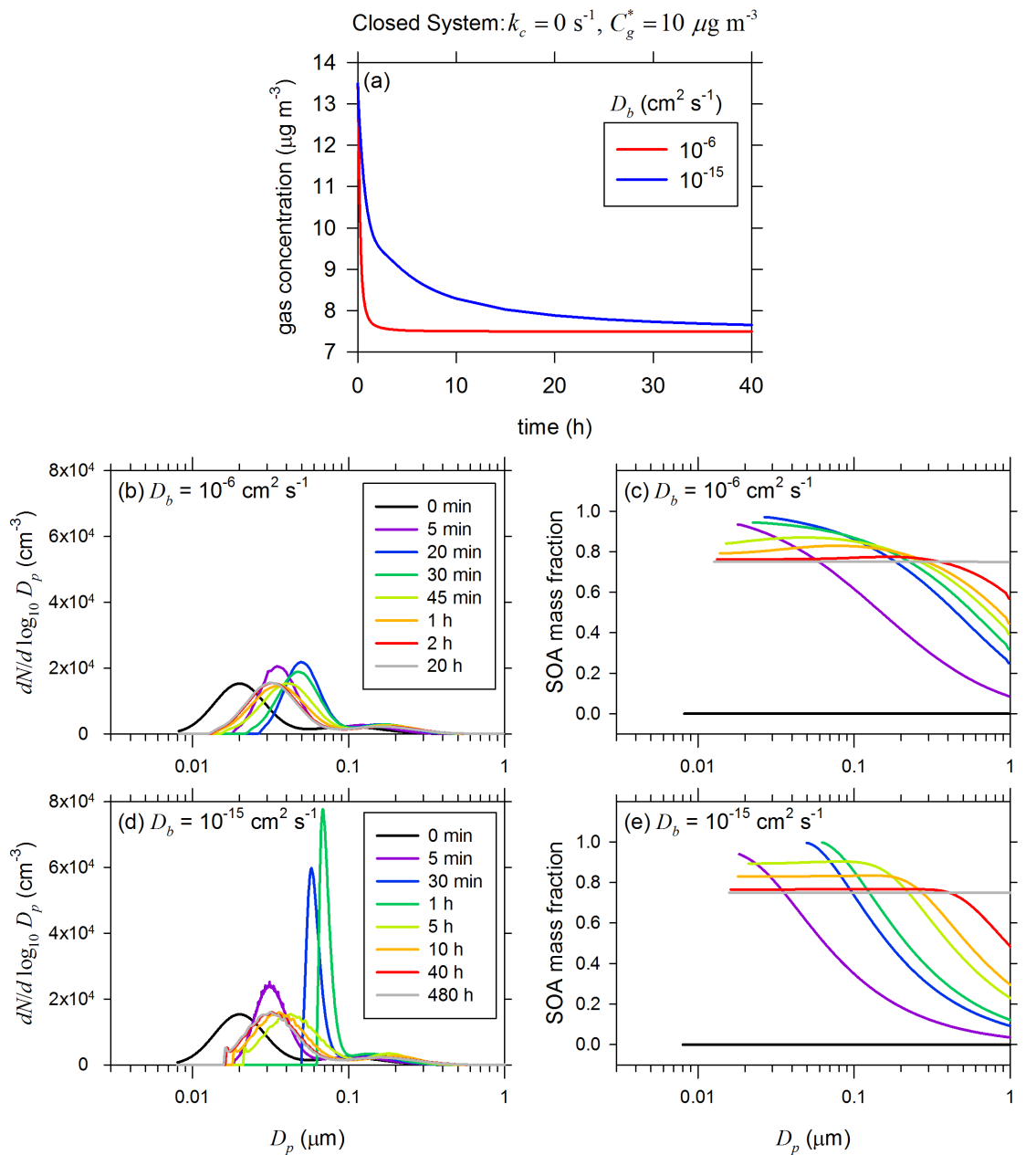
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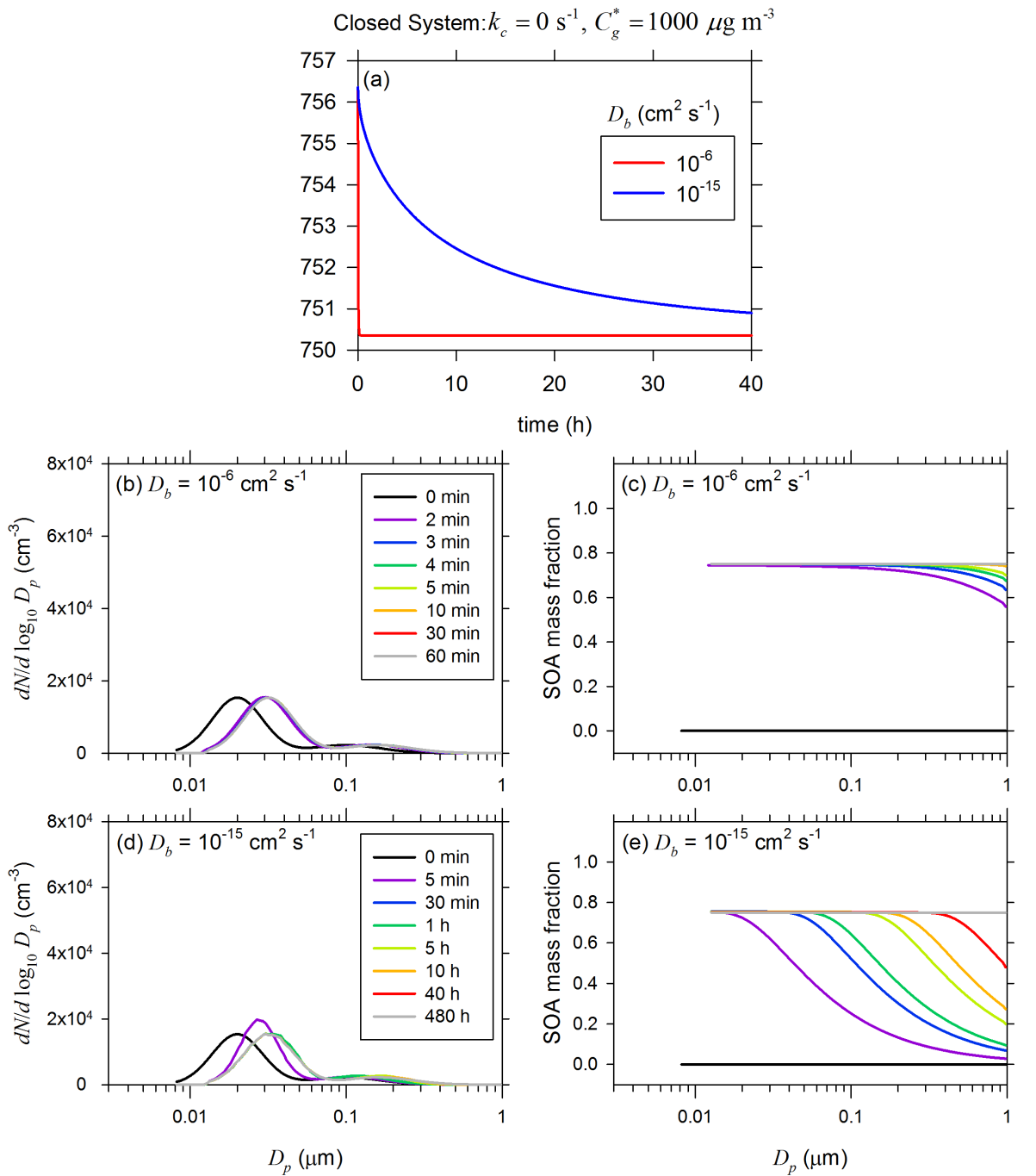
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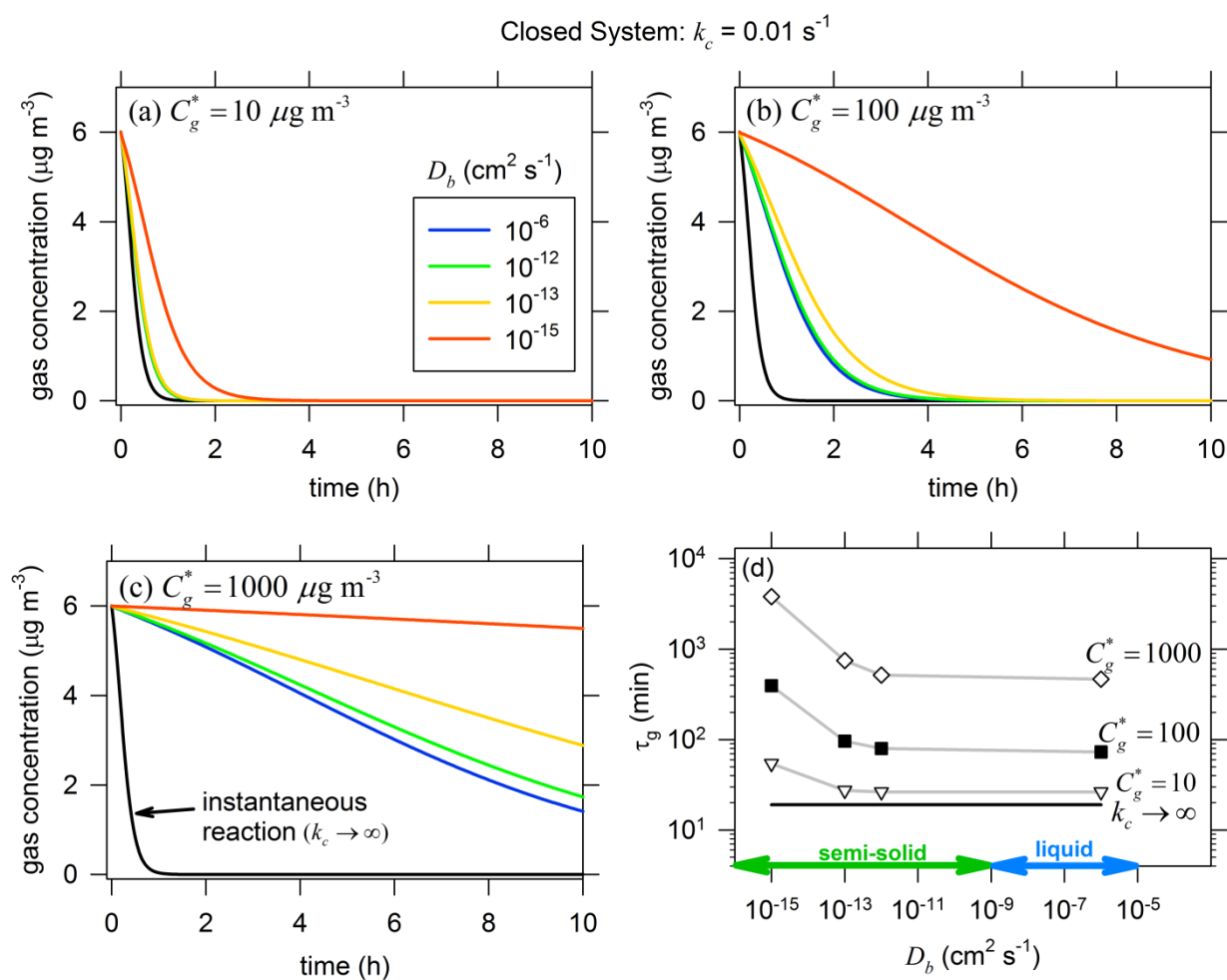
3 Figure 13. Results for kinetic SOA partitioning due to Raoult's law ( $k_c = 0 \text{ s}^{-1}$ ) for  $C_g^* = 10$   
 4  $\mu\text{g m}^{-3}$ : (a) Gas-phase concentration decay for  $D_b = 10^{-6}$  and  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$ , (b) aerosol  
 5 evolution for  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ; (c) SOA mass fraction evolution for  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ; (d)  
 6 aerosol evolution for  $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ ; and (e) SOA mass fraction evolution for  $D_b = 10^{-15}$   
 7  $\text{cm}^2 \text{ s}^{-1}$ . In both cases, the final (i.e., equilibrium) concentration of the newly formed SOA is 6  
 8  $\mu\text{g m}^{-3}$ .



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3 Figure 14. Same as Fig. 13, except  $C_g^* = 1000 \mu\text{g m}^{-3}$ .

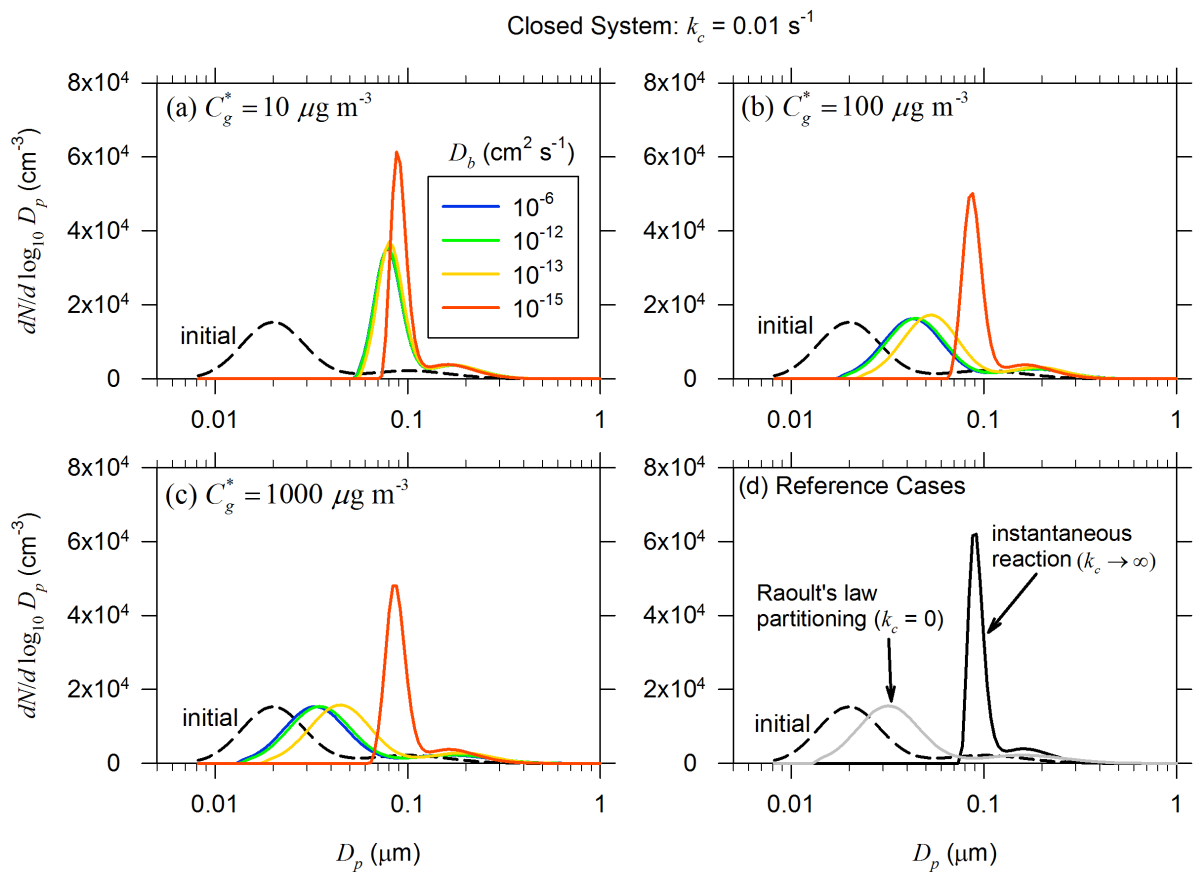


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3 Figure 15. Gas-phase concentration decay due to kinetic SOA partitioning with particle-phase  
 4 reaction ( $k_c = 0.01 \text{ s}^{-1}$ ) for bulk diffusivities ranging from  $10^{-6}$  to  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$  and three gas  
 5 volatilities: (a)  $C_g^* = 10 \mu\text{g m}^{-3}$ ; (b)  $C_g^* = 100 \mu\text{g m}^{-3}$ ; and (c)  $C_g^* = 1000 \mu\text{g m}^{-3}$ . Each plot  
 6 also shows gas-phase concentration decay for the reference case of instantaneous reaction  
 7 (black line,  $k_c \rightarrow \infty$ ). In each case, the final concentration of the newly formed SOA is  $6 \mu\text{g}$   
 8  $\text{m}^{-3}$ . Panel (d) shows the plot of gas-phase concentration decay timescale ( $\tau_g$ ) as a function of  
 9  $D_b$  for the different gas volatilities.

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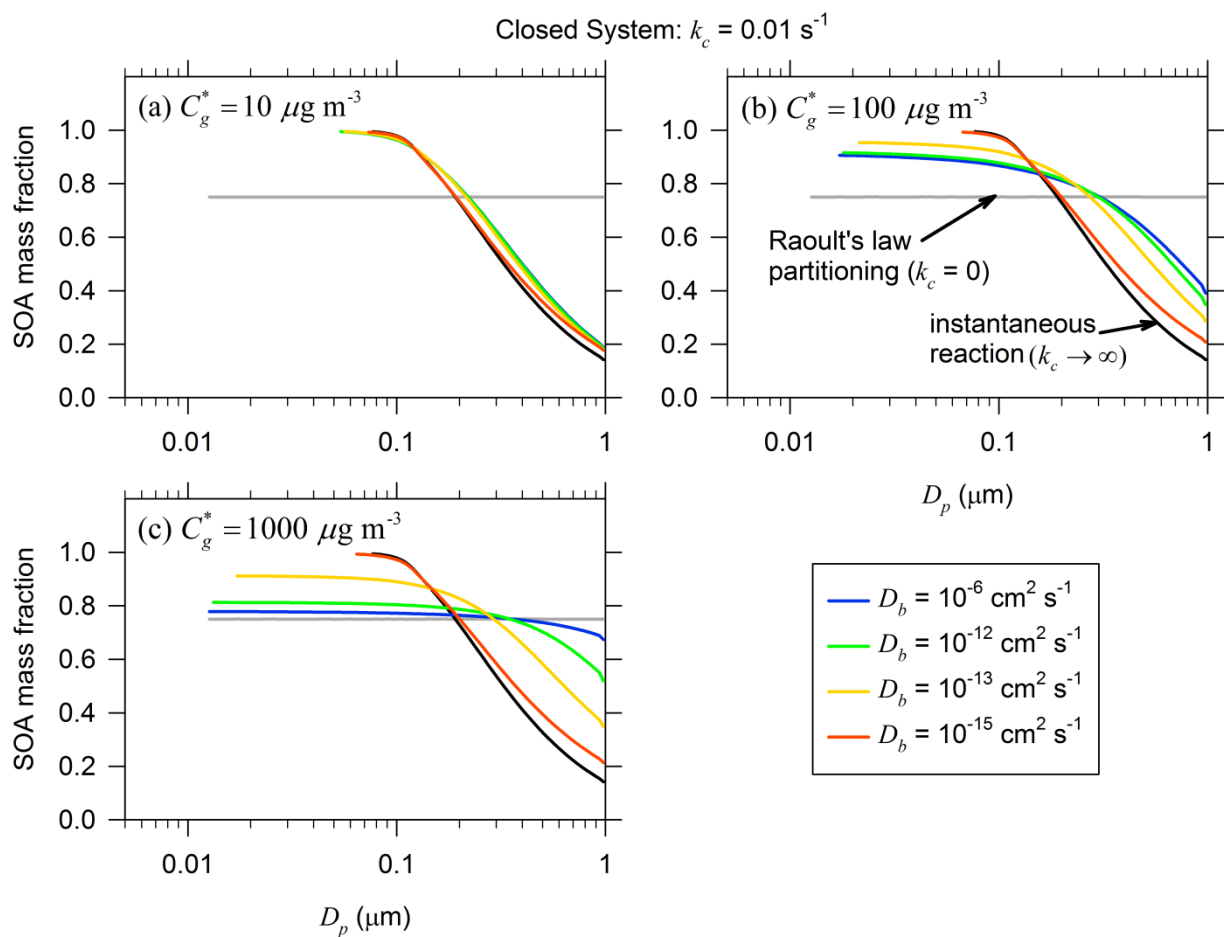
3 Figure 16. Initial (dashed line) and final (solid lines) aerosol number size distribution due to  
 4 Raoult's law gas-particle partitioning coupled with particle-phase reaction ( $k_c = 0.01 \text{ s}^{-1}$ ) for  
 5 bulk diffusivities ranging from  $10^{-6}$  to  $10^{-15} \text{ cm}^2 \text{ s}^{-1}$  and three gas volatilities: (a)  $C_g^* = 10 \text{ } \mu\text{g m}^{-3}$   
 6  $\text{m}^{-3}$ ; (b)  $C_g^* = 100 \text{ } \mu\text{g m}^{-3}$ ; and (c)  $C_g^* = 1000 \text{ } \mu\text{g m}^{-3}$ . Panel (d) shows the final size  
 7 distributions for the two reference cases: instantaneous reaction (black line;  $k_c \rightarrow \infty$ ) and  
 8 Raoult's law partitioning (gray line;  $k_c = 0$ ) for any  $D_b$  and  $C_g^* > 0$ . As illustrated in Fig. 15,  
 9 the time required to reach the final state differs significantly for different cases, but the final  
 10 SOA formed in each case is  $6 \text{ } \mu\text{g m}^{-3}$ .

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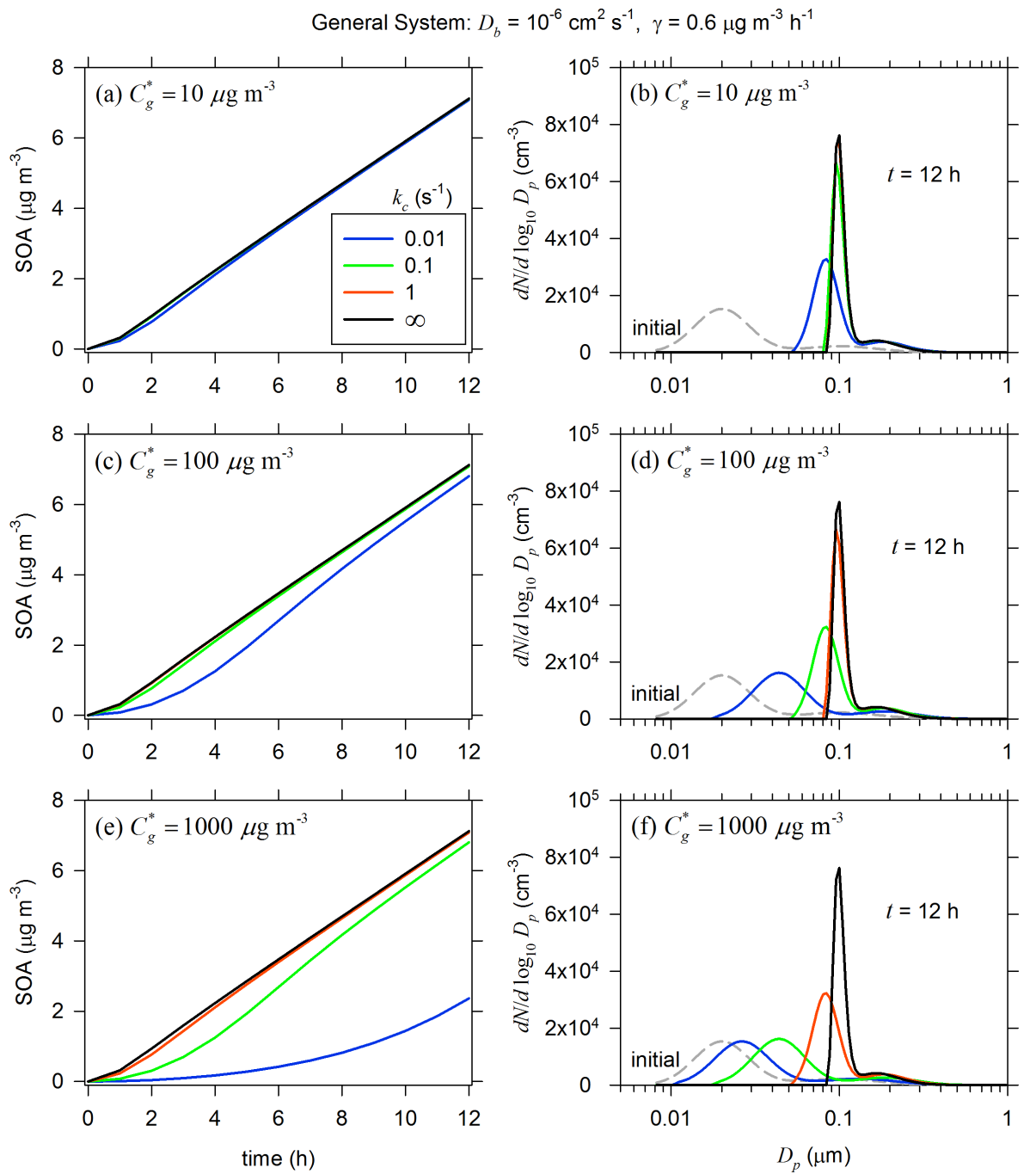




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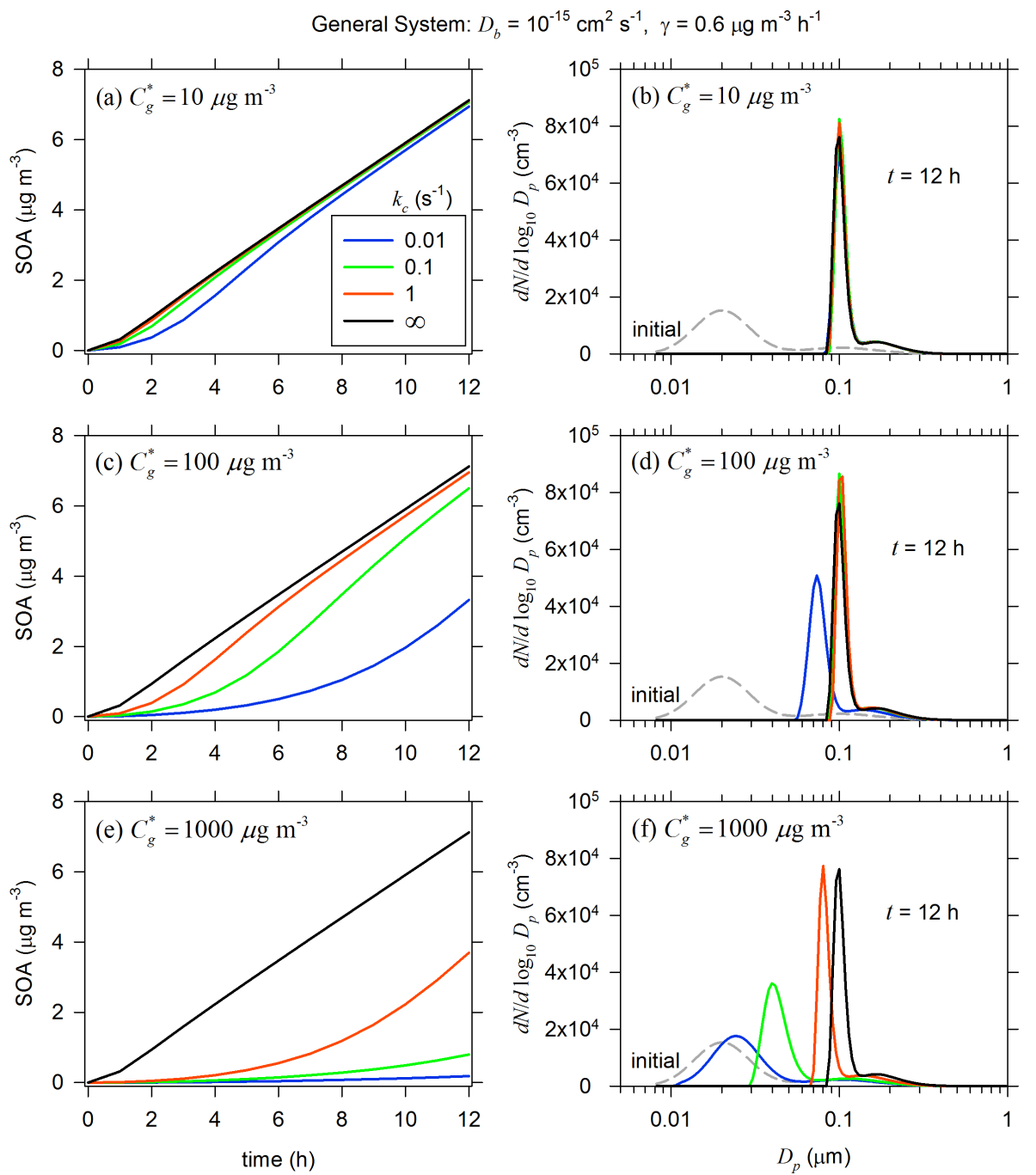
3 Figure 17. Final size distributions of the newly formed SOA mass fraction for different  $D_b$   
 4 values and: (a)  $C_g^* = 10 \mu\text{g m}^{-3}$ ; (b)  $C_g^* = 100 \mu\text{g m}^{-3}$ ; and (c)  $C_g^* = 1000 \mu\text{g m}^{-3}$ . Each panel  
 5 also shows the reference plots for instantaneous reaction (black line;  $k_c \rightarrow \infty$ ) and for  
 6 Raoult's law partitioning (gray line;  $k_c = 0 \text{ s}^{-1}$ ) for any  $D_b$  and  $C_g^* > 0$ .



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3 Figure 18. Temporal evolution of total SOA mass concentration (left column) and aerosol size  
 4 distribution (right column) at  $t = 12 \text{ h}$  for  $D_b = 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $\gamma = 0.6 \mu\text{g m}^{-3} \text{ h}^{-1}$ ,  $k_c = 0.01$  to  $\infty$   
 5  $\text{s}^{-1}$ , and three different solute volatilities: (a, b)  $C_g^* = 10 \mu\text{g m}^{-3}$ ; (c, d)  $C_g^* = 100 \mu\text{g m}^{-3}$ ; and (e,  
 6 f)  $C_g^* = 1000 \mu\text{g m}^{-3}$ .



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2 Figure 19. Same as Fig. 18, except  $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ .

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