

We thank both referees for reviewing of our manuscript. Our point-by-point responses are in blue. When appropriate, the responses also list all the relevant changes made in the revised manuscript.

Referee #1

General remarks: This is a well written paper that extends the model for kinetic gas-particle partitioning to include particle-phase diffusion and chemical reaction. The paper also provides evaluation of the theoretical framework of this model with implementation in MOSAIC and comparison of results to a finite-difference solution. Further, growth dynamics of the Aitken and accumulation mode particles are studied at several combinations species volatility, particle-phase diffusivity and particle-phase reaction rate constant. Although the model is immensely complex, and requires number of parameters that are very hard to derive from experiments, the model evaluation advances scientific understanding of kinetic partitioning of SOA and can act as a template to design future SOA formation algorithms for implementation in 3-D Eulerian models. I recommend publishing the manuscript in ACP only after taking into account the following minor changes/additions

Specific comments:

1. One of the major drawbacks of the model is the failure to account for SOA formed through aqueous-phase pathways (Carlton et al, Atmos. Chem. Phys., 13, 10203-10214, 2013). This can be particularly important in areas such as Eastern US and other urban centers where sulfate-rich conditions increase the particle-phase liquid water and subsequently aqueous-phase SOA. This should be highlighted as one of the limitations of the current proposed framework for inclusion in 3-D Eulerian models.

Thanks for mentioning this issue. MOSAIC already performs kinetic partitioning of inorganic gases (H_2SO_4 , HNO_3 , HCl , and NH_3) to size-distributed particles and predicts liquid water associated with inorganic species as a function of relative humidity. While the focus of the present work is on kinetic partitioning of organic gases to particulate organic phase, the new framework can be readily adapted to kinetically partition water soluble organic gases into the particulate aqueous phase if that is the only liquid phase in the particle. However, additional research is needed to extend the present framework to mixed inorganic-organic particles that experience liquid-liquid phase separation (i.e., coexistence of both aqueous and organic phases). We have now cited Carlton and Turpin (2013) and have added this point in the last paragraph of Sect. 3.1.2 and clarified it in the Summary and Implications section.

2. Although the paper focuses on the interplay between organic solute volatility, particle-phase diffusivity and particle-phase reactivity, some discussion on previous studies using accommodation coefficients to impose kinetic constraints on SOA formation arising from mass-transfer during phase transition would be helpful to set up a broader context of the current formulation (Bowman et al., Atmospheric Environment 31, 3921-3931; Saathoff et al., Atmos. Chem. Phys., 9, 1551–1577, 2009; Parikh et al., Atmospheric Environment 45 (5), 1126-1137).

Thanks for pointing this out. We have added the following text in section 3.1 to set up the broader context of the present work: “Previously, the interfacial mass accommodation coefficient (α) has been often used as a tunable parameter to fit the observed kinetic limitation to mass-transfer during SOA partitioning (Bowman et al., 1997; Saathoff et al., 2009; Parikh et al., 2011). However, α does not correctly capture the mass transfer limitations due to particle-phase diffusion and chemical reaction occurring within the bulk of the particle. In the present framework, the interfacial and bulk particle phase mass transfer limitations are represented separately, with the appropriate dependence for the latter on particle size.”

3. A major limitation of this model is the requirement of size-dependent diffusion parameters and kinetic rate constants for actual particle-phase chemical reactions (the specification of such reactions is still incomplete). Also several combinations of species volatility, particle-phase diffusivity and particle-phase reaction rate constant can lead to the similar aerosol size distributions, making it difficult to verify the parameters experimentally – particularly requiring size distributions of isolated SOA chemical species that are formed as products of particle-phase reactions. The burden of acquiring parameters for the model for it to be implemented in larger-scale models is very high – this caveat should be stressed and the focus of the summary and implications section should be on key scientific findings from the model, rather than suggesting it can be implemented in larger-scale models.

Our view is that there is growing experimental evidence of the effects of particle phase state and particle-phase reactions on SOA partitioning dynamics. The model framework presented here facilitates the representation of these effects in a computationally efficient manner, which can be eventually implemented in large scale models. This is the strength of the new framework rather than the present model's limitation. We have devoted only one sentence to highlight this important feature of the model in the Summary and Implications section, and have left it unchanged. The rest of the material in this section already focuses on summary of the key scientific findings from the present model analysis. We do agree that determining all the relevant phase state parameters and kinetic rate constants important for SOA formation (from different precursors and under different conditions) is a major effort, and expect a community-wide collaborative effort to address the set of new scientific and technical needs of the next generation SOA models. We have revised summary point (e) in the text to emphasize this need.

Referee #2

1. (General comment): There are a large number of equations in the manuscript; I found some of these hard to follow. If it is important that the derivation of these equations (e.g., Eq. (3) or Eq. (7)) be understood by most readers, the authors should provide a more detailed derivation in the supplemental material. My feeling is that if the reader will accept the derived results without fully understanding the derivation (as I did) they will still be able to make use of the equations and understand the work as presented.

The solution of equation (1) can be carried out by first solving the pure diffusion problem in the absence of reaction. This is the standard problem of diffusion (or heat conduction) in a sphere. Solutions can be found in the classic books: Crank, *Mathematics of Diffusion* (1975) and Carslaw and Jaeger, *Conduction of Heat in Solids* (1946). The pure diffusion solution can be extended to the case of first-order reaction using the method of Danckwerts, on page 330 of Crank. Eq. (7) is quite easily obtained by integrating Eq. (3) over the volume of the particle. Thus we feel it is not necessary to include the step-by-step solutions for these equations in the supplementary material.

2. Page 28636, line 3: It seems that the symbol k_c refers only to the bulk reaction as it is defined as the pseudo-first order approximation. Do the authors differentiate surface reactions from bulk reactions? If not, the decision to disregard surface reactions should be justified (see e.g., the importance of the surface reaction of OH and Cl⁻ in Laskin et al. 2003 among many others).

Bulk and surface reactions are not explicitly differentiated in the present framework. A reaction would essentially become a “surface reaction” if the reaction timescale ($\tau_c = 1/k_c$) is much smaller compared to the particle-phase diffusion time scale [$\tau_{da} = R_p^2/(\pi^2 D_b)$], such that there is sufficient time for the solute to be completely consumed by the reaction at or near the surface before it can diffuse into the bulk of the particle. These bulk vs. surface reaction scenarios are already discussed in Sect. 2 and illustrated in Fig 3. The reaction between OH and Cl⁻ in Laskin et al. (2003) was treated as a very fast chemical reaction (a net probability for uptake and reaction of 0.85) and the transport of OH from the gas phase to the surface was essentially gas-phase diffusion limited. Such reactions are already handled in the present framework. Special cases such as adsorption on solid surfaces followed by chemical reaction are presently not implemented in the framework, but can be easily added as and when necessary.

3. Page 28638, line 8-10: The decision to invoke the pseudo-first order (PFO) approximation needs to be more fully justified. As discussed in Eq. 8 of Berkemeier et al. (2013), when the reacto-diffusive length is expressed in terms of a PFO rate constant it is implicit that the reactant in excess is well mixed depthwise throughout the particle. In my opinion this calls into question the validity of using a PFO rate constant throughout this work as the bulk reactant need not be homogeneously distributed depth-wise, e.g., when the bulk of the particle is solid or nearly-solid. The first-order approximation essentially means that we model the dynamics of chemical reaction in the particle with a time scale, the inverse of k_c . If the time scale for the reaction is long as compared to that for diffusion, then the reaction takes place essentially uniformly in the particle. If the time scale for the reaction is short as compared to that for diffusion, then the solution predicts that the reaction proceeds as a front that propagates slowly into the particle. This latter case would be appropriate for a semi-solid particle, for example. Thus, the solution itself automatically accommodates both extremes of time scale. The only issue of the validity of the first-order assumption is whether the actual chemistry itself can be modeled by a single time scale. In the case of a chemically complex SOA system, the PFO representation provides the type of order-of-magnitude estimate that is desired, especially when trying to parameterize the model for use in regional and global models. However, it may be possible to parameterize the PFO rate constant for a condensing solute in terms of its second order rate constant multiplied by the average concentration of the reactant solute in the particle phase even when the reaction time scale is shorter than that for diffusion. Additional work, beyond the scope of the present manuscript, is needed to test and validate this approach. We have acknowledged this issue at the end of Sect. 3.2 in the revised draft manuscript.
4. Page 28639, line 18: The statement here that the timescale of diffusion varies as the radius squared is true in the case of Fickian diffusion. However, in glassy particles, diffusion fronts may move linearly inward, leading to a linear dependence on particle radius (see Zobrist et al. 2011), if the material being taken into the particle is a plasticizing agent such as water.

This point concerning the timescale of diffusion in glassy particles is well taken. We have added a clarifying statement in the text concerning this issue.

5. Page 28641, line 3-8: Were the times QSS calculated using an assumption of Fickian diffusion (see note 6)?

Yes.

6. Page 28642, line 9-11: the assertion that all particles with $k_c > 10^{-2} \text{ s}^{-1}$ are in quasi-steady state seems to be very important. The argumentation that supports it (lines 5-8) needs to be expanded for those that are less intimately familiar with the results of this study.

This result is inferred directly from Fig. 6b, which shows that $\tau_{QSS} \leq 0.7 \text{ min}$ for solutes reacting with $k_c = 10^{-2} \text{ s}^{-1}$ in particles of any size and any bulk diffusivity. The typical timescale for changes in the bulk gas phase concentrations due to transport and chemical reaction is of the order 10 min or more. Thus, from a practical standpoint, the particle-phase concentration profiles of solutes reacting with $k_c > 10^{-2} \text{ s}^{-1}$ (which have $\tau_{QSS} < 0.7 \text{ min}$) may be assumed to be at quasi-steady state in particles of any size and any D_b value. We have clarified this point in the second last paragraph of Sect. 2 of the revised manuscript.

7. Page 28644, line 14-15: Using Raoult's Law implies that the surface is in equilibrium with the gas phase. This assumption needs to be supported given that particles can often be out of equilibrium with the gas phase.

The bulk of the particle can be out of equilibrium with the gas phase, but phase equilibrium at the interface is achieved rapidly. We have added the following text in the manuscript to support this assumption: "The timescale to achieve interfacial phase equilibrium between $C_{g,i}^s$ and the particle-phase concentration of i just inside the surface, A_i^s (mol cm⁻³(particle)) is at least (Seinfeld and 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 $\bar{v}_i = (8\Re T / \pi M_i)^{1/2}$ where \Re is the universal gas constant ($8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$), T (K) is temperature, and M_i is the molecular weight of the solute. For representative values of $D_{b,i} \leq 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $M_i = 300 \text{ g mol}^{-1}$, $T = 298 \text{ K}$, and α_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

3.3 Future Considerations

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

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

Second, while the present framework allows particles of different sizes and composition to have different bulk diffusivities, it cannot explicitly treat the potential variation of diffusivity within a given particle of complex morphology. Examples include black carbon or solid ammonium sulfate particles coated with organics as well as particles with non-ideal internal mixtures of hydrophobic and hydrophilic organics. The diffusion-reaction process inside such complex and potentially non-spherical particles will again have to be parameterized based on the average bulk properties, with possible guidance from more detailed finite difference models where applicable.

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

Minor comments:

1. Page 28637, line 12 (equation 4): Is this really just the ratio of the particle radius to the reactodiffusive length? If so, it would be helpful to point this out for those readers that are not intimately familiar with this sort of framework.
Yes, the dimensionless parameter q can be viewed as the ratio of particle radius to the reactodiffusive length. We have added text to this effect (before Eq. 4) in the manuscript.
2. Page 28639, lines 16-17: If the phrases “surface-area controlled” and “volume controlled” have a specific definition, a reference would be appropriate here. These phrases imply to me that the behavior of the system scales with radius squared (surface area) or cubed (volume). However, Brekemeier et al. (2013) recently showed that several possible responses to changes in radius occur,

ranging from no effect on the normalized time to react a well-mixed particle limited by chemical reaction in the bulk (Brx) to an inverse-square dependence on particle size for systems limited by bulk diffusion (Bbd). Note that these scenarios are all for systems in which the bulk loss dominates the reactive uptake, and that Table 4 of Berkemeier et al. is normalized so that the intuitive volume controlled cubic dependence on radius appears as zero.

We have rephrased that sentence to: “Thus, the particle growth is volume reaction-controlled when the concentration profile is uniform and tends to be surface reaction-controlled at the other extreme (Seinfeld and Pandis, 2006).”

3. Page 28642, line 2-4: Instead of separating particles by D_b , it seems that q would be a better metric for which particles will be in steady state. Since these are non-reacting particles q is necessarily zero, but perhaps an analog such as $R_p/\sqrt{D_b}$ would be more appropriate.

Unfortunately, q is not a unique indicator of which particles will be in steady state. For example, a particle with $R_p = 10^{-5} \text{ cm}$, $k_c = 10^{-1} \text{ s}^{-1}$, and $D_b = 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ has $q = 1$ and $\tau_{QSS} = 0.008 \text{ min}$. Another particle with $R_p = 10^{-5} \text{ cm}$, $k_c = 10^{-4} \text{ s}^{-1}$, and $D_b = 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ also has $q = 1$, but $\tau_{QSS} \sim 30 \text{ min}$. The first particle would reach quasi steady state much more rapidly compared to the second particle.

4. Page 28644, line 13: Are there any assumptions that go into Eq. (14)? If so, they should be re-stated here.

We have briefly described the source of Eq. (14) and cited Seinfeld and Pandis (2006) for further details on the use of this correction factor.

5. Page 28648, line 2: The symbol for particle-side mass transfer k_b conflicts with the PRA framework definition (Poschl et al. 2007) and is potentially confusing as many people use this symbol for the PFO bulk chemical reaction. Could a different symbol be used for the quantity?

The particle-side mass transfer symbol has been changed to k_p and the particle-side film thickness is now denoted by δ_p .

6. Page 28654, line 15-17: the authors note that the y-axis labels on figure 11 should be interpreted as the decadal logarithm. Why not include this directly on the y-axis label?

“ \log_{10} ” is now directly included on the y-axis labels.

7. Page 28659, line 3-5: do all small particles grow much faster than large ones, or only semi-solids? The text as written implies that only semi-solid particles experience this difference in growth rate.

In general all small particles grow faster than the large ones. But if all particles (small as well as large) are semi-solids (in the present case with $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$), there will be a steep gradient in Q across the size distribution (e.g., From Fig. 7 we see that $Q \approx 0.7$ for $D_p = 0.02 \text{ }\mu\text{m}$ and $Q \approx 0.1$ for $D_p = 0.2 \text{ }\mu\text{m}$). In contrast, $Q \approx 1$ for liquid particles of all sizes. This steep gradient in Q for semi-solid particles is responsible for the much faster growth of small particles than the large ones when compared to the liquid particle case.

We have therefore clarified the sentence in question as indicated by the red text: “However, significant narrowing is still seen for $D_b = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ due to the steep gradient in Q across the size distribution, which causes the small semi-solid particles to grow much faster than the large semi-solid ones when compared to the corresponding liquid aerosol case where $Q \approx 1$ across the entire size distribution.”

8. Page 28666 Line 7: The reference to Eq. (S12) seems out of place here and might be a typo. This is indeed a typo and has been corrected to Eq. (B3).
9. Page 28681, Figure 6, panels b-d: what would happen if the lines were plotted using different values of q instead of different values of D_b ? Might this simplify the figure by collapsing some of the variation between panels?
For a given k_c , the plot of τ_{QSS} vs. D_p will yield horizontal lines for different values q . However, we have chosen to plot the lines for different values of D_b so that the effects of all three independent variables (k_c , D_p , and D_b) can be understood at a glance rather than having to calculate D_b values for different combinations of k_c , D_p , and q . And because q by itself is not a unique metric for steady state (as exemplified in response to minor comment #3), it is not possible to collapse the different k_c panels into one.