

Interactive comment on “Modeling kinetic partitioning of secondary organic aerosol and size distribution dynamics: representing effects of volatility, phase state, and particle-phase reaction” by R. A. Zaveri et al.

Anonymous Referee #2

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This manuscript presents an upgrade to the MOSIAC model that includes diffusion and chemical reactions in the particle phase. In general the paper is well written and well organized. The authors present a detailed analysis of their upgraded model and show that its results are comparable with a finite difference equation which requires fewer simplifying assumptions. I recommend it for publication in ACP provided that the following concerns can be addressed.

Substantive comments:

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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.

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)

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.

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.

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

6. Page 28642, line 9-11: the assertion that all particles with $k_c > 10^{-2} \text{ s}^{-1}$ are in quasi-

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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.

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.

8. Page 28646 – 28647: Is there a transition regime between the two approximations? How accurate is the assumption that behavior changes suddenly from one approximation to the other?

9. Page 28661, section 5: are there any systems that are not well-represented by this framework? Are there transition regimes that potential users of this framework must be aware of?

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.

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 Brekemeier et al. is normalized so that the intuitive volume controlled cubic dependence on radius appears as zero.

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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.

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

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?

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?

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.

8. Page 28666 Line 7: The reference to Eq. (S12) seems out of place here and might be a typo.

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?

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