

Interactive comment on “Kinetic multi-layer model of gas-particle interactions in aerosols and clouds (KM-GAP): linking condensation, evaporation and chemical reactions of organics, oxidants and water” by M. Shiraiwa et al.

Anonymous Referee #1

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This manuscript describes development of a kinetic model simulating gas and particle phase mass transport and chemical reactions. Developing such a model is timely and the manuscript is for the most part easy to follow. I have, however, a number of suggestions / concerns that should be addressed before the manuscript can be considered for publication in ACP;

1. Chapter 2, model description, is on the whole quite long and could be condensed somewhat. Some specific suggestions on this:

- Equations 11-13 are quite basic and probably unnecessary
- The chapter is filled with equations of the form $J=k*[Z]$. Perhaps it is not necessary to write explicitly out the specific equation for each combination of subscripts.
- The description of equations of chemical reactions on pages 33697-33699 and then again on p. 33701 are largely similar and the latter could be mostly omitted.

2. Some information on the model should however, be added and/or clarified: Chapter 3.1 mentions that equations are solved in Matlab, chapter 3.2 does not mention anything of such nature and chapter 3.3 mentions Matlab and even the ODE solver used. As the paper presents the new model KM-GAP, this kind of technical information should be described in some detail, and already before chapter 3.

3. On p. 33693 (and onwards) it is mentioned that KM-GAP treats each species semi-volatile and the distinction between volatile and non-volatile compounds is removed in KM-GAP. Yet the example in section 3.3 implies that the compounds can still be treated as volatile or non-volatile. This feature bears clarification.

4. The authors should discuss the validity of ideal mixture assumption (Eq. 6) for the thin layers of material they are dealing with.

5. Eq. 22 suggests that 1) the presence of adsorbates always decreases the surface accommodation coefficient compared to an adsorbate-free surface and 2) any accommodation takes place only as the incoming molecule meets a molecule of its own species. These two assumptions are worth mentioning.

6. Eq. 26: is the bulk diffusion coefficient used for the transport between sorption and quasi-static surface layer the liquid or gas phase coefficient?

7. Continuing from previous comment: the use of diffusion coefficient and bulk diffusion concepts in general seems dubious at best when the situation is such that molecules are moving distances of the order of their own diameter. Could the authors comment on this?

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8. Furthermore, the form $J=k*[Z]$ for the transport equation combined with the estimate for a transport rate coefficient k obtained with Fick's 1st law (e.g. Eq.26) looks unusual: 1) how exactly is Eq. 26 derived? 2) the concentration gradient looks to be between the concentration in a specific layer and a vacuum instead of a difference between the neighboring layers? Also, the subscripts of k in Eqs. 26 and 27 seem to be backwards compared to the notation given in appendix A.

9. The transport rate coefficient from quasi-static surface layer to first bulk layer given in Eq. 35 has an added curiosity: if one plugs in Eq. 35 the bulk-to-quasi static coefficient as given by Eq. 34, one sees that the surface-to-bulk coefficient depends on the thickness of the first bulk layer. This appears counterintuitive, why would transport from the surface to bulk depend on the arbitrary, purely computational choice of number of bulk layers. Could the authors comment on this?

10. The very next equation, Eq. 36, however gives another expression for the transport rate coefficient for quasi-static surface to bulk transport which doesn't make use of the bulk layer thickness. Even if the subscript b_1 , denoting 1st bulk layer, of Eq. 35 is changed to b for Eq. 36, it is clear that the two coefficients are the same as any transport from surface to bulk is to bulk layer one by construction of the model. The right hand sides of the two equations are however only equal when the thickness of the first bulk layer is one effective molecular diameter. This discrepancy requires explanation, and specifically it needs to be made clear which expression the model uses.

11. In the sentence starting on line 17 on p. 33701 it is mentioned that an adequately large number of bulk layers is required to ensure that the assumption that each bulk layer is homogeneously mixed. As bulk diffusion is used to describe the fluxes between layers, there is necessarily a limit on how small a layer can be for the diffusion treatment to be reasonable. The authors should comment on this also, and how the two requirements can be reconciled.

12. Continuing on the assumption of homogeneously mixed bulk layers: the authors

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could comment in chapter 3.3 on how reasonable this assumption is for runs with fewer number of layers ($n=5$) especially if the assumption is not valid, since they report that the observed results do not change when going from 5 to 200 layers.

13. In general, it would be good if the authors could demonstrate the sensitivity of their results to the various simplifying assumptions, most importantly: 1) ideal mixing; 2) use of diffusion coefficient as a measure for transport over a layer with molecular thickness. This could be done by a set of sensitivity simulations where the related quantities are varied within a reasonable range.

Minor corrections:

- Eq. 14: in accordance to the notation used elsewhere in the paper subscript X should be Z
- Line 17 on p. 33696: “as described below in Eq. 18” should read “as described above in Eq. 14”
- Line 8 on p. 33697 “i.e. H₂O” should probably read “e.g. H₂O”, unless the authors suggest H₂O to be the only adsorbate species
- Line 9 on p. 33698: subscript bs should be ss
- Line 23 on p. 33699 (Eq. 33): subscript bs should be b1
- Line 3 on p. 33701: psi in parentheses is redundant for this sentence
- Line 20 on p. 33704: “in units of g g⁻¹” is an odd way to say that the ratio is unitless

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 33689, 2011.

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