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Discussions

Interactive comment on "Modelling non-equilibrium secondary organic aerosol formation and evaporation with the aerosol dynamics, gas- and particle-phase chemistry kinetic multi-layer model ADCHAM" *by* P. Roldin et al.

M. Shiraiwa (Referee)

m.shiraiwa@mpic.de

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Comments to Roldin et al., ACPD 2014

General comments:

The novel aerosol model ADCHAM was developed that includes detailed gas and particle phase chemistry, and particularly a kinetic multilayer module. ADCHAM was applied to several experimental data, demonstrating the usefulness of this comprehensive model. Overall I found this study is a very nice piece of work, achieved with big efforts by the authors. However, some details of the model including parameters and processes included in the model are not clear and need to be clarified. There are several assumptions that I feel not fully justified as detailed below. I support publication in ACP, after below comments are implemented.

Specific comments:

P773, L21 – P774, L2: The recent study of Shiraiwa & Seinfeld, GRL, 2012 showed that equilibration timescale of SOA partitioning becomes indeed long if particle adopt a semi-solid state. Reference to this paper would be appropriate here.

P777, L25: The internal time step of ADCHAM is 1-10ms. However, some processes, for example, desorption proceeds in much shorter timescale of nanoseconds with Tau_d = 1e-9 s (Table 1). I am wondering whether 1-10 ms is a good choice for reliable calculations.

P783, L8: Please justify thin layer thickness of 1 mm. I guess this value might be critical. Have you done sensitivity studies?

P784: Regarding first-order vapor loss rate to chamber. kg,w may depend on chamber size and mixing of chamber. Matsunaga and Ziemann determined its value using a relatively small chamber. For example, at Caltech chamber the smaller loss rate (kw of on the order of 1e-6 – 1e-4 s-1) was observed (see Loza et al., ES&T, 2010 and supplement in Shiraiwa et al., PNAS, 2013). What are the exact orders/values used in ADCHAM simulation? At P784, L10, 50% of compound was estimated to deposit on chamber wall. How this value will change if smaller loss rate is used? Please compare and discuss.

P784, L24: Is this the same for all substances? Shouldn't it be scaled with the mean free path of the molecule? What values did you get after fitting?

P785: When full-moving method is used, how do you treat coagulation? Do you have a new diameter grid for coagulated particles or do you merge into the existing diameter grid? In the latter case, how do you deal with difference of chemical composition between coagulated and pre-existing particles?

P786, L1: It is mentioned that no interaction coefficients of AIOMFAC are available for PANs, organonitrates and peroxides. This is not entirely true; Zuend & Seinfeld, ACP, 2012 (Appendix A and Table A2 of that paper) introduced peroxide-ion interaction coefficients in AIOMFAC, based on a polarity series and analogy approach.

P789, L6: Is R6 correct? I wonder such 3-body reaction is very slow even in the condensed phase. You need references to justify this reaction and reaction rate coefficient.

P790, L12: What do you mean treat as reactive uptake? Do you use uptake coefficients? Please specify equations to calculate reactive uptake process. I am wondering why you do not treat R2b same as R2a: let aldehyde partition into particle surface, then react at surface. Do you have any evidence that such reaction occurs upon collision of gas molecule to surface (e.g., Eley-Rideal mechanism)? Eley-Rideal mechanism may apply for uptake of very reactive gases such as OH and NO3 (Pöschl et al., ACP, 2007; Shiraiwa et al., ACP, 2009), but I doubt it also applies for aldehydes.

P790, L6: What is the difference between reactions R1-R6 and R7+R8? Why do you need implicit dimer formation when you have explicit dimer formation?

P792, L12: The latest update of KM-GAP also includes thermodynamics (Shiraiwa et al., PCCP, 2013) and simplified gas- and particle-phase chemistry (Shiraiwa et al., PNAS, 2013).

P 792, L15: How is adsorption/desorption treated? How does competition for adsorption sites work if there is no sorption layer? Does the first bulk layer have other properties than all others?

P 792, L22-27: It would be nice to have an explanation why this is split.

P 793, L6-8: This is not always true for KM-SUB. It does not always use identical width for bulk layers. Moreover, for KM-GAP, the layers shrink and grow.

P793, L15: Just a comment: In KM-GAP, the factor of 4/pi is omitted, based on direct derivation by Fick's law.

P793, Eq16: This equation holds in absence of chemical reactions. Please state this.

P793, L11-12: How is surface concentration treated, in cm-2 or cm-3? If treated as cm-2, how is it converted into a bulk concentration for this calculation?

P793, L22-24: This is a big assumption. Particularly small oxidants or water molecules can easily diffuse into solids. For example, bulk diffusivity of H2 into glass/SiO2 is ∼1e-8 cm2 s-1 (Bird et al., 2007) and that of ozone in amorphous solid protein is ∼1e-10 cm2 s-1 (Shiraiwa et al., PNAS, 2011). If you assume no bulk diffusion for solids in ADCHAM, no water would be taken up by glassy particles (in contrast to Zobrist et al., PCCP, 2011). Also there are no dissolution effects.

P794, L9: When the number of layers increased, then do you also increase number of differential equations?

P794, L16-18: Do you arbitrarily assume bulk diffusivity of organics as Dy=0? Such treatment may affect which molecules contribute to theta_s arbitrary. Is there any legitimation to do this?

P796: Is it only ozone that is considered to undergo reversible adsorption? It is not clear whether organic molecules are also treated as same way as ozone, or are they directly transported into the first bulk layer using eq(1)? I wonder why ozone and other organics are not treated in the same way (either with condensation or reversible adsorption).

P797: Why eq28 and 29 do not have transport terms, but only reactions? You have two equations for Xi, eq16 and 29. Do you decouple and solve mass transport and chemical reactions separately for Xi? Why do you treat ozone and Xi differently?

P798: ADCHAM includes many processes: gas- and particle-phase chemistry, coagulation, thermodynamics, diffusion in the bulk, wall loss, etc. In the section of model applications, all processes are not always included and some are switched off. I suggest having a table, specifying which processes are included in certain application.

P800: I would suggest putting current section 3.3 to section 3.2, directly after modeling DOP evaporation. SOA evaporation is direct follow-up of DOP evaporation from the same publication.

P802: The AIOMFAC model treats organic acids as undissociated (p9158, Zuend et al., ACP, 2011). How did you introduce the dissociation products and their activity coefficients? This cannot be done without modifying AIOMFAC or using the activity coefficients of the undissociated compounds. Please clarify.

P803, L22: Recently, Zhou et al., Faraday D., 2013 estimated bulk diffusivity of a-pinene 2e-14 cm2 s-1 at dry condition. This study can be used to justify the use of high diffusivity.

P804, L14-16: I wonder if the diffusion scheme (mass-balance to keep volume layer intact, as described on P794) has an influence on a comparison of modeling results and this estimation formula. It seems that diffusion scheme in ADCHAM tend to be shorter (for example, compared to KM-GAP), as diffusion could only be limited by this mass balance effect.

P804, L17-19: What are fitted parameters and fitted values for these experiments? How is the model fitted? Please clarify.

P806, L13: Is NH3 allowed to adsorb on the sorption layer, or is it directly partitioned into the first bulk layer?

P810, L8-10 & P813, L27-28: I would not agree with this assumption. Why organic molecules cannot adsorb/absorb on non-volatile oligomers? With this assumption, if particle surface is fully covered with oligomers, then no organic molecules are allowed to partition into the particle phase. I wonder why such unphysical assumption is necessary.

P810: Oligomer implies that it consists of multiple monomers. In the model, only dimer (even though dimer is a part of oligomer) is included and I would suggest using the word dimer for clarification when you discuss the modeling results. Otherwise it sounds that further oligomerization (trimer, tetramer, etc.) is treated in the model.

P810, L21: Please put a reference here.

P813, L10-12: What are weakly and tightly bound surface oligomers? How do they differ in the ADCHAM model? What is the chemical identity for surface and bulk oligomers?

P814, L4-7: Do you have any justification for this assumption? I think that it is too simplified. Based on the Langmuir adsorption mechanism which commonly applies for adsorption of gas molecule to the surface, the surface concentration of gas molecule X, [X]s, can be described using the gas-phase concentration [X]gs as follows (eq86 by Poschl et al., ACP, 2007):

[X]s = Kads [X]gs / (sigma* (1+Kads [X]gs)

where sigma is molecular cross section of X and Kads is adsorption coefficient. Thus, [X]s may not be simply proportional to [X]gs (cpinal(g)).

P814, L22: In the section 8 of Ziemann & Atkinson, Chem. Soc. Rev., 2012, reaction rate coefficients of dimerization are reviewed extensively. I suggest comparing your values with them.

P815, L10: It is still not clear for me the difference between short-lived surface oligomer and longer-lived bulk oligomer. Are their chemical identities different? What is their chemical lifetime (short vs. long)?

P817, L1: Why “layers” in plural form? Isn’t it only one surface layer?

P817, L27 and P818, L1: Are these formation rate and decomposition rate fitted? In what range were they varied? Please compare with values reviewed by Ziemann and Atkinson, 2012.

P818, L 4: The difference of bulk diffusivity between monomer and dimer seems to be too small. This contradicts with the assumption that only dimers block the surface, so that no monomers can evaporate.

P823, L19: The range of kO3 values seems reasonable, but it may be as high as 1e-15 cm3 s-1. You could compare with kBR values listed in Table 6 in Berkemeier et al., ACP, 2013, which derived kBR values as 1.7e-17 – 1.7e-15 cm3 s-1 by fitting to multiple data sets of oleic acid ozonolysis.

P827, L26 & P831, L2-3: Are these values fitted values? Please justify or compare with literature values. For example, kf can be compared with Ziemann & Atkinson, 2013 (kf = 1e-4 – 0.06 M-1 s-1). Please note that Shiraiwa et al., PNAS, 2013 found that heterogeneous reaction rate for formation of peroxyhemiacetal was enhanced by two orders of magnitude in the presence of carboxylic acid (kf = 12 M-1 s-1, 2e-20 cm3 s-1).

P832: In the present manuscript the results of salt formation are based on modeling a system without sulfuric acid and with rather high gas phase concentration of ammonia. Recent study by Yli-Juuti et al. (2013) modeled nanoparticle growth in the atmospheric conditions with also sulfuric acid present. Their results suggest that only a small fraction of organic acids forms salt in the particle phase, unless ammonia/amine concentration is high, and that mainly sulfate salts are formed. Pointing out clearly the potential effect of high ammonia concentration and lack of sulfuric acid on the conclusion drawn here and reference to Yli-Juuti et al. (2013) paper would be appropriate here.

P833, L5: I suggest adding several more references in addition to Abramson et al.

P855, Fig. 3: The surface layer seems to be thicker than monolayer, but I guess it is kept as monolayer? What does the double arrow mean (mass transport?)? Please clarify in the figure caption.

Minor comments for edition.

P775, L27: Please spell out 2D-VBS.

P777, L24: Put “relies” instead of “rely”.

P792, L15: Delete either “a” or “one”.

P793, L2: Space missing before DXi.

P803, L29: “is not a” should be “are not”.

P806, L13: “That can explain”: Here is a word too much, or missing.

P806, L21: “are” should be “is”.

P808, L25: “Form” should be “From”.

P823, L10: Space between “O3” and “and”.

P825, L1: Space between “NO2” and “and”.

P832, L25: Space between “NH3” and “in”.

References:

Berkemeier, T et al.: Kinetic regimes and limiting cases of gas uptake and heterogeneous reactions in atmospheric aerosols and clouds: a general classification scheme, Atmos. Chem. Phys., 13, 6663-6686, 2013.

Bird, R. B., Stewart, W. E., and Lightfoot, E. N.: Transport Phenomena (2nd Ed.), John Wiley & Sons, Inc., New York, 2007.

Loza, C. L., Chan, A. W. H., Galloway, M. M., Keutsch, F. N., Flagan, R. C., and

Seinfeld, J. H.: Characterization of vapor wall loss in laboratory chambers, Environ. Sci. Technol., 44, 5074-5078, 2010.

Pöschl, U., Rudich, Y., and Ammann, M.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions - Part 1: General equations, parameters, and terminology, Atmos. Chem. Phys., 7, 5989-6023, 2007.

Shiraiwa, M., Garland, R. M., and Pöschl, U.: Kinetic double-layer model of aerosol surface chemistry and gas-particle interactions (K2-SURF): Degradation of polycyclic aromatic hydrocarbons exposed to O3, NO2, H2O, OH and NO3, Atmos. Chem. Phys., 9, 9571-9586, 2009.

Shiraiwa, M., and Seinfeld, J. H.: Equilibration timescale of atmospheric secondary organic aerosol partitioning, Geophys. Res. Lett., 39, L24801, 2012.

Shiraiwa, M., Yee, L. D., Schilling, K. A., Loza, C. L., Craven, J. S., Zuend, A., Ziemann, P. J., and Seinfeld, J. H.: Size distribution dynamics reveal particle-phase chemistry in organic aerosol formation, Proc Natl Acad Sci USA, 110, 11746-11750, 2013.

Shiraiwa, M., Zuend, A., Bertram, A. K., and Seinfeld, J. H.: Gas-particle partitioning of atmospheric aerosols: interplay of physical state, non-ideal mixing and morphology, Phys. Chem. Chem. Phys., 15, 11441-11453, 2013.

Yli-Juuti, T., Barsanti, K., Ruiz, L. H., Kieloaho, A. J., Makkonen, U., Petaja, T., Ruuskanen, T., Kulmala, M., and Riipinen, I.: Model for acid-base chemistry in nanoparticle growth (MABNAG), Atmos. Chem. Phys., 13, 12507-12524, 2013.

Zhou, S., Shiraiwa, M., McWhinney, R., Pöschl, U., and Abbatt, J. P. D.: Kinetic limitations in gas-particle reactions arising from slow diffusion in secondary organic aerosol, Faraday Discuss., 165, 391-406, 2013.

Ziemann, P. J., and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chem. Soc. Rev., 41, 6582-6605, 2012.

Zobrist, B., Soonsin, V., Luo, B. P., Krieger, U. K., Marcolli, C., Peter, T., and Koop, T.: Ultra-slow water diffusion in aqueous sucrose glasses, Phys. Chem. Chem. Phys., 13, 3514-3526, 2011.

Zuend, A., Marcolli, C., Booth, A. M., Lienhard, D. M., Soonsin, V., Krieger, U. K., Topping, D. O., McFiggans, G., Peter, T., and Seinfeld, J. H.: New and extended parameterization of the thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups, Atmos. Chem. Phys., 11, 9155-9206, 2011.

Zuend, A., and Seinfeld, J. H.: Modeling the gas-particle partitioning of secondary organic aerosol: the importance of liquid-liquid phase separation, Atmos. Chem. Phys., 12, 3857-3882, 2012.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 769, 2014.