Atmos. Chem. Phys. Discuss., 11, C15750–C15756, 2012
www.atmos-chem-phys-discuss.net/11/C15750/2012/

Atmospheric
Chemistry
and Physics
Discussions

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.

M. Shiraiwa et al.

m.shiraiwa@mpic.de

Received and published: 1 March 2012

Referee General Comment:

This paper describes KM-GAP, a multiphase model of gas-particle interactions that treats explicitly mass transport and chemical reaction of semi-volatile substances, and that resolves concentration gradients within the particle. KM-GAP is the latest addition to a series of models with increasing complexity (K2-SURF, K2-SUB, KM-SUB) that are all based on the formalism put forward by Poeschl, Rudich, Ammann. The model

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

development that distinguishes KM-GAP from the previous model versions is that it includes condensation and evaporation (and therefore particle growth and shrinking) and associated heat fluxes. The authors present the model description and apply it to model experimental data from three case studies. The paper fits well within the scope of ACP, and addresses an important topic. This model represents a very useful tool to investigate processes such as the aging of organic substances on a very detailed level, with less simplifying assumptions than traditional models typically have and suffer from. I recommend this paper for publication after the following questions and comments have been addressed.

Response:

We thank Anonymous Referee #3 for the review and the very positive evaluation of our manuscript. The constructive suggestions for improvement are very welcome and will be implemented upon revision. Detailed responses to the individual comments are given below.

Referee Comment 1:

Since it is the focus of this paper, the model description needs some improvement in organization and precision. Specifically, from section 2 it is not clear what system of coupled differential equations is actually solved. What are the dynamic variables? Clearly, eqs. 1-5 are part of the system, but there are more, such as eq. 15, and also the equations for particle temperature and environmental temperature, which appear much later. It would help this paper if these were clarified.

Response:

The dynamic variables are the number of molecules in each layer, droplet temperature and ambient temperature. We will specify what system of coupled differential equations is actually solved in each section.

Referee Comment 2:

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Then, after the governing equations are defined, there needs to be a section on the numerical implementation. The authors mention much later that the Matlab solver ode23tb is used. Does this apply to all cases or only the one presented in 3.3?

Response:

Yes, Matlab solver of ode23tb was used for all presented simulations. We will clarify it in the beginning of section 3 in the revised manuscript as below.

“In this study the coupled differential equations were solved in Matlab software with an ordinary differential equation solver (ode23tb), which integrates a system of differential equations using second and third order Runge-Kutta formulas. The computational costs for one simulation were less than one minute on a standard desktop computer.”

Referee Comment 3:

I echo the comment by Referee #2 about the phrase in the abstract that “unlimited numbers of species” can be simulated. Clearly this is not the case in practice, and should be rephrased.

Response:

The computational time for simulating the system presented in this study was less than one minute using Matlab software on a standard desktop computer. Of course the computational cost would increase if more number of species and reactions are included. We will mention that computational cost can be a limiting factor in the revised manuscript.

Referee Comment 4:

It looks like the number of layers is predefined in this model. Consequently, when the particle grows, the thickness of the layers becomes larger. Does this introduce problems when the particle grows by large amounts? Could it be necessary to introduce more layers?

Response:

For water growth it is not a problem as the assumption of homogenous mixing in each bulk layer holds due to fast bulk diffusivity (low viscosity) of water molecules. This assumption might break down for highly viscous particles. In this case we need to use either very high number of layers or introduce more layers in the course of simulation. For clarification we will add the below sentences in the revised manuscript.

“The lower limit of physically meaningful layer thickness corresponds to the molecular diameter of the involved chemical species, and the upper limit for correct treatment of bulk diffusion depends on the diffusivity. In (semi-)solid matrices with low diffusivity, the mixing times are long and concentration gradients can be steep, so that relatively thin layers should be used (>10 layers) (Shiraiwa et al., 2011a). In liquid matrices with high diffusivity, the mixing times are short and concentration gradients are small, so that relatively thick layers can provide sufficient resolution (<10 layers) (Shiraiwa et al., 2011a).”

Referee Comment 5:

Section 3.2: What is n for these model runs? Also, I would like to know more about the wall losses mentioned in this section. Are these particle wall losses, gas phase wall losses or both? The expression how these wall losses are incorporated should be added to the equations.

Response:

n is 5 for the model run in section 3.2. We will add this information it in the revised manuscript. Particle wall loss was not considered. The loss of DOP to the denuder is considered using a simple first-order wall loss coefficient (kw), introducing –kw[Z]g in the right hand of eq(16). We will clarify it in the revised manuscript as below.

“The loss of DOP to the denuder is considered using a first-order wall loss coefficient (kw) and adding the term –kw[DOP]g to the right hand side of eq(16). We assume that the core of the chamber is well-mixed and the loss occurs via molecular diffusion (1st Fick's law) through a layer adjacent to the denuder wall to estimate kw. We varied the thickness of the denuder wall up to the half-height of the chamber (∼3 cm). Particle losses to the wall and coagulation were not considered."

Referee Comment 6:

Furthermore, the calculations for the DOP experiment are conducted assuming that the particles stay monodisperse during the experiment, this means assuming no coagulation. While for this particular experiment, this assumption may be appropriate due to the low number concentrations and relatively short time scales, it would be good to point out this assumption since it could be a limitation when applying the model to other conditions.

Response:

We did not consider coagulation and will clarify this in the revised manuscript.

Referee Comment 7:

Sensitivity studies with respect to number of bulk layers. The authors mention that varying the number of layers between 5 and 200 does not impact the results of oleic acid degradation. I am curious to know how few layers would be sufficient?

Response:

We could go below 5, but then we lose the information of bulk concentration profile. To reproduce the experimental data, one layer is sufficient as already shown in the KM-SUB paper (Fig, 2a, Shiraiwa et al., 2010). This is because degradation kinetics of oleic acid is limited by surface accommodation of ozone. For high resolution and to avoid the congestion of the concentration profile plot (Fig. 5), we use high number of layers.

Referee Comment 8:

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

p. 33693, l. 18: Strictly speaking, these equations do not describe a mass balance, but a number balance.

Response:

We agree and will clarify this in the revised manuscript.

Referee Comment 9:

Equations 1-5: Define n.

Response:

We will define n in the revised manuscript, which is the number of bulk layer.

Referee Comment 10:

Equation 6: Over what quantity is this summation?

Response:

NZi,bk VZi is summed up over i (number of species) as specified in the equation.

Referee Comment 11: Do we need eq. 14?

Response:

We like to keep eq.14 because γZi is one of the most important and frequently used parameters in kinetic models and experiments.

Referee Comment 12:

- Eq. 15: add “m=1”

- Something needs to happen with the symbol for the Knudsen number in eq. 19 and 20, the typesetting looks like K is multiplied with n_{Z_i}

- Page 33703, l. 9: typo: surface tension

Response:

m=1 will be added. We will check Kn carefully how it appears upon proof reading. Typo will be corrected.

Referee Comment 13:

Eq. 58: What is the summation index in this equation?

Response:

The summation index is m and this will be added in the revised manuscript.

Referee Comment 14:

Figure 1(b), the fluxes below J_abs and J_des, should these read J_s,ss and J_ss,s?

Response:

Thanks for pointing it out. We revised to Js,ss and Jss,s.

Referee Comment 15:

Table A1: Line with J_ads,Zi says flux of adsorption and desorption (need to mention J_des,Zi somewhere).

Response:

Following your comment, Jdes,Zi is added in Table A1.

References:

Shiraiwa, M., Pfrang, C. and Pöschl, U.: Kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB): the influence of interfacial transport and bulk diffusion on the oxidation of oleic acid by ozone, Atmos. Chem. Phys., 10, 3673-3691, 2010.

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