

Interactive comment on “Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions: Part 1 – general equations, parameters, and terminology” by U. Pöschl et al.

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Received and published: 20 February 2006

We would like to thank Markku Kulmala for his constructive comments and suggestions, which are highly appreciated and will be taken into account upon manuscript revision, together with the earlier comments and suggestions from Referee #1, Dr. Remorov, and Dr. Sander (overview of interactive discussion and comments on Pöschl et al., 2005a: http://www.cosis.net/members/journals/df/article.php?a_id=1863&).

A point-by-point response to the comments of Dr. Kulmala is given below. For the readers' convenience, we also include a copy of his comments prior to our response.

Comments by M. Kulmala (Kulmala, 2005):

1) I think that the general idea is an excellent one, and in principle it has everything (except heat fluxes) in it 2) However, there are several points, which need to be clarified a) it is too early to say that this is a master mechanism or even to suggest it as a master mechanism, since - it is still too complex - it should be verified with couple of experiments - see also comments/criticism below b) on different layers presented in Figure 2. I think that you have too many layers there. Is it making the whole thing too complicated. E.g. how one can ever separate sorption layer and quasi-static surface layer for small aerosol particles or for liquid droplets. Is there never a hope to receive parameters for all those layers? c) thermal fluxes are missing d) The results of and comparison with condensation/evaporation studies are completely missing. I mean studies made by Paul Wagner and myself. There is a recent paper by Winkler et al., (2004 Phys. Rev. Letters) and the other one Kulmala and Wagner, J. Aerosol Sci. 32, 833-841, 2001, which should be mentioned in page 2151 and compared somewhere. e) I started to look more carefully the accommodation coefficients and uptake coefficients defined in the paper and my own ones (Kulmala and Wagner, 2001), and I think that some more work is needed in future for comparison and clarification. f) different mechanisms like Langmuir-Hinshelwood etc. should be defined in appendix.

Response by U. Pöschl, Y. Rudich, and M. Ammann:

1) We appreciate the positive general evaluation of our manuscript and concepts. With regard to the inclusion of heat fluxes we refer to point 2c) below and to our earlier response to Referee #1 (Pöschl et al., 2005b).

2a) As pointed out in the abstract, introduction, and conclusions of our manuscript, we do not suggest that the presented formalisms would already represent a master mechanism. Nevertheless, we do propose these formalisms as the basis for the construction of a master mechanism of aerosol and cloud surface chemistry and gas-particle interactions, and we hope that it will help to end the Babylonian confusion of incon-

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sistent and incompatible terminologies and formalisms applied in different studies for the description of atmospheric gas-particle interactions and surface processes (chemistry/physics, lab/field/model, aerosol/cloud, alphas/gammas, etc.; Fuzzi et al, 2005; Pöschl et al., 2005a; Pöschl, 2005a). Moreover, we would like to reconfirm that the proposed double-layer surface model and unambiguous definition of elementary steps of mass transport and chemical reactions represent a minimum of detail and complexity required for the description of aerosol and cloud surface chemistry, and thus for consistent description of atmospheric gas-particle interactions including surface and bulk processes as detailed below.

2b) In our companion papers, especially in Part 2 (Ammann and Pöschl, 2005), we have already outlined and discussed the results of several experimental studies which have clearly demonstrated that the kinetics of heterogeneous reactions at the surface of aerosol particles or surrogate surfaces (non-linear concentration and time-dependencies of surface composition and rate parameters), can hardly be described in a physically meaningful way without invoking competitive co-adsorption of gas molecules in a sorption layer. Competitive co-adsorption, however, can hardly be described without the assumption of a quasi-static surface layer which defines the surface area and adsorption sites which define and limit the competitive adsorption process.

In fact, most studies of gas-particle interactions in aerosols and clouds which are not composed of liquid water droplets, have reported non-linear concentration dependencies which are most easily and efficiently described by Langmuir adsorption isotherms or Langmuir-Hinshelwood reaction mechanisms (combination of reversible and competitive co-adsorption of gas molecules and rate limiting surface reactions of adsorbed species with each other or with quasi-static surface layer components; Pöschl et al., 2001; Ammann et al., 2003; Ammann and Pöschl, 2005; Pöschl, 2005a; Pöschl et al., 2005a; and references therein).

The near-surface gas phase and near-surface particle bulk as defined in our model framework are essentially the same as in earlier model formalisms linking interfacial

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mass transport to diffusion in the gas phase and particle bulk. These had mostly referred to “concentrations at/near the surface” without providing a descriptive definition and illustration of the model domain (compartment) which is effectively characterized by these “concentrations at/near the surface”. As illustrated by the the examples given in Part 2 of our companion papers (Ammann and Pöschl, 2005), many of the kinetic parameters required for consistent description of chemical reactions and mass transport within and across sorption layers and quasi-static surface layers can be derived from existing literature data - not only for solid particles (e.g. soot interacting with O₃/NO₂) but also for liquid droplets (e.g. aqueous droplets interacting with SO₂).

On the other hand, we do not at all claim or suggest that it would be necessary to resolve sorption and quasi-static surface layers and the kinetics of all (quasi-)elementary molecular processes in systems where only bulk reaction or condensation processes are considered, and where competitive co-adsorption and chemical reactions at the surface can be assumed to have no significant influence. Under such conditions, the multiple elementary steps and kinetic parameters of mass transport from the gas phase onto the surface and into the bulk of the particles can be convoluted into a single process and parameter (“mass accommodation” or “condensation”). For details see the comparison and distinction of the terms “surface accommodation”, “bulk accommodation”, and “mass accommodation” below (points 2d and 2e) and in our discussion paper (Pöschl et al., 2005a, pp. 2148-2150).

2c-d) As already pointed out in our response to Anonymous Refere #1, the development and presentation of the proposed model framework have been focussed on consistent description of aerosol and cloud surface chemistry and gas-particle interactions of reactive trace substances, rather than on phase transitions of major gas phase and particle components with substantial uptake/release of latent heat (bulk condensation or evaporation, melting or freezing). Nevertheless, we are planning to address the heat transfer aspect upon revision of the manuscript. The consideration of heat transfer and related temperature changes has no direct effect on the proposed

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kinetic model framework terminology and formalisms. If required, heat flux and energy balance equations can be flexibly added and coupled to the presented mass transport and reaction rate equations (uptake/release of heats of adsorption/desorption, condensation/evaporation, mixing/dissolution, solvation/segregation, etc.). Based on the composition-dependent heat capacities and conductivities of the particles and gas phase in the investigated aerosol or cloud system, uptake or release of heat can be converted into temperature changes, which in turn can be taken into account in the determination of temperature-dependent kinetic parameters (Arrhenius equations, etc. - section 4.1 of Pöschl et al., 2005a).

In our discussion papers we have already outlined perspectives for the application of the proposed model framework to the condensation/evaporation of (semivolatile) particle bulk components (Pöschl et al., 2005a, pp. 2150-2152), and we have demonstrated that the presented general formalisms can be simplified and reduced to earlier formalisms for special cases where surface effects are negligible (Pöschl et al., 2005a, pp. 2148-2168, Ammann and Pöschl, 2005).

On the other hand, we had intended and still do intend to postpone an in-depth discussion of bulk condensation and evaporation processes to follow-up studies. Otherwise, it would be necessary to substantially expand a manuscript which is already fairly long and has been criticized for being too comprehensive (Referee #1, 2005; Pöschl, 2005b). Nevertheless, we will attempt to clarify some aspects below and in the revised manuscript, and we are planning to include the suggested references upon revision.

In practice, the investigation and description of bulk condensation and evaporation processes of atmospheric particles do not generally require a resolution of sorption and quasi-static surface layers and of all (quasi-)elementary molecular processes at the particle surface. For description of non-reactive aerosol and cloud particle growth by uptake of semivolatile vapors, it will usually be sufficient to determine and use a bulk accommodation coefficient (“mass accommodation coefficient”) for the description of the molecular kinetics of gas-to-particle mass transfer, and a simple bulk evaporation

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rate coefficient for the reverse process. In many cases, it may even be sufficient to consider only gas phase diffusion as the rate limiting process and neglect the molecular kinetics of mass transfer at the surface (gas-particle interface) completely.

If, however, there is a demand or need to resolve molecular kinetics at the gas-particle interface, the proposed model framework enables the description and linkage of elementary steps of molecular motion and interaction as well as macroscopic observables within a consistent set of terms and formalisms. As detailed in our discussion paper (Pöschl et al., 2005a, pp. 2150-2152), the double layer surface model would enable efficient description of the elementary steps of multilayer adsorption and bulk condensation of semivolatile species at the gas-particle interface as follows: Transfer from the quasi-static surface layer to the sorption layer as a (formal) kinetic step which can be pictured as a thermal activation process transforming a quasi-static surface component (with relatively low potential energy) into an adsorbate species (with relatively high potential energy) which can either desorb into the gas phase or return to the quasi-static surface (thermal deactivation). In the sorption layer, the semivolatile species would competitively inhibit the adsorption of other semivolatile or volatile species; in the quasi-static surface layer, on the other hand, they would provide sorption sites (area) for gas molecules.

In any case, however, it would be beneficial to use consistent and compatible terminologies for the different physicochemical processes relevant for atmospheric aerosol and cloud chemistry, physics, and gas-particle interactions (Fuzzi et al., 2005; Pöschl, 2005a).

2e) With regard to the paper by Kulmala and Wagner (2001) and the large body of scientific literature on aerosol and cloud particle formation, growth, and non-reactive gas uptake, we fully agree that further comparison and clarification is needed. In fact, we are looking forward to pursuing this work in collaboration with Dr. Kulmala and other colleagues.

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At this point, however, we would just like to like to clarify some basic differences and relations between the terminologies and formalisms used by Kulmala and Wagner (2001; “KW2001”) and by Pöschl, Rudich, and Ammann (2005a; “PRA2005”):

flux (KW2001) = flow (PRA2005, IUPAC recommendation)

flux density (KW2001) = flux (PRA2005, IUPAC recommendation)

α_m (KW2001) = $S + \gamma_{gsr}$ (PRA2005)

γ (KW2001) = γ_{eff} (PRA2005)

In KW2001 only the effects of gas phase diffusion are mechanistically described in the formalisms relating gas phase concentrations, mass accommodation coefficient, and uptake coefficient. PRA2005, however, explicitly consider and separate the effects of gas phase diffusion, surface processes (adsorption and chemical reaction), and surface-bulk transfer.

As demonstrated by numerous experimental studies and outlined by PRA2005, surface processes are important for heterogeneous and multiphase atmospheric chemistry, especially for the concentration and time dependence of reactions involving solid or highly viscous liquid particles and multiple reactive species.

For simple systems and physicochemical processes such as bulk condensation or evaporation of water droplets, surface processes can certainly be convoluted and implicitly taken into account in simple overall rate equations and parameters as outlined by KW2001.

Nevertheless, a lack of consistent and explicit distinction between surface and bulk accommodation seems to be a likely explanation for some of the apparent discrepancies between different studies and values reported for the “mass accommodation” coefficient of water vapour on liquid water (Winkler et al., 2001: approx. 1.0, not < 0.4; Davidovits et al., 2005: approx. 0.2, not > 0.3 at 273 K; see also Davidovits et al., 2004, and references therein).

Moreover, we consider it more intuitive, straightforward, and versatile to formulate gas phase diffusion corrections on the basis of γ (net uptake; C_g and section 2.2 of PRA2005) rather than α (gross uptake; equations 6-12 and section 2.2 of KW2001), because gas phase diffusion effects can play a role only if $\gamma > 0$ (significant net uptake) and are always negligible when γ is close to 0 (insignificant net uptake), even if α is close to unity.

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