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Atmospheric
Chemistry
and Physics
Discussions

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.

U. Pöschl et al.

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In an earlier interactive comment we had already expressed our appreciation for the efforts of Referee #1 in reviewing our two model framework companion papers, and we have responded to the referee’s concerns about the length of these manuscripts (Pöschl, 2005a). Here we respond to the referee’s scientific and technical comments on Part 1 of our companion papers (Referee #1, 2005).

With regard to the referee’s introductory statement that “the model comprises a set of rate equations to be solved in quasi-steady manner”, we would like to point out that the general rate equations presented in sections 2 and 3 of Pöschl et al. (2005a) are neiter based on nor dependent on (quasi-)steady-state approximations. Only the special cases outlined in section 4 are based on the assumption of (quasi-)steady-state conditions.

Before proceeding with detailed responses to the numbered comments, we would like to point out that most of the referee's critical remarks about the scientific contents of our companion papers ask for more detailed information and consideration of additional aspects. This clearly demonstrates that it would be more than difficult to reduce the overall volume of the kinetic model framework presentation (total length of manuscripts) without omitting relevant information and aspects.

Response to General Comments

Comment 1: Many phase transition processes may include significant release/absorption of heat. The paper does not say anything on coupling between mass and heat transfer.

Response: 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 this aspect upon revision of the manuscript.

The consideration of heat transfer and related temperature changes has no direct effect on the proposed 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, solvatation/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., 2005).

Comment 2: The model includes a plenitude of different parameters, coefficients etc.; it would be good to have some hints for most important of them how to find values for them or possibly how to estimate their values using other known parameters and thermodynamical relations.

Response: Most parameters are highly dependent on the chemical composition and physical conditions of the investigated aerosol or cloud system. Some examples are given in Part 2 of the companion papers (Ammann and Pöschl, 2005). Further considerations and exemplary applications are certainly desirable and will be provided in follow-up studies. At this point, however, they go beyond the scope of the two companion papers and would further increase the length of the already relatively long manuscripts.

Comment 3: The paper makes a reader's position difficult with some long sentences and long concepts, for example "pseudo-first-order quasi-static surface transformation rate coefficient" or sentence "Again the transfer. . . ." below Eq. 61; the paper must be polished from these.

Response: We are planning to shorten long sentences and to check options for a simplification of terminology upon revision of the manuscript. Terms like "pseudo-first-order quasi-static surface transformation rate coefficient", however, cannot be shortened and simplified arbitrarily, because this would lead to ambiguities and inconsistencies. In our opinion, scientific terminologies and treatises should be as simple and concise as possible, but not at the expense of completeness and precision.

Comment 4: The concept of "kinetic theory of condensed phases" is used in several places; what is it exactly, is there some certain well-established kinetic theory?

We consider "kinetic theory" as an umbrella term for the explanation and description of properties of matter by molecular motion. With the formulations "kinetic theories of gases, condensed phases, and interfaces" and "kinetic theory of condensed phases" we have referred to the wide-spread application/extension of basic concepts from the kinetic theory of gases to condensed phases and interfaces, in particular to the description of molecular transport (diffusion) by thermal motion (random walk). We are planning to check and clarify these formulations upon revision of the manuscript.

Comment 5: Quasi-steady approximation (QSA) is used for coping with time dependence, some criteria should be given when QSA is acceptable when not, the question is not just reducing the time increment but of the ratio of the characteristic time scales of modelled processes vs. the time scales of governing processes; it is not always clear what are the most important governing physical process in each cases.

Response (see Comment 2): Most parameters are highly dependent on the chemical composition and physical conditions of the investigated aerosol or cloud system. Some examples are given in Part 2 of the companion papers (Ammann and Pöschl, 2005). Further considerations and exemplary applications are certainly desirable and will be provided in follow-up studies. At this point, however, they go beyond the scope of the two companion papers and would further increase the length of the already relatively long manuscripts.

Comment 6: The model is 1-dimensional but deals with, for example, spherical particles; how is the geometry taken into account for example if the bulk diffusion is important; I am not satisfied with the answer that the model reduces to some resistance/conductance formulation with "semi-theoretical" geometry corrections and terms; if the model carry the label "comprehensive" it should be more rigorous as regard the treatment of geometries; on the other hand some models with a detailed geometrical framework may have only gas phase "layers" and bulk, omitting sorption layer, quasi-static surface layer and near-surface bulk, it would good to know under what conditions or for which systems the extra layers are important.

Response: Development and presentation of the proposed model framework have been focussed on consistent description of physico-chemical processes at the surface of aerosol and cloud particles, i.e. at the interface of gas phase and condensed phase, rather than on mass transport and chemical reactions within the particle bulk. The unambiguous terminology, flux-based rate equations, and kinetic parameters proposed for the description of surface processes can be flexibly combined with formalisms describing the fluxes and rates of mass transport and chemical reaction in the particle bulk. If required, the influence of particle geometry can be taken into account by means of appropriate boundary conditions for the coupled differential equations or correction factors for the (quasi-)steady-state solutions. An example for such formalisms and references to related studies have been given in section 3.5.1 of our manuscript. Further considerations and exemplary applications are certainly desirable and will be provided in follow-up studies. At this point, however, they go beyond the scope of the two companion papers and would further increase the length of the already relatively long manuscripts. Nevertheless, we are confident that the kinetic model framework proposed and illustrated in our companion papers is more comprehensive than any other model formalism for aerosol and cloud surface chemistry and gas-particle interactions published in the scientific literature that we are aware of.

With regard to the practical relevance of sorption layer, quasi-static surface layer, and surface (sorption layer) saturation effects, general dependencies on kinetic parameters have been outlined and discussed in sections 3.6, 4.1, and 4.3 of Part 1 of our two model framework companion papers (Pöschl et al., 2005a). Exemplary practical applications and numerical simulations are illustrated in Part 2 (Ammann and Pöschl, 2005). Most of the relevant kinetic parameters are highly dependent on the chemical composition and physical conditions of the investigated aerosol or cloud system. Generally speaking, surface effects tend to be small or negligible for liquid droplets and low trace gas concentration levels, but they can be important for solid particles and high trace gas concentration levels. Experimental evidence has been provided by numerous laboratory studies as referenced in our companion papers.

Response to Detailed/Technical Comments

Comment 1: To orientate the reader, each sub-section in Sections 2 and 3 could shortly tell what are well-known things and what are possibly novel items to be presented in the section; that could be said in the beginning of each section.

Response: As outlined in the introduction of Pöschl et al. (2005a), most of the individual components of the presented model framework (equations, parameters, definitions) are not conceptually new by themselves, but they have been taken from kinetic formalisms already existing in atmospheric and aerosol science, physical chemistry, and chemical engineering. To our knowledge, however, our manuscript is the first scientific publication, in which these individual components from different fields of research have been reformulated and combined in a consistent way, making them universally applicable for the to atmospheric aerosol and cloud surface chemistry and gas-particle interactions.

In other words: While only few of the individual bits and pieces of the proposed model framework are conceptually new by themselves, essentially all definitions and equations have been reformulated and synthesised in an unprecedented universal and consistent way.

The key aspects of this reformulation and synthesis have been clearly outlined in the manuscript abstract and conclusions: simple and descriptive double-layer surface model (sorption layer and quasi-static layer); straightforward flux-based mass balance and rate equations; clear separation of mass transport and chemical reactions; well-defined rate parameters (uptake and accommodation coefficients, reaction and transport rate coefficients); clear distinction between gas phase, gas-surface, and surface-bulk transport (gas phase diffusion correction, surface and bulk accommodation); clear distinction between gas-surface, surface layer, and surface-bulk reactions (Langmuir-Hinshelwood and Eley-Rideal mechanisms); mechanistic description of concentration and time dependencies; flexible inclusion/omission of chemical species and physicochemical processes; flexible convolution/deconvolution of species and processes; and full compatibility with traditional resistor model formulations. We are planning to ceck if these aspects can be further clarified upon revision of the manuscript.

Comment 2: Section 2.2. Gas phase diffusion: "flow regime" and "transport flow", I would replace "flow" by "flux".

Response: In contrast to the generic term "flow", we are using the term "flux" exclusively for a specific physical quantity. In accordance with the IUPAC compendium on chemical terminology ("gold book") the term "flux" is defined as the flow rate of the investigated species through a cross-section perpendicular to the flow divided by the cross-sectional area. We are planning to check and clarify these aspects of terminology upon revision of the manuscript.

Comment 3: In Eqs. 16 and 17, should alpha appear there?

Response: For consistency, and within the terminology of the proposed model framework, the use of α instead of γ in Equations (16) and (19) would not be appropriate. The depletion of a certain molecular species in the gas phase close to the surface depends on its net uptake onto and into the particle rather than its gross flux into the particle bulk. For example, α and C_g can be unity while β_F, β_{FS}, γ, and F_g are zero under solubility equilibrium conditions.

Comment 4: In the beginning of Page 2124: "F-S is most appropriate under isothermal conditions"; the works by Paul Wagner and Markku Kulmala and their co-workers have shown that F-S works well also under non-isothermal conditions.

Response: Thanks. We are planning to check and include this information upon revision of the manuscript.

Comment 5: In the beginning of p. 2130: ". . . or thermal accommodation coefficient."; thermal accommodation is really different thing from mass accommodation.

Response: We agree, but if we are not mistaken, the term "thermal accommodation

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coefficient" has been used to describe accommodation of molecules in a sorption layer (adsorption), confirming the need to resolve the "Babylonian" confusion of kinetic parameters in the investigation of atmospheric aerosol and cloud surface chemistry and gas-particle interactions. Nevertheless, we are planning to double-check the given references and modify our statement if it is incorrect.

Comment 6: before Eq. 31, I suppose inserting Eq. 2 and not 3?

Response: Yes, thanks. We are planning to correct this error upon revision of the manuscript.

Comment 7: below Eq. 50, "rapid surface bulk-mass transport (low-viscosity liquid droplets"; how is viscosity related to bulk transport, due to some flow processes, circulation etc. or just due to relationship with diffusivity?

Response: Our argumentation had been focussed on molecular diffusivity, but indeed bulk flow and circulation might also play a role in (large) liquid droplets of low viscosity. We are planning to clarify this aspect upon revision of the manuscript.

Comment 8: Eq. 28 has some "-" signs but Eq. 83 has only "+" signs, should they be consistent?

Response: In contrast to the mass balance equation (28), the inequation (83) does not contain any minus signs, because it refers to the gross rates of production, loss, and transport rather than net production (production minus loss) and net transport. If minus signs were inserted in analogy to Eq. (28), large rates of chemical loss and surface-to-bulk transport would not be properly taken into account.

Comment 9: P. 2165: why is Henry's law coefficient proportional to S_{Xi}*, by the classical definition, the coefficient should be temperature dependent constant; the so called effective Henry's law coefficient may depend also on pH.*

Response: Thanks for pointing out this erroneous formulation. The statement on page 2165 is meant to refer to gas-particle partitioning coefficients (solubilities) but not to

Henry's law coefficients (limiting case of infinite dilution; section 3.5.2). We are planning to correct this error upon revision of the manuscript.

Comment 10: Conclusions and outlook: "multiple condensed phases (solid/liquid, surface/bulk, homogeneous/heterogeneous. . . .)", solid and liquid are phases but others mentioned are not.

Response: Thanks for pointing out this imprecision. We are planning to correct it upon revision of the manuscript by referring to "different condensed pases, interfaces, and mixing states (...)" rather than "multiple condensed phases (...)".

Comment 11: Conclusions, item (i); what is meant by "flexible convolution/deconvolution"?

Response: With regard to physicochemical processes, "flexible convolution/deconvolution" means that the framework formalism and terminoloy are sufficiently general and self-consistent to allow both: (a) the deconvolution and description of individual elementary processes whenever it is necessary; and (b) the convolution of multiple elementary processes whenever it is possible and convenient (Pöschl et al., 2005b).

For example, the transport of molecules from the gas phase into the particle bulk can be described by different but fully consistent parameters and rate equations, depending on the properties of the investigated aerosol or cloud system. Deconvolution of the overall process into surface accommodation and surface-bulk transfer enable the description of surface reaction and saturation effects. If such effects are insignificant, the rate coefficient of surface accommodation and surface-bulk transfer can be convoluted into a single bulk accommodation coefficient (Pöschl et al., 2005a, pp. 2150, 2154, 2168).

With regard to chemical species, the presented formalisms allow to resolve the formation, interaction, and decomposition of unlimited numbers of highly reactive and short-lived intermediates at the particle surface via consecutive or competitive gas-surface,

surface layer, and surface bulk reactions. This can be important with regard to the atmospheric abundance of hazardous air pollutants in densely populated areas and the influence of meteoroloical conditions, local emissions, and long range transport on aerosol health effects (e.g. Franze et al., 2005; Pöschl, 2005b; and references therein).

On the other hand, a master mechanism of aerosol chemistry based on the proposed kinetic model framework would also enable systematic lumping (grouping) of the hundreds and tousands of organic species and reactions in air particulate matter into surrogate species (substance classes with fairly uniform physicochemical properties) and reactions (reaction types with fairly uniform patways and kinetics), which appear to be appropriate for efficient description of atmospheric aerosol aging and climate effects on global scales (Pöschl, 2005b).

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