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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Internal mixing of the organic aerosol by gas phase diffusion of semivolatile organic compounds” *by* C. Marcolli et al.

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We are very grateful for your comments.

To a) We do not consider the equilibration process under varying temperatures as principally different from the one under isothermal conditions. Evaporation and condensation of semivolatile species always takes place. In thermodynamic equilibrium evaporation equals condensation and the gas/particle partitioning does not change. When the temperature varies, a net change of the gas/particle partitioning occurs leading to a faster equilibration in the case of a temperature increase and to a slower one in the case of a temperature decrease.

To b) We add a paragraph that mentions the importance of chemical reactions: Page 5798, line 12, we insert after “effect”: Moreover, chemical reactions are not taken into account for the calculation of equilibration times. For example, neutralization reactions by ammonia can reduce the effective Henry's law constants for organic acids and prolong the mixing time of species such as oxalic acid. Also, polymerization reactions may lower the vapor pressure and increase the amount of non-volatile organic matter.

To c) We think that for the case provided by Neususs et al. the volatility is not the key factor that determines partitioning of the dicarboxylic and the hydroxyl-dicarboxylic acids between the different size fractions. Rather, the equilibrium partitioning will depend on the physical properties of the different size fractions such as acidity and hydrophilicity as it is discussed in the paper by Neususs et al.

To d) Equation (1) of our paper describes the relaxation of organic species in the two-distribution aerosol system, i.e. of both liquid phases i ($i = 1, 2$) and the gas phase. On the other hand, the analytical treatment of Meng and Seinfeld (1996) is restricted to individual subsystems each consisting of the gas phase and one liquid phase i and assumes mass conservation within such a subsystem only. Thus each subsystem's relaxation is governed by a single exponential equilibration with a unique time constant. These individual subsystem time constants are approximated for the two limiting cases of a large gas phase reservoir or a large liquid phase reservoir. We apply mass conservation for the entire system consisting of the gas phase and all liquid phases. This leads to the system of coupled differential equations (4) and their analytical solution in equation (5). Mathematically speaking, (5) solves the two-dimensional system (4) of linear differential equations with constant coefficients whereas the analytical treatment of Meng and Seinfeld (1996) addresses the one-dimensional case of the decoupled subsystems. The time evolution of (5) is more complex than a single exponential relaxation and can be non-monotonous, as indicated in Figure 1. Such a behavior is captured by Meng and Seinfeld (1996) solely in their numerical, non-analytical treatment. This is expressed more clearly in the revised manuscript where the last sentence of section 2 (page 5795, line 15 -17) is changed to: "The non-monotonous time evolution of the liquid phase as displayed in Figure 1 results from superposition of exponential relaxations with different time constants as seen in equation (5). Such a time evolution cannot be expressed by simpler analytical treatments given in the literature (e. g. Meng and Seinfeld, 1996) which neglect the liquid phase coupling and thereby describe the equilibration of each liquid phase by a single monotonous time exponential."

To e) In Fig. 1, the data is presented for accumulation mode particles with r = 100 nm, not for ultrafine particles. We think that equilibration by gas phase diffusion is more important for the accumulation mode than for ultrafine particles. For ultrafine particles, the time constants would be smaller, however, for an accurate prediction the Kelvin effect should also be taken into account. The dotted line in Fig. 1 shows the time evolution of a polydisperse aerosol distribution.

To f) We change Figure 2 and use now the molecular weights indicated on the x-axis to calculate the equilibration times. We also change the manuscript accordingly.

To g) We add the molecular weights to Figure 3.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5789, 2004.

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