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Atmospheric
Chemistry
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Discussions

Interactive comment on “Parameterization of N_2O_5 reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate” *by* J. M. Davis et al.

J. M. Davis et al.

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We appreciate the compliments and thoughtful criticism provided by Anonymous Referee #1 (2007). We have given all of the suggestions careful consideration and revised our manuscript accordingly, as described in detail below.

Major concerns

1. *Justification for restricting the scope to* NH_4^+*-*SO_4^{2-}*-*NO_3^- *(A S N) systems is unsatisfactory.*
In the revised manuscript, we have augmented our justification for excluding other particle types from the parameterization. Ignoring the fact that a thorough treatment of those data would greatly lengthen our manuscript, we note that the available labora-

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tory measurements of γ on organic acids, soot, and dust have been parameterized adequately in a recent modeling study (Evans and Jacob, 2005). This text appears in the first paragraph of Section 2 in the revised manuscript.

We agree that an improved parameterization of γ on sea-salt particles is warranted given the abundance of laboratory data on NaCl, $NaNO_3$, and natural sea salt. Global modeling studies as well as simulations around coastal urban areas may benefit from such a parameterization. Given our current focus on continental domains such as the eastern United States, we maintain that a detailed parameterization of γ on sea-salt particles is outside our scope.

We fully acknowledge that a key limitation of our parameterization is that it excludes the effects of organic coatings (see Sections 2 and 5.1 of the original manuscript). Indeed, many atmospheric particles are composed of inorganic salts which are internally mixed or coated with organic material. As discussed by Anttila et al. (2006), a prerequisite to computing γ on organic/inorganic mixtures is an accurate parameterization of γ for the inorganic particle core. Therefore, our equations may be viewed as a necessary foundation for future research that will parameterize the suppression of γ when inorganic ammoniated particles are mixed or coated with organic material. In our revised manuscript, this sentence has been added to the abstract.

Though we did not expand our parameterization to explicitly treat other particle types, we have now examined the laboratory measurements of γ on NaCl, $NaNO_3$, sea-salt, and malonic-acid particles, in an effort to assess the dependence of γ on relative humidity (RH) in the A S N system. This examination is discussed in a new appendix (Appendix A) as described in the following response.

2. *Above 50% RH, strong dependence on RH is questionable.*

In response to these insightful comments, we have added an appendix to the revised manuscript. In Appendix A, we examine all laboratory measurements of γ on water-soluble particles (in which RH was varied and T held constant) to seek independent confirmation of the trend at high RH reported by Kane et al. (2001). Though that trend has not been confirmed in other published studies, none of the other studies provide

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physical rationale for rejecting the KAN01 data (e.g., error in experimental procedure). In addition, our personal correspondence with M.-T. Leu (principal investigator in the KAN01 study) yielded no information that would cast doubt on the KAN01 data at high RH. For these reasons, we decided not to change the RH dependence in our original parameterization.

Instead, we provide an alternative parameterization for γ_1 and γ_2 in Appendix A, based on a statistical analysis of all measurements except the KAN01 data. In this analysis, we include a new threshold variable to allow for the possibility that no effect on γ is discernible at high RH. Following the same stepwise model selection procedure used to derive the original parameterization, we obtain a model with a threshold RH of 46%. This is in fair agreement with the studies on NaCl, sea-salt, and malonic-acid particles, as well as the HAL03 data on ammoniated sulfate particles, which suggest no RH dependence above ~ 50%. In the appendix, we point out some shortcomings of the alternative parameterization. We also provide supplementary material that illustrates the alternative parameterization in a manner analogous to Figs. 2 and 4.

In the main body of the manuscript (Section 2.1), we have moderated our original statement that an increase in γ with RH is the most prominent feature in the laboratory data. The new sentence reads, “For all three compositions studied here, a prominent feature is that γ increases with RH although the reliability of this trend at high RH is unclear (see Appendix A).”

Anonymous Referee #1 (2007) suggests that our original parameterization of γ at high RH exceeds the N_2O_5 uptake coefficient on pure water by a factor of three, so we examined the available measurements on pure water. The most recent data evaluations (Sander et al. (2003, 2006)) recommend a value of 0.02 for γ on water ice, but there is no recommendation for the best value on liquid water. Uptake coefficients on liquid water range from 0.01 to 0.06, and Sander et al. (2006) provide some indication that the high values exhibit more consistency with MOZ88 and HU97 than the low values (see Note 25 below Table 5-2). Using our alternative parameterization, one obtains maximum values of 0.065 and 0.025 for γ on aqueous NH_4HSO_4 and $(NH_4)_2SO_4$ particles, respectively. Thus, the alternative parameterization at high RH is in good agreement with the uptake coefficients on pure liquid water. Using our original parameterization, maximum values of 0.08585 and 0.053 are obtained. Even these do not greatly exceed the reported uptake coefficients on pure liquid water. From this cursory analysis, it seems that additional laboratory measurements which aim to reduce the uncertainty of γ on pure liquid water would help us constrain our parameterizations in the limit when RH approaches 100%. A call for laboratory measurements on pure liquid water has been added to Section 5.2 of the revised manuscript.

3. *In place of Fig. 3, consider alternative methods to test the validity of both the T and RH components of the parameterization.*
We considered several plotting configurations before arriving at the format shown in Fig. 3. The reviewer‘s suggestions – “to show how the parameterization does when T is fixed and RH varies, and when T varies but RH is fixed” – do not produce useful figures due to the limited size of the dataset. Consider the aqueous NH_4HSO_4 dataset, for example. It contains 35 data points in total, but the measurements are collected at 26 different RH values and 9 different temperatures. The largest cross section (17 data points) is at 295 K with varying RH, but 15 of those values are from a single study (KAN01). Plotting our results against this cross section of data would merely test whether the statistical parameterization reproduces the RH dependence in the KAN01 data. Our objective is to concisely illustrate the overall performance of the parameterization against a variety of laboratory measurements. Ultimately, we found Fig. 3 to be the best format for achieving this objective.

Other Comments

1. *Alter the first line of abstract to reflect focus on A S N systems.* Both the manuscript title and the abstract’s second sentence clearly convey our focus on A S N particles and the paper is “comprehensive” with respect to these species. We have added a sentence to the abstract that elaborates on our exclusion of organics. When taken in context, we feel that the abstract’s first sentence is in no way misleading.

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2. *Organic coatings and organic mass are separate issues.* We have altered the first paragraph of Section 2 so this distinction is now clear. In response to Brown (2008), we also added two sentences to the conclusions that discuss the limitations imposed by excluding organics from our parameterization.

3. *Removal of 4 MOZ88 data points is questionable.* We agree with the referee's reasoning and have added back in the four MOZ88 data points. Figure 1, Table 1, and the first paragraph of Section 2.1 have been updated accordingly. We repeated the statistical analysis using all 67 aqueous ammoniated sulfate data points. This produced a slightly different parameterization (see Eqs. (4 – 5) and Table 3 of the revised manuscript) than our original result, which was based on 63 data points. Figures 2 – 4 have been modified based on the new parameterization, but they are visually similar to the original plots.

4. *Below the equation for threshold temperature, provide range of j values that were considered.* We have added an explanatory note below that equation.

5. *For dry particles, RH dependence may be due to an increase in surface-adsorbed water.* We thank the referee for pointing us to the study by Sumner et al. (2004). We looked into this further and found some studies in which the heterogeneous uptake of HNO_3 on crystalline salts increased with RH due to increases in surface-adsorbed water. It is possible that the reactivity of N_2O_5 on solid ammoniated sulfate particles is influenced by a similar process. We modified the last paragraph of Section 4.1 to mention this possibility and added two relevant references to the bibliography as well.

6. *The FOL03 data are in agreement with all other data sets except KAN01.* We have removed the sentences in Section 4.2 that questioned the FOL03 data point at 79.7% RH. In addition, we have taken the referee's suggestion to solve Eqs. (1 – 2) without the KAN01 data. The alternative parameterization is provided in Appendix A of the revised manuscript, as described above in response to Major Concern #2.

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