**Atmospheric
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Comment

Interactive comment on "Homogenous nucleation of sulfuric acid and water at atmospherically relevant conditions" *by* D. Brus et al.

Anonymous Referee #2

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Brus et al. present results of homogenous nucleation studies of the binary sulphuric acid water system from flow tube experiments. They build upon a recently developed system (Brus et al., 2010) that controls the levels of H_2SO_4 and water vapour and is supplemented with state of the art measurements of H_2SO_4 by CIMS and nucleation mode particles by PSM (1.5 nm cut-off). Thus, nucleation rates are determined as function of sulphuric acid concentration for typical ranges of ambient temperature (5-25°C) and relative humidity (10-57%). The subject of this presentation is of interest for this journal as it contributes new observations for a better understanding of the mechanism of gas-to-particle conversion. It also compares the results with recent field observations. It is well written and mostly well structured. However, there are substantial uncertainties in the description of the sulphuric acid distribution in the flow tube and accordingly the levels of sulphuric acid are questionable. As this paper relates

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nucleation rates to sulphuric acid concentrations, this is a central issue and revisions are requested.

The following general comments should be addressed by the authors:

1. Experimental – this section should contain all relevant information on the measurements including more details of H2SO4 CIMS, the aerosol particle measurements by TSI CPC, and the loss of H2SO4 in the flow tube and sampling tube (these latter could be done in a separate section, but moved from the Results section as this paper aims at a presentation of nucleation results and the distribution of H2SO4 sets the experimental conditions).

With respect to H2SO4-CIMS, a more thorough description is needed as discrepancies show up and experimental issues related to this should be presented in the Experimental. For example, no information about upper limits of measuring H2SO4 are given, depending on the CIMS system configuration, concentrations exceeding 109 molecules/cm^3 might deplete the NO3- ion concentration in the ionisation zone of the CIMS and thus reduce the sensitivity. Furthermore, the principle of ionisation should be explained and it should be discussed which H2SO4 clusters can be ionised by NO3-. It should be clearly stated that dimers, trimers, etc. of H2SO4 are measured as one sulphuric acid molecule only. Furthermore, the rate constant for charging reactions with higher order acid clusters depend, according to Viggiano et al. (1982), on the reduced mass and the dipole momentum of the acid. As clusters are expected to arrange such that their dipole moments partly compensate each other, lower reaction rate constants and ionisation rates are expected. Accordingly, dimers and higher momentum acid clusters are not measured quantitatively, and estimates of dimer/monomer ratios etc. should be handled with great caution, e.g. ratios of monomer/dimers of 100 deduced from these observations are expected to be overestimated. Moreover, in usual operation, higher order acid clusters are decomposed in the collision dissociation chamber, and the experimental part needs to be accomplished by information on the method used to determine dimers.

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Finally, the use of the inlet line of 1 m should be described and characterized in the experimental part. Especially, care has to be taken to demonstrate that the flows in the CIMS and corresponding calibration factors are not affected by this inlet line.

2. The authors ascribe losses of H2SO4 in the flow tube (and the sample tube) mostly to wall losses, which appears questionable. A related point, the discrepancies between the different methods to determine H2SO4 remains largely unresolved, there is only a short and insufficient discussion of these issues on page 25970.

Wall losses are presented which are according to Tables 1 and 2 in the range of factor 20 (combined loss in flow tube and sample tube CIMS). Such high loss rates principally bare the potential of high uncertainties in the H2SO4 concentrations, these uncertainties in the nucleation area need to be discussed. Furthermore, according to Brus et al. (2010), the observed losses relative to initial concentrations increase with increasing concentration of H2SO4 (Figs. 12 and 13 in this reference). Such a dependency is not expected for a first order loss process to the wall surfaces. On the other hand, it is clearly demonstrated that the H2SO4 mass in the observed particles is at most 3% of the initial gaseous H2SO4 (p. 25970). But the authors should consider and discuss the distribution of clusters containing H2SO4 and estimate the number of sulphuric acid molecules in all these clusters which are below the detection threshold of the particle counters. This sulphuric acid does not show up quantitatively in the CIMS measurements either (see above). Thus, the open part of the H2SO4 balance is expected to be in clusters and some small part also adsorbed to the walls.

Furthermore, the discrepancies between CIMS, bubbler-IC quantification and mass balance of H2SO4 should be further addressed. To better separate effects, experimental set-ups with smaller H2SO4 concentrations could help to better understand the nature of the loss process, e.g. linear and non-linear processes. In comparing the CIMS and bubbler approach, it should also be thought of possible artefacts in the bubbler. As no information on the bubbler is provided, it is hard to estimate but the potential of a diffusion limitation of higher clusters to reach the interface in the bubbles should

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be considered which could underestimate the contribution of larger clusters. Finally, the mass balance approach can not address potential losses at the Teflon filter at the end of the furnace, and it does not differ between single acid molecules and clusters.

Though some of these arguments remain speculative, they might be helpful in resolving or better discussing the discrepancies between the three methods for assessing the sulphuric acid concentration in these experiments. If the reason for the discrepancy is not resolved, the authors should think of new experiments in the flow tube to better understand what is going on. At least, the uncertainty of H2SO4 concentrations used in this paper should include the range of discrepancy between the different methods.

3. The nucleation rates are calculated for a certain H2SO4 concentration. It is not made clear to the reader, how one can speak of a specific H2SO4 concentration in a flow tube when concentrations change by factors of 5 (table 1).

4. It is not discussed why nucleation rates are identical at the lowest investigated H2SO4 concentration (Fig. 2) for all temperatures. The different slopes do not explain this phenomenon (p. 25968, l. 22, and conclusion) but only describe it. If real, this would imply that for atmospheric conditions with usually less than 5 107 molecules / cm^3 there is no temperature dependence of the nucleation mechanism discernable.

Technical/Minor Comments

1. Please check the given units for nucleation rates which should be given in /(cm^3s) and not cm^3/s

2. p. 25960, l. 19-20: the impact of anthropogenic emissions is rather vague, be more specific.

3. p. 25963, 1st §: this is a complete repetition from the Brus et al., 2010 paper, and should be shortened and referenced.

4. p. 25964, l. 3: the uncertainty should be further specified and it should be explained how it was derived (see also above).

5. p. 25964, l. 21: spelling error in "diethyl-glygol"

6. section 3.1: It is recommended to move this to the experimental section (see above).

7. p. 25967, l. 26: a factor of "-2" would not make much sense, instead it should be uncertainty by factor 2.

8. p. 25968, l. 19: change to ". . . order of magnitude when decreasing. . ."

9. p. 25972, l. 2-4: Please, make clear that there were different CIMS systems involved

10. p. 25972, l. 5: Please correct "Hohnepeissenberg" in "Hohenpeissenberg"

References

Viggiano, A. A., R. A. Perry, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld (1982), Stratospheric negative-ion reaction rates with H2SO4, J. Geophys. Res., 87(C9), 7340–7342, doi:10.1029/JC087iC09p07340.

Brus, D., Hyvärinen, A.-P., Viisanen, Y., Kulmala, M., and Lihavainen, H.: Homogeneous nucleation of sulfuric acid and water mixture: experimental setup and first results, Atmos. Chem. Phys., 10, 2631-2641, doi:10.5194/acp-10-2631-2010.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 25959, 2010.