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Interactive comment on “Laboratory studies of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ binary homogeneous nucleation from the SO_2+OH reaction: evaluation of the experimental setup and preliminary results” by L.-H. Young et al.

Anonymous Referee #2

Received and published: 2 May 2008

General comments:

This paper presents valuable laboratory work of binary homogeneous nucleation relevant to atmospheric new particle formation. The instrumentation used in the study is novel, and the construction of the new instrument is well documented. Experimentally measured, accurate nucleation rates of sulfuric acid + water are very much needed, as questions still arise of this nucleation pathway. Therefore, the paper is well suited for publication in the ACP.

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There are, however, some concerns over the methodology used in this study, and the following items should be addressed in the revised paper. My main concern over the experiments conducted is the stability of the instrument. In flow based nucleation experiments, nucleation is assumed to take place in a steady state. In principle, the steady state could be maintained as long as needed, several hours at least. However, the authors show no proof of the operating stability. In stead, looking at figures 4,5,6,10 and 12 it appears that the measured particle concentration is typically exhibiting a rising trend. The authors should perform a stability test on their instrument, or at least explain why they assume their instrument to be in a steady state only minutes after changing the experimental parameters such as the SO₂ concentrations.

Another general comment is about the figures. Nearly all figures are presented as timelines. I would suggest presenting more figures as quantitative relations and only the most necessary figures as timelines. Which figures might be changed is in the discretion of the authors.

Specific comments:

The orders of the paragraphs in the introduction should be considered. Now there is first discussion about sulfuric acid vapor generation (starting at line 12, page 6905), then discussion about flow based methods (from the line 22) and then focus is again on sulfuric acid vapor generation (line 10, page 6906). Furthermore, the authors should make a note that sulfuric acid vapor from liquid samples can be made by two ways: saturating a carrier gas with the vapor from a liquid pool or vaporizing the sulfuric acid liquid at high temperature. This has direct effect on the corrosion problem mentioned line at 10, page 6906.

Page 6909, line 14. The authors assume that nucleation occurs on the whole length of the nucleation chamber. Is it possible that nucleation occurs already in the mixer? Could this have an impact on the results or would this effect be negligible?

2.3 Particle measurements. The five to ten times lower particle concentrations obtained

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with the DMA + CPC compared to a stand-alone CPC are worrying. Some questions come to mind to validate the data. Did the authors make an intercomparison for example from the lab air? Was inversion made on the SMPS data? Was the RH of the sheath air controlled? If the differences of the concentrations cannot be consolidated, I would recommend using only the stand-alone CPC data for concentration. SMPS size distribution data are still likely valid, and very valuable information.

Page 6911, line 8. "when condensation and coagulation growth are negligible". Only coagulation should be negligible.

3.1 SO₂, OH, H₂O and O₂ effects on H₂SO₄ and particle production. The authors say that the step (3) illustrated in figure 4a is not expected from the reactions R1-R3, as both sulfuric acid concentration and particle number should show zero. From figure 4b, a clear decrease of both can be seen in step (3). What would happen if step three was kept on a longer time? Complementary to that; did the authors make test runs starting with SO₂ on, but UV light off? Did particles/ sulfuric acid appear? If so, this could be an indication of an unknown production process of sulfuric acid/particles (just as the authors correctly suggest and further elaborate in chapter 4.6) and should be a subject of further studies later on. It would be interesting to see if the problem remains if SO₂ concentrations were on the same order of magnitude as the OH-concentrations. According to the authors, the minimum RH attained was 4%. Where does the humidity come to the system? What is the accuracy of the RH sensor/has it been calibrated? The authors state that the standard SO₂ gases were diluted for the experiments. How was this made? The resulting nucleation behavior should really be independent of the original gas concentration, as long as the concentration entering the mixing chamber is the same. If I understood correctly this is not the case. Any ideas behind this? Which measurements should be considered more valid; the ones from 1ppm SO₂ or 100ppm SO₂?

3.2 Nucleation time (t_n) dependence of particle numbers (N) and [H₂SO₄] These measurements are interesting. I was wondering, in principle, the residual sulfuric acid

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concentrations could be linked to the initial OH-concentrations with the wall loss factors, thus consolidating the different sulfuric acid concentrations observed with different nucleation times (at these particle concentrations, the condensational loss of vapor should be close to negligible). Did the authors try to do this?

Page 6917, line 25. "...larger N and Dp at higher tn, consistent with the predictions from nucleation theories." I do not see a point making this relation, larger N is quite trivial ($N = t \cdot J$) and larger Dp occurs due to there being more time for condensational growth. Please elaborate? The same sentence occurs in the abstract, by the way.

3.5 The 34SO2 experiments. The authors should consider whether this chapter brings any added value to the manuscript.

4.1 Uncertainties in the particle measurement. According to the authors the reproducibility of the instrument can be examined when the same experimental condition is repeated several times. While this is certainly true, I would still draw attention in making sure that the instrument is really at steady state when repeating the experiment. In the referee's opinion, this might not be the case in figure 10.

Page 6921, line 17. "On the other hand, enhanced condensation growth will allow more particles to grow larger than 3 nm, leading to an increase of N and subsequently an overestimated (Kulmala et al., 2006)" This is very confusing. The paper by Kulmala 2006 deals with activation of clusters (NOT necessarily pure sulfuric acid clusters.), and the situation is quite different from the experiment. Surely the nucleation rate cannot be overestimated, this is the only way particles form in the experiment. The authors should carefully revise the remaining paragraph as well especially when talking about condensation.

Page 6921, line 26. "...condensation is needed for nucleation." This term is not correct. Nucleation is the very first step of the phase transition, only after nucleation can condensation take place. The authors are correct that condensation in the experiment is unavoidable; otherwise no particles would grow big enough to be detected!

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Page 6923, line 26. "A recent refined kinetic quasi-unary nucleation model...[H₂SO₄] has to be at least 10¹¹ cm⁻³ to observe significant binary J...". Would be nice to see the same for classical nucleation theory. I think this should be also in the paper by Yu (2006).

Fig 3. Should the y-axis really be log WLF, or just WLF in logarithmic scale?

Fig 5. Is there a reason why the axis values for H₂SO₄ are different in figures a and b? Also time axis's are different.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 6903, 2008.

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