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Atmospheric
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Discussions

Interactive comment on "Evolution of particle composition in CLOUD nucleation experiments" *by* H. Keskinen et al.

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Review of "Evolution of particle composition in CLOUD nucleation experiments" by Keskinen et al.

This paper estimates the evolution of particle composition during the growth of particles from diameters of ∼1-2 nm to diameters larger than 50 nm. The paper uses a combination of instruments to estimate the organic vs. inorganic fraction across this complete size range.

I feel that the paper is lacking a discussion (and possibly a very useful analysis) of *why* the inorganic to organic composition changes with size. Once this and other (more minor) comments have been addressed, I recommend this paper be published

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in ACP.

General comment

There was no discussion in the paper regarding why the organic composition increases during growth. Pierce et al. (2011) and Donahue et al. (2011) estimated that this occurs because of small particles reaching equilibrium with the vapor phase more quickly than larger particles, and only the lowest volatility organics can condense onto the smallest particles. However, in your experiments, there is the confounding factor that the gas-phase production of sulfuric acid and low-volatility organics may be occuring at different rates. If the sulfuric acid is being formed more rapidly than the low-volatily organics, this may also cause the particles to increase in organic composition later, as they grow. Please add a discussion of these possibilities.

In my opinion, the usefulness of the paper could increase greatly if additional analysis were done to quantify why/how the organic composition increases during growth. The relative sulfuric acid vs. organic aerosol formation rates could be determined from looking at the bulk mass from the AMS and the concentrations of the precursors (if they are monitored). If the oxidative timescale of both the precursors is similar or both smaller than the growth timescale, then the change in composition with growth is likely due to only the lowest-volatility organics condensing to the small particles with higher volatilities being able to condense as the particles grow. It should be possible to estimate a volatility distribution based on the change in organic fraction with time. However, one thing that might make this estimate tricky is that multi-generational organic chemistry will be causing the organic volatility distribution to evolve even as the particles grow. Either way, please consider this analysis. Co-authors Riipinen and Donahue should have good thoughts on this.

Pierce, J.R., Riipinen, I., Kulmala, M., Ehn, Petaja, T., Junninen, H., Worsnop, D.R., Donahue, N.M.: Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events, Atmospheric Chemistry and Physics, 11, 9019-9036, doi:10.5194/acp-11-9019-2011, 2011.

Donahue, N.M., Trump, E.R., Pierce, J.R., Riipinen, I.: Theoretical Constraints on Pure Vapor-Pressure Driven Condensation of Organics to Ultrafine Particles, Geophysical Research Letters , 38, L16801, doi:10.1029/2011GL048115, 2011.

Specific comments

P31073 L20-22: Why are different size ranges given (e.g. 2-63 nm vs. 2-50 nm)? And when you say “sulfuric acid” volume fraction, I think you mean “sulfate” or “inorganic”. I didn’t see any evidence in the paper that the aerosols were very acidic (i.e. un-neutralized sulfuric acid) at 2 nm (though this may be related to a mis-understanding that I have in a later comment).

P31074 L15-18: This is not totally accurate. The sentence makes it seem as if we call the entire particle an “SOA particle” when SOA condenses onto the particle (even if the particle is not entirely SOA).

P31074 L21: Why is “state-of-the-art” italicized?

Introduction: The intro focuses largely on the hygroscopic growth of particles, but it doesn’t discuss much about the growth of nucleated particles (by inorganics vs. organics). The contributors to aerosol growth appear to be on of the main focuses of the results, so they should be motivated in the introduction.

P31076 L20-23: Please give a few more details on the GR analysis here. I believe this is where you calculate the maximum growth rate due to H2SO4 vapours (measured from the CIMS) alone and compare this to the actual growth rate. This gives an estimate of the amount of sulfuric acid condensing vs. the amount of organics condensing.

P31077 L1-2 and P31079 L17: The size ranges for CCNC measurements differ.

P31083 L14: Measured organic fraction from which instruments?

P31083 L21-24: Diffusivity/molar mass is not the only (or necessarily the primary)

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driver for the timescale of reaching equillibrium. Higher volatility species reach equilibrium faster because condensation/evaporate occurs more rapidly to drive towards equillibrium.

P31084 L17: “10 : 10”, please make “10:10”. This confused me for a bit.

Discussion of Fig. 1B: Approximately how many sulfuric acid molecules are in a 1.2 nm cluster. This would be a useful reference to have.

Section 3.2.1: Why are API-TOF results not shown for this run?

P31086 L14: Need comma between CCNC and O-TDMA.

Figure 3 and P31086 L13: “runs C-G”. Figure 3 only shows 1 run, right (or maybe 2)? How could this be runs C-G? I guess I can kinda pick out 5 separate bananas (3 of the 5 are faint). Please make your definition of a “run” clear in the text. I was thinking that a “run” was a full experiment, but maybe each run is the injection of precursors, which could happen many times during a single experiment?

P31088 L1: Why “(Fig. 1)” here? I was confused and trying to look in Figure 1 for where you might be extrapolating some value from it (but you aren’t extrapolating anything from it, right?). Best to remove “(Fig. 1)”, I think.

P31089 L18-end-of-paragraph and Figure 5c: When you say “SA”, do you mean unneatralized sulfuric acid, or do you mean “sulfate” or “inorganics”? I was assuming that you meant un-neutralized sulfuric acid, but then I was confused when I read the sentence starting at L25 that only mentions AS and AbS, not SA. If it is un-neutralized sulfuric acid, it is very acidic, and you should mention this.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 31071, 2012.