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Comment on acp-2022-364

Anonymous Referee #1

Referee comment on "Water uptake and the gas-particle partitioning of nitrate aerosols"
by Hoang Duong Do et al., Atmos. Chem. Phys. Discuss.,
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This paper investigates through H-TDMA experiments the uptake of water onto pure ammonium sulfate and ammonium nitrate particles, mixtures of the two, and then with an added organic species (glyoxal). The experimental data are compared to two thermodynamic models, ISORROPIA and E-AIM.

The paper claims to identify three issues with thermodynamic models:

- They do not consider the period when a particle may have not yet reached the DRH and so the particles are dry, but most thermodynamic models are run in the metastable mode which assumes the particles are deliquesced. (See comment below on applicability of experiments to the real atmosphere; whether particles are ever dry in the ambient atmosphere and stable mode applies).
- They do not correctly predict DRH for mixtures. (If particles are always deliquesced, is this still a significant issue?)
- They do not include contribution of organic species to particle water. (This has been discussed for other locations in some detail and is not noted in this paper, see example Guo et al. <http://www.atmos-chem-phys.net/15/5211/2015/>)

Overall, the paper is confusing, and the experimental setup does not mimic actual ambient atmospheric conditions and so the conclusions that suggest the thermodynamic models are wrongly applied or deficient may not be justified. The paper needs substantial work.

This paper should really discuss the classic work of Tang and Munckelwitz on water uptake by salts. Tang and Munckelwitz report results from single particle levitation experiments, likely some of the earliest and most precise work in this area. As one example publication see, JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 99, NO. D9, PAGES 18,801-18,808, SEPTEMBER 20, 1994). There are more.

How do the authors handle the possible loss of NH₃ and/or HNO₃ to interior surfaces during the experiments? Since both NO₃⁻ and NH₄⁺ in the particle phase are semi-volatile and surfaces are a sink, there will be continual evaporation of these compounds from the particles. Is this an issue and possible cause for discrepancies with the model predictions?

Figure 1 schematic is confusing. First, is the gas phase HNO₃-NH₃ reaction important as a source for particle NH₄⁺ and NO₃⁻. If so, state how you know this. I suspect that HNO₃ and NH₃ partitioning is the important route, thus I do not understand the line in the Fig caption that states: thus I do not understand the line in the Fig caption that states: The partitioning of HNO₃(g)-NO₃(p) and NH₃(g)-NH₄⁺(p) can be viewed as the formation of ammonium nitrates(p) by the reaction of ammonia and nitric acid in the gas phase. Second, the red arrow to the particle phase of NH₄NO₃ implies it is a one-way path, yet it is semi-volatile. Is the idea that the NH₄NO₃ formed in the gas phase dissociates in the particle aqueous phase and then these two ions establish equilibrium with their gas phase components? Overall, I do not understand this aspect of the figure, why is it included, how does it support the findings of the paper?

Why is SO₂ oxidation by only OH? In Figure 1. Are the authors claiming this is the main route to forming SO₄⁼.

The word aerosol means particle within a gas, in many cases in this paper the term aerosol should really be particle or aerosol particle.

Line 179 typo, change all over to over all? Also, this line is very important and possible explains the discrepancy in Fig 3 for AN. (Note, a similar statement is made later in the paper). The issue is likely that the AN aerosol was never truly dry when exiting the dryers and so the H-TDMA experiments are really for a deliquesced aerosol and the comparison to a dry aerosol in Fig 3a (ISORROPOA stable mode) is not valid. Note that the data does basically agree with Fig 3b which compares to a deliquesced aerosol (ISORROPIA metastable). This point should be made very clear in section 3.2.

I do not understand the following arguments:

Line 301-302 which states; When the fraction of nitrates is small, particles of the ammonium-sulfate-nitrate system will become dry ammonium sulfate aerosols in the RH range of 30 to 70% by evaporating ALWC, nitrates and ammoniums significantly.

Line 310 to 311 which states; a barrier created by ammonium sulfate aerosols that suppress ALWC and nitrate accumulation in the RH range of 30 to 70%.

To better explain my confusion, maybe it would work to follow what happens in the atmosphere to an aerosol particle over periods of changing RH (i.e., a diurnal cycle). Say a pure AS particle is somehow formed in the ambient atmosphere (not sure how this would happen, but this is what the experiment simulates). Within one night the RH likely exceeds the AS deliquescent point of about 80% RH, so the particle takes up water, then as the RH decreases the next day the water follows the upper curve of the hysteresis as it dries. Since the RH likely never drops below the crystallization RH of about 37% the particle from now on is always wet, it moves along the upper curve of the hysteresis. The only way it will shift to a dry particle (AS crystal), the lower hysteresis part of the curve, is if the RH drops below the crystallization point sometime during the day, which requires a RH

The fundamental question about this work is that the experiments don't seem to mimic the RH levels of what ambient particles experience – they are likely never completely dry (10% RH), which is how they start out in these experiments (I am sure there is never a 10% RH in the ambient boundary layer pertinent to this study). The main question is then, would the results of this work change if the particles started off wet (deliquesced)? Or another way to put this, describe the situation where a crystallized salt exists in the Korean boundary layer so that the use of the metastable mode in the thermodynamic models is incorrect.