Our responses to the short comments from A. Nenes et al.

Comment on Wang et al. (by A.Nenes, R.Weber, H.Guo, A.Russell, and P.Vasilakos)

Comments from A. Nenes et al:

We feel that the manuscript contains conceptual issues that need to be addressed. Below is what we consider the main ones.

The authors claim that thermodynamic models cannot be applied to ambient aerosol, because the system is "too complicated" due to the presence of organics. This discredits decades of research and aerosol model development and the extensive literature to evaluate them, without much proof on behalf of the authors. Instead, the authors chose, without supporting evidence, to come up with a much simpler (and considerably less accurate and evaluated) conceptual model of aerosol acidity, one that presumably uses the presence of aerosol oxalate as the "smoking gun" of aerosol neutrality, and the proposed NO2-enhanced sulfate production mechanism of Wang et al. (2016). This conceptual model, a fundamental premise of the paper, is incorrect; one can show (using the approach of Meskhidze et al. 2003 and Guo et al. 2016) that a considerable fraction of oxalic acid can partition to strongly acidic aerosol (see figure below). In a manuscript we have just submitted to ACPD (Nah et al., submitted), we use comprehensive field data to verify that the semivolatile partitioning of oxalic acid follows thermodynamic predictions just like for semivolatile inorganic ions, and is in agreement with modeled pH.

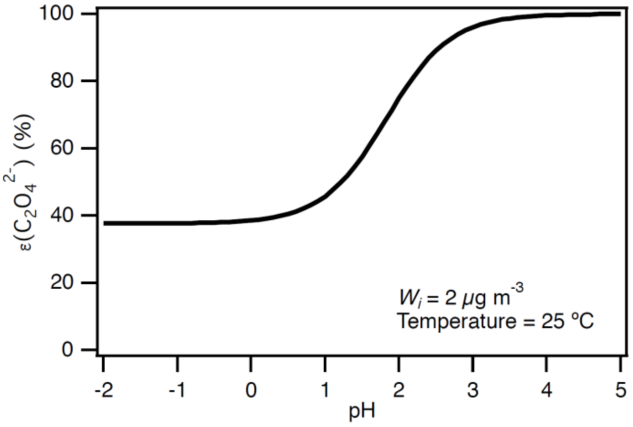

Figure 1: Fraction of total oxalic acid (particle/[particle+gas]) that partitions to the aerosol phase as a function of aerosol pH. Note that there is always some oxalate in the aerosol phase, even at very low pH (where it is undissociated), due to the high solubility (Henry's Law constant) of oxalate. Calculations based on Nah et al. (submitted).

Reply : We thank Dr. Nenes et al for their interesting comments. Before giving the detailed comments, we would like to say that we didn't intend to discredit anyone, instead, we only showed our experimental results and discussed the potential mechanism leading to the rapid formation of sulfate during the haze events in China by simulating heterogeneous oxidation of SO_2 by NO_2 on oxalic acid seed particles in a smog chamber. Our chamber results can successfully explain the mechanism of the rapid formation of sulfate in China during the wintertime haze periods. The SO_2 uptake coefficient calculated from our laboratory chamber simulations is consistent with that observed in Beijing haze periods (Wang et al., 2016, 2018) but cannot be explained by using the ISORROPIA-II model.

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Noteworthy is that Song et al (2018) carried out pH calculations (with the E-AIM model) for Beijing conditions and found that oxalic acid does not modulate aerosol pH considerably. This is in part because oxalate ion constitutes a relatively small fraction of the total ions in solution. The data presented in Wang et al. also shows that relatively minor amounts of oxalate are in the aerosol, so pH cannot be strongly affected. Regarding the discussion on the other effects of organics on pH predictions (such as liquid-liquid phase separation effects and water

Reply: The oxalic acid concentration in aerosols calculated by Song (2018) is not minor, which varies from 0.01 μmol m^{-3} to 0.32 μmol m^{-3} and is comparable and even higher than sulfate (0.1μmol m^{-3}). Oxalic acid is often found to be the most abundant dicarboxylic acid in the atmosphere. However, water-soluble organic acids in urban atmospheric aerosols consist of hundreds of species with molecular weight ranging from the smallest formic acid to the very big humic acid like compounds. All of these organic acids are responsible for the aerosol acidity. Therefore, one cannot say that pH cannot be strongly affected by organic acid because oxalic acid in the aerosols is minor. As we discussed in the manuscript, acidity of an ambient aerosols is not only determined by inorganic species but also by organic compounds (e.g., organic acid, carbonyls and amines).

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Partitioning calculations for evaluating pH predictions: The authors raise issues with the use of comparisons between predicted and measured partitioning of semivolatile species as a way to assess the thermodynamic model performance. Here we attempt to clarify the issue……

Reply: As for this point, see the short comments from Song (2018)

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Song et al. (2018) finally show that the difference in pH between stable and metastable states may not significantly differ when the two solutions drastically differ in their predicted liquid water (one still requires however evaluation of the pH against partitioning measurements to believe them!). Therefore, asserting that uncertainty in which phase state is assumed invalidates the pH prediction is without merit.

Reply: Song et al (2018) pointed out that pH predicted by ISORROPIA-II model between stable and metastable modes are similar when the model code errors are fixed, and high pH values predicted by the thermodynamic mode under stable mode is due to the model code errors. We think this issue needs a confirmation from the model developer, i.e., Prof. A. Nenes et al. Until now, Guo et al (2017a, 2017b) and many other researchers (e.g., Liu et al., 2017) have claimed that the pH predictions with ISORROPIA-II model by using the metastable mode are remarkably better than that by using the stable mode, on the basis of model evaluation from measured and predicted NO_3^- and NH_4^+. However, we found that the predicted concentrations of NO_3^- and NH_4^+ by using both the metastable and stable modes are nearly identical (see Wang et al., 2018) but the pH values predicted with these two phase states are significantly different, which is recently ascribed by Song et al (2018) to the model code errors.

Comment from Nenes et al :

One point that needs to be emphasized is that "bulk" (or beaker-scale) arguments, essentially do not consider the critical issue of equilibrium with the gas phase and the implications thereof, as pointed out by S. Song in his comment. The number of moles in the gas phase can be comparable or far exceed those in the aerosol phase; therefore volatilization of compounds (such as ammonium, oxalate, nitrate and chloride) to establish equilibrium can completely change the composition of the aerosol vs. the expectations obtained from beaker-scale thermodynamics. Understanding this unique but often neglected aspect of the aerosol system is critically important. Thermodynamic models based on the equilibrium assumption consider this, bulk beaker-scale conceptual models do not.

Reply: We agree on the comment that the equilibrium of a volatile species between the gas and aerosol phases is different from that on a bulk beak-scale. The problem here is that several recent studies using the thermodynamic model estimated the particle acidity and sulfate production rate by treating the PM exclusively as a mixture of inorganic salts dominated by ammonium sulfate and neglected the effects of organic compounds. Noticeably, the estimated pH and sulfate formation rate during pollution periods in China were highly conflicting among the previous studies.

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