

Interactive comment on “Particle acidity and sulfate production during severe haze events in China cannot be reliably inferred by assuming a mixture of inorganic salts” by Gehui Wang et al.

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Song calculated the acidity of the aerosol mixture of ammonium sulfate and ammonium oxalate by using the thermodynamic model and stated that pH of the 0.1 M ammonium sulfate aerosols mixed with different molar ratio of ammonium oxalate is nearly the same (around pH= 4.3, see the figure given by Song). We think this model calculation needs experimental validations. We agree with Shaojie Song and A. Nenes et al that the equilibrium with the gas phase could be significantly different between beaker-scale and aerosols. Due to the tiny size and complex compositions, pH of atmospheric aerosols cannot be measured directly and is, instead, often estimated by

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thermodynamic models based on some simplified assumptions. The uncertainty of the pH estimation is significant in some cases. Our lab chamber simulation results showed that SO₂ could be efficiently oxidized by NO₂ into SO₄²⁻ on the ammonium oxalate aerosols, which is derived from the reaction of seeded oxalic acid particles with NH₃(g), under the high humid conditions with ammonia neutralization, but such a conversion does not efficiently happen on the ammonium sulfate seeds under the same conditions. Such a difference indicates that pH of aqueous ammonium oxalate aerosols is high enough for the SO₂ conversion.

We agree with Shaojie Song that the equilibrium of dissolution and dissociation of ammonia in water can be expressed as: $\text{NH}_3(\text{g}) + \text{H}^+(\text{aq}) \leftrightarrow \text{NH}_4^+(\text{aq})$, but the concentration of H⁺ in aqueous aerosols is also equilibrated with all anions, e.g., sulfate (SO₄²⁻) and oxalate (C₂O₄²⁻). Since C₂O₄²⁻ is a weak acid, it would exist in part as C₂O₄H⁺/C₂O₄H₂ by combining some H⁺. Therefore, pH of ammonium oxalate aerosols should be different from that of ammonium sulfate aerosols, which is the reason why sulfate is efficiently produced on oxalic acid particles but not ammonium sulfate particles under high RH conditions with NH₃ neutralization.

Our reply to the specific comments

(1) As for the statement related to SO₂ and NO₂ solubility, we removed the phrase of “NO₂ solubility” and revised the sentence.

(2) Song et al claimed that the assumed particle phase states do not significantly impact pH predictions and the higher pH values of 6.9 ± 1.33 under stable mode in Xi'an were affected by the ISORROPIA-II model code errors. As commented by the model developers, A. Nenes et al, this explanation still requires evaluation.

(3) As for the contribution of organics to aerosol water contents, our lab measurement shows that the growth factor of oxalic acid is about 1.5 at a RH90% conditions (Figure 2) (Wang et al., 2018), which is comparable to ammonium sulfate, suggesting that the contribution of organic compounds to aerosol-associated water could be significant in

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some cases, and cannot be neglected.

References:

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