Short Comments on "*Particle acidity and sulfate production during severe haze events in China cannot be reliably inferred by assuming a mixture of inorganic salts*" *by Wang et al. (2018)*

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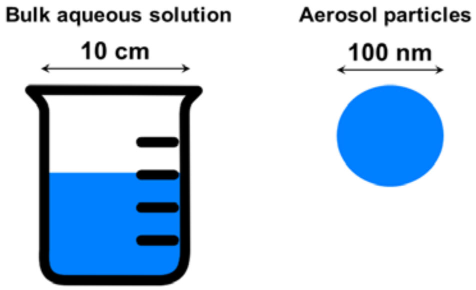
Wang et al. (2018) discussed particle acidity and sulfate production for haze events in China by laboratory and field experiments. I think this paper may benefit from the following general and specific comments.

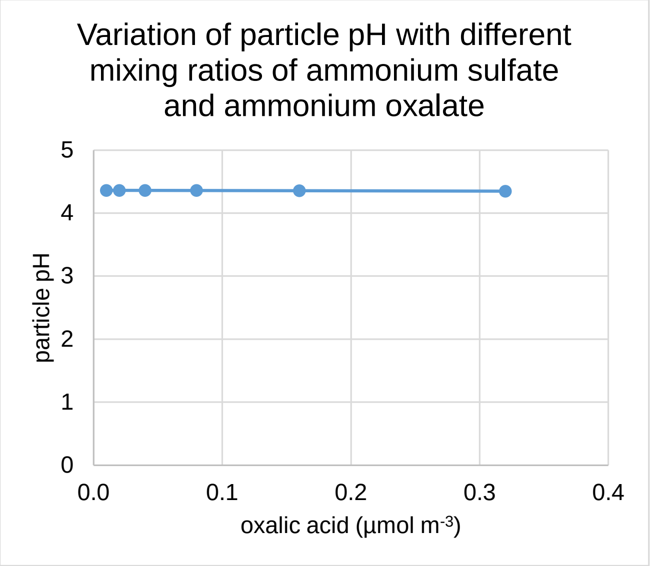
A general comment on laboratory experiments

I find this paper's discussion on the laboratory experiments of sulfate production and particle acidity confusing. In Section 3.1, this paper wrote, "*The ammonium oxalate is less acidic than ammonium sulfate*". An example was given to support this statement: "*the pH value of 0.1 M ammonium oxalate is 6.5, which is one unit higher than that of ammonium sulfate (the pH value of 0.1 M $(NH_4)_2SO_4$ solution is 5.5)*". This paper also suggested that the distinct sulfate production rates in Wang et al. (2016) and (2018) are due to the distinct acidity for ammonium oxalate seed and ammonium sulfate seed particles. The abstract of this paper wrote, "*Ammonium sulfate and oxalic acid seed particles exposed to vapors of SO_2, NO_2, and NH_3 at high relative humidity (RH) exhibit distinct size growth and sulfate formation. Aqueous ammonium sulfate particles exhibit little sulfate production because of high acidity, in contrast to aqueous oxalic acid particles with significant sulfate production because of low acidity*".

I think that the statement, "*The ammonium oxalate is less acidic than ammonium sulfate*", is true for the bulk aqueous solution, but false for the aerosol particles under the experimental conditions in Wang et al. (2016) and (2018). The major difference between the bulk aqueous solution and aerosol particles is in their time scale of reaching the thermodynamic equilibrium with the gas phase. The time required for the thermodynamic equilibration of 100 nm aerosol particles should be very short (in minutes or less), while this characteristic time of bulk aqueous solution is much longer. Thus, we do not need consider the issue of thermodynamic equilibrium when determining the acidity of bulk aqueous solution but usually we have to consider this for aerosol particles.



Using the E-AIM thermodynamic equilibrium model (*http://www.aim.env.uea.ac.uk/aim/aim.php*), it is easy to calculate that the pH values of 0.1 M ammonium oxalate and 0.1 M ammonium sulfate bulk aqueous solutions are 6.4 and 5.4, respectively, at 298 K. This is obvious, as the acidity of sulfuric acid ($pK_a = -3, 1.99$) is stronger than that of oxalic acid ($pK_a = 1.25, 4.14$). I also calculated the pH values for aerosol particles with the E-AIM model under the following situations (which should be consistent with laboratory experiments by Wang et al.): temperature = 298 K, RH = 90%, NH_3 = 20 μmol m^{-3} air, $(NH_4)_2SO_4$ = 0.1 μmol m^{-3} air, and the levels of oxalic acid increase from 0 to 0.32 μmol m^{-3} air (representing the mixing of ammonium oxalate and ammonium sulfate). One characteristic of the experimental conditions is that NH_3 is super rich, that is to say, $[NH_3] >> [SO_4^{2-}] + [C_2O_4^{2-}]$, and therefore a large amount of NH_3 can exist in the gas phase and buffer the pH of the aqueous solution. The equilibrium of dissolution and dissociation of ammonia in water can be expressed as: $NH_{3(g)} + H^{+}_{(aq)} \leftrightarrow NH^{+}_{4(aq)}$. The figure below shows that the calculated particle pH values do not vary with different mixing ratios of ammonium sulfate and ammonium oxalate. Thus, the statement in this paper, "*aqueous ammonium oxalate/$(NH_4)_2SO_4$ particles exhibit a lower acidity than that of $(NH_4)_2SO_4$ particles*" does not stand.



The above E-AIM model calculations suggest that the pH values for aerosol particles of ammonium oxalate and ammonium sulfate, under the experimental conditions, should be nearly the same (difference < 0.02 pH unit). Then, **the interesting question is: why the sulfate production is different for the oxalic acid and ammonium sulfate seed particles in the laboratory experiments**? I learn from Wang et al. (2016) and (2018) that these experiments have "*comparable concentrations for* SO_2*,* NO_2*, and* NH_3" and the aerosol particles are "*in the same phase-state (aqueous)*". It would be great if the authors can provide more insights into this question. The inputs of these E-AIM model calculations are attached at the end of this file, and I am happy to conduct additional thermodynamic model calculations, if requested.

Specific comments:

Page 8, Line 180: The solubility of NO_2 should not change with particle acidity as it does not dissociate.

Page 11, Lines 244-259: On the pH predictions under the metastable and stable mode, this paper wrote, "*More recently, it was suggested that the large discrepancy in predicting pH is attributable to the differences in the model assumptions (Song et al., 2018)*". The citation seems not clear. This Song et al. (2018) study demonstrated that there were coding errors in the stable mode of the ISORROPIA-II standard model, and that the assumed particle phase states do not significantly impact pH predictions. The pH values of 6.96±1.33 under the stable mode in Xi'an winter 2012 were affected these coding errors.

Page 11, Lines 261-265: "*Guo et al. (2017) and Liu et al. (2017) assumed negligible particle water associated with the organic aerosol mass. Such an assumption is clearly invalid since aerosols typically contain a large portion of WSOM in China, including organic nitrogen species and acids.*" The particle water associated with organics should be much smaller compared to that associated with inorganic salts, given the small hygroscopicity parameter (κ) of organics. A very recent paper, Wu et al. (2018), estimated aerosol water contents under Beijing winter haze conditions, by the ISORROPIA-II model using inorganic salts measurements and by the combination of the measured size-resolved hygroscopic growth factors and particle number size distributions, and showed that these two methods agreed well with each other. This Wu et al. (2018) study demonstrated the minor contribution of organic compounds to aerosol water contents.

Reference

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Table. Summary of inputs for the E-AIM (version II) model calculations. The temperature in all of the problems is 298 K. The concentration units of input chemical species are mol m^{-3} air or µmol m^{-3} air.

Problem No.	Type	Input
1	Bulk aqueous solution, 0.1 M ammonium oxalate	H_2O = 55.6 mol m^{-3}, NH_4^+ = 0.2 mol m^{-3}, $H_2C_2O_4$ = 0.1 mol m^{-3}
2	Bulk aqueous solution, 0.1 M ammonium sulfate	H_2O = 55.6 mol m^{-3}, NH_4^+ = 0.2 mol m^{-3}, SO_4^{2-} = 0.1 mol m^{-3}
3	Aerosol particles	RH = 90%, NH_3 = 20 µmol m^{-3}, SO_4^{2-} = 0.1 µmol m^{-3}, $H_2C_2O_4$ = 0 µmol m^{-3}
4	Aerosol particles	RH = 90%, NH_3 = 20 µmol m^{-3}, SO_4^{2-} = 0.1 µmol m^{-3}, $H_2C_2O_4$ = 0.01 µmol m^{-3}
5	Aerosol particles	RH = 90%, NH_3 = 20 µmol m^{-3}, SO_4^{2-} = 0.1 µmol m^{-3}, $H_2C_2O_4$ = 0.02 µmol m^{-3}
6	Aerosol particles	RH = 90%, NH_3 = 20 µmol m^{-3}, SO_4^{2-} = 0.1 µmol m^{-3}, $H_2C_2O_4$ = 0.04 µmol m^{-3}
7	Aerosol particles	RH = 90%, NH_3 = 20 µmol m^{-3}, SO_4^{2-} = 0.1 µmol m^{-3}, $H_2C_2O_4$ = 0.08 µmol m^{-3}
8	Aerosol particles	RH = 90%, NH_3 = 20 µmol m^{-3}, SO_4^{2-} = 0.1 µmol m^{-3}, $H_2C_2O_4$ = 0.16 µmol m^{-3}
9	Aerosol particles	RH = 90%, NH_3 = 20 µmol m^{-3}, SO_4^{2-} = 0.1 µmol m^{-3}, $H_2C_2O_4$ = 0.32 µmol m^{-3}