

## ***Interactive comment on “Technical note: Comparison and interconversion of pH based on different standard states for aerosol acidity characterization” by Shiguo Jia et al.***

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I believe I reviewed a very similar ms to this one (submitted to another journal) in 2017. I presume it was rejected.

Below are what I see as some of the most important issues regarding our understanding (from measurement or from models) of aerosol acidity. I don't think that the authors really grasp them or the problems involved, and that this proposed Technical Note does not provide the clarity and guidance that are needed by the field.

1. Any discussion of pH ought to start with a recognition of what it is, which is not some

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"absolute" but depends on either how it is measured or the model used to calculate it. See for example the first sentence of Buck et al. (Pure Appl. Chem. 74, 2169-2200, 2002):

"The concept of pH is unique among the commonly encountered physicochemical quantities listed in the IUPAC Green Book in that, in terms of its definition,

$\text{pH} = -\lg a$

it involves a single ion quantity, the activity of the hydrogen ion, which is immeasurable by any thermodynamically valid method and requires a convention for its evaluation."

So, for example, values of model-calculated  $\text{H}^+$  activities depend on how the model "splits" mean activity coefficients of cation-anion pairs (which are measurable) into single ion activities (which are not). This may not be a problem if all the calculations of thermodynamic properties (gas/aerosol equilibrium for example) are made with one model, but it should nonetheless be recognised. The measurement of pH is tied to the defined pH of the buffer used to calibrate the instrument. The buffer needs to be chemically similar to the solution being measured. Measured and modelled pH may not be comparable.

2. The  $\text{H}^+$  content of an aerosol should never be calculated from charge balance, for reasons that are so obvious that they hardly need repeating here (chemical analysis may not include all charged species; real  $\text{H}^+$  content is likely to be small relative to the amounts of the other cations and anions and is obtained as the [small] difference between two large and uncertain numbers). The use of measurements of gas phase  $\text{NH}_3$  or  $\text{HNO}_3$ , in addition to the major ion composition of the aerosol, as constraints on aerosol acidity seems the sensible approach to me. I'm aware that the group of Jose Jimenez uses this method. I expect there are others.

3. The relationship between solute activities on different concentration scales - the basis of equations 1 to 10 of the authors - is textbook material. See for example

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Chapter 2 of "Electrolyte Solutions" by Robinson and Stokes. The authors haven't cited this or any other chemistry textbook.

4. The rough correlation between pH on the molarity scale and on the other scales is to be expected, as is clear from eq (9), and this part of their discussion doesn't really add to the content of the ms.

5. Discussions of aerosol acidity need to address the fact that "pH" will go up and down with the diurnal cycle of RH, while the H<sup>+</sup> content of the aerosol might remain more or less the same.

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