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Atmospheric Chemistry and Physics
Discussions

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

Anonymous Referee #2

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Particle acidity is an important property in terms of aerosol chemistry and its impact on health and climate. Due to the importance, there has been an increasing amount of publication investigating particle pH through thermodynamic models in recent years, which is a step forward compared to the problematic ion balance or molar ratio because of particle liquid water and non-ideality effect (activity coefficient). Without a consensus on the pH definition, it would be difficult to compare various studies, and this may lead to misunderstanding or misinterpretation of particle pH. Although some particle acidity studies state clearly the pH definition used in the analyses, there are some papers not talking about the definition at all. In the latter case, some studies probably take the approach of molality-based or molarity-based because they take a pH of 7 as neutral.

This paper shows the two pHs are very close and the minor difference is caused by particle density (for dilute water solution, no difference is expected from the two pHs). In general, this paper hits an important point (i.e., pH definition) that has not been paid enough attention to by the community and fits the scope of a technical note on ACP. However, some revisions are needed before considering a publication.

There are several "circular" statements as pointed out by the other reviewer Andreas Zuend. The differences between pHx, pHc, pHm are all expected from their definitions. This is the key point of this paper: the difference between pHc and pHm is small (within 0.2 pH units, caused by particle density), but pHx is significantly higher than pHc and pHm (pHx – pHm = 1.74). The E-AIM (or any other model) predicted pHs are supposed to be consistent with the rule, if one model is used consistently in this analysis. Therefore, it is not a real support by field data (used as E-AIM input) as claimed on line 13 Page 5. Relating to this, the author should consider changing the saying of "observed" (Line 18 Page 1) in the abstract. The presented result is all based on a thermodynamic model prediction of pH but not measured pH.

From a boarder view of an application, this paper could be more beneficial by showing the default pH scales given by widely used thermodynamic models. The E-AIM model has been discussed in detail, however, ISORROPIA or AIOMFAC or any other model is not mentioned. For example, ISORROPIA gives pH in the model output and the pH scale is molality-based (Fountoukis et al., 2009; Guo et al., 2015). If a literature doesn't specify the pH scale, this piece of info could be very helpful to readers.

The section 3.3 is problematic without discussion of uncertainty, especially considering that the presented pH in this study is solely based on particle data (no gas data used to constrain pH). The predicted pH uncertainty is propagated from the particle ionic composition data (6% reported by Chen et al. (2016)) and RH, T. It is not easy to estimate particle pH uncertainty. Guo et al. (2015) estimated a pH uncertainty of 13% using another model, ISORROPIA, and in forward model for their dataset. Even though the two data points (S-I and S-II) are selected for the largest deviation from the

1:1 line, small differences (7% or 8%) in hydrogen ion activity are found, which seem to be within uncertainty range. Hennigan et al. (2015) and other papers have pointed out that forward mode is superior over reverse mode in terms of particle pH prediction accuracy. For one reason, reverse mode is more sensitive to particle measurement uncertainty (likely the cause for occasionally very high pH seen in Figure 1). For the other reason, particle pH is sensitive to gas-particle partitioning of semivolatile species (e.g., NH4+, NO3-, and Cl-), as long as the species is not totally in gas phase or particle phase. The forward mode predicted pH can then be validated if predicted and observed gas-particle partitioning agree. In contrast, the reverse mode predicted pH could not be verified in the same way. The Line 7 on Page 7 seems to suggest there is no advantage of using forward mode calculation and this is misleading to potential users.

As Andreas Zuend points out, it would be nice to mention the possible differences between predicted pH via different models at the end of section 3.4. Even if the same inputs are given to models, 100% agreement in pH is not expected due to differences in assumptions and approaches. There are a number of studies comparing thermodynamic models and exploring the differences (Hennigan et al., 2015; Liu et al., 2017; Pye et al., 2018; Song et al., 2018).

Minor comments:

- Toning down the statement of “for the first time” is suggested. Thermodynamic specialists must have known the difference between pH scales. The elucidation in the paper is based on established equations on textbooks and doesn’t sound to me like a groundbreaking finding. The paper is of value to minimize the gaps in the current understanding of pH definitions.

- The units in Equation (3) (mol/kg water) and (6) (mol/dm3) look redundant. However, more explanations in the text are needed. Equation (3) is defined based on the mass of water, while Equation (6) is defined based on the volume of particle, which includes

the volumes of water (solvent) and other solutes. If Equation (6) is defined solely on the volume of particle water, there would not be any difference with Equation (3). This is not clear in the text.

- Proper reference as suggested by Simon Clegg.

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