

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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1 General comments

Acidity is an important characteristic of liquid aerosol particle phases, which often tend to be highly acidic, as expressed by a low pH value. This technical note addresses several issues arising from the existence of distinct ways to define “pH”. The authors discuss the differences between pH defined on molality, molarity and mole fractions scales and the importance of using thermodynamically correct conversions among these scales when field data is compared. This scale-dependence of pH is an im-

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portant point indeed. While this reviewer has been aware of the pH scale dependence and its potential pitfalls for a while, it is an issue appropriate for a “technical note” outlining the proper thermodynamic scale conversion (theory) and providing discussion of related practical issues in aerosol acidity evaluations from field data.

However, the present manuscript contains a number of flaws, several of which are further discussed under specific comments below. The interactive comment by Simon Clegg (<https://www.atmos-chem-phys-discuss.net/acp-2018-85/acp-2018-85-SC1.pdf>) summarizes the main concerns shared by this reviewer. Major revisions are necessary to transform this manuscript into a paper that contains (i) a thorough discussion of the thermodynamic scale conversions as well as (ii) an appropriate discussion of the general issues with pH estimation of field aerosol samples, given that the actual H^+ concentration is not routinely measured and other properties like water content and cation/anion balances may suffer from substantial measurement uncertainty and artifacts. While the latter point is not the focus of this technical note, mostly ignoring the issues of that point is not appropriate either. Errors from incorrect H^+ concentration estimations, e.g., by use of an ion charge balance, as done in this study (and others), may frequently be more substantial than the errors from pH value comparisons without proper pH scale conversion. Therefore, a discussion of issues with aerosol acidity determination and pH scale intercomparison must include both.

2 Specific comments

1. Abstract, line 16: Stating that this issue is addressed “for the first time” is rather bold given that the theoretical framework for activity coefficient and pH scale conversions has been known for decades (even though it may be true that it is a frequently ignored issue, therefore it is worthy of attention by the atmospheric chemistry community).

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2. Abstract, line 18: "Using hourly ionic species measurements in Guangzhou, China, it is observed that pH_x (mole fraction based) is always 1.74 pH unit higher than pH_m (molality based)". This is clearly misleading, since the pH unit difference is not truly based on observation. It is a circular argument also made at other places in the manuscript. The 1.74 pH unit difference is in fact coming from the application of such a theory-based difference and using the same thermodynamic model to compute the pH values in different scales based on H^+ activity coefficient prediction from the same samples.
3. Page 2, line 9: The authors state; "The acidity of aerosols can be quantified by parameters such as strong acidity, free acidity, cation-to-anion ratio and ammonium-to-sulfate ratio. However, these parameters neglect the effect of liquid water content or the dissociation of ions and acids (Pathak et al., 2004; Hennigan et al., 2015)." First, a definition of what strong acidity and free acidity represents is not given. Second, it is incorrect that free acidity neglects water content, as the partial dissociation of species like bisulfate is very much dependent on water content and therefore affects free acidity. Pathak et al. and Hennigan et al. do not seem to make such a point.
4. Equation (1): Define the meaning of "lg".
5. Equation (2): This equation and its description is flawed. (1) What are the terms of "1000" in the numerator and denominator? The authors likely use these for conversion from units of kg to g. If so, the mathematically correct way of writing this would be to write $1000 \frac{g}{kg}$ in the equation and it would be necessary to state that the molar masses are supposed to be used in units of $\frac{g}{mol}$ rather than the standard SI unit of $\frac{kg}{mol}$. Otherwise it is simply incorrect and a potential source of confusion. However, since the ACP recommendation is to use SI units whenever possible, there is not need for these unit conversion terms at all (they would be 1). (2) This expression is only correct for the special case where the only

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solvent for the ions is water. However, in the more general case, there may be other solvents, such as organic compounds mixed with water and the ions in a liquid phase. In that case, the distinct molar masses of the organics must be accounted for in the activity coefficient conversion expression. Hence, since this is a key part of the discussion about different thermodynamic composition scales and reference and standard states, it should be shown correctly for the general case. A rigorous derivation of such scale conversions is, e.g., shown in the PhD thesis by Zuend (2007) (page 45 – 47 there), which shows different versions of the scale conversion formula. One of which (useful here) is $\ln[\gamma_i] = \ln[f_i^*] + \ln\left[\frac{x_i}{m_i M_w}\right]$ where γ_i is the molality scale activity coefficient of ion "i" (e.g. H^+) and f_i^* the mole fraction scale activity coefficient, both with reference state of infinite dilution in pure water; x_i the ion mole fraction with respect to dissociated ions, m_i the ion molality and M_w the molar mass of water. Since solvents other than water are also included in both the mole fraction and molality expressions for ion "i", this is a general expression. From this scale conversion of ion activity coefficients, it is readily shown that the difference in pH values is generally given by $pH_x - pH_m = -\log_{10}[m^\circ M_w]$, where m° denotes unit molality (= 1 mol/kg) (similar to Eq. (8) in the manuscript, but note the difference in units, the given Eq. (8) is not dimensionless in the log).

6. As pointed out in the comment by Simon Clegg, thermodynamic models differ in the way single-ion activity coefficients are calculated (since only mean cation/anion pair activity coefficients are measurable) and of course they also differ in the expressions, such that even with the correct conversion of activity coefficients or pH values between scales, different models may predict different pH_m (or pH_x) values for the same input composition. Furthermore, only some models account for the influence of organic species in the mixture (e.g. AIOMFAC can be used for that, while ISORROPIA is only for inorganic aqueous mixtures) and differences in predicted pH may partially stem from organic interactions with ions

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and treatment of phase separation, see Pye et al (2018).

7. Equation (4): Similar to above comment. A general expression should be shown, with proper use of units.
8. Page 4, line 3: the last sentence there makes little sense. The pH values can be compared when the scale effect is accounted for; the point is that one should not expect the values to be equal.
9. Page 4, line 13: "This is supported by our field data". Again, this is a circular argument. The $\text{pH}_x - \text{pH}_m$ scale difference is used in the evaluation of the pH values, so of course it will show as consistent, but the measurements are no proof for that. Also, the fact that the difference should be a constant in pH units is clear from the theory, as long as the same thermodynamic model is used to compute the activity coefficients (which may not be the case when different studies are compared).
10. Page 7, line 6: The discussion in this paragraph is not sufficient to address the other very important issues when aerosol acidity is attempted to be assessed from field measurements. It is also clear from theory and comparisons that organic compounds will affect aerosol acidity, maybe not dramatically but noticeably, since their interactions with water and H^+ ions are affecting the activity of H^+ . Last sentence in paragraph: "The relationship between pH_x , pH_c and pH_m established in this study is valid regardless of the method selected to estimate aerosol acidity." This is true only for the scale conversion, since it depends on proper application of thermodynamic theory only (which has been known for decades and is not a novelty of this study). However, when aerosol sample acidity is estimated in practice, different models are used for activity coefficients (e.g. ISORROPIA, E-AIM, AIOMFAC) or unit activity coefficients are assumed (not recommended). Moreover, different methods are applied to determine the approximate H^+ amount, which is a critical problem in acidity evaluation, see Hennigan

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et al (2015). Therefore, the difference in reported pH values is not just due to the offsets between these different pH scales. The authors have failed to make this important point very clear.

11. Table 1: The definitions include many mistakes and typos; e.g., pH_m is not molarity based, the last two entries are confusing and not correctly described and reference states of activity coefficients are missing.

References

- Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles, *Atmos. Chem. Phys.*, 15, 2775-2790, 10.5194/acp-15-2775-2015, 2015.
- Pathak, R. K., Yao, X., and Chan, C. K.: Sampling Artifacts of Acidity and Ionic Species in PM_{2.5}, *Environ. Sci. Technol.*, 38, 254-259, 10.1021/es0342244, 2004.
- Pye, H. O. T., Zuend, A., Fry, J. L., Isaacman-VanWertz, G., Capps, S. L., Appel, K. W., Foroutan, H., Xu, L., Ng, N. L., and Goldstein, A. H.: Coupling of organic and inorganic aerosol systems and the effect on gas-particle partitioning in the southeastern US, *Atmos. Chem. Phys.*, 18, 357-370, doi:10.5194/acp-18-357-2018, 2018.
- Zuend, A.: Modelling the Thermodynamics of Mixed Organic-Inorganic Aerosols to Predict Water Activities and Phase Separations, Phd thesis, ETH Zurich, Zurich, Switzerland, doi:10.3929/ethz-a-005582922, <http://e-collection.ethbib.ethz.ch/view/eth:30457>, 2007.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2018-85>, 2018.

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