Response to Prof. Clegg

Comments are in black, responses in blue and the revised text in red.

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.

Response:

We thank Prof. Simon Clegg for the helpful comments.

First of all, we would like to apologize for the mistakes made in Eqs. 4 and 9 in the original manuscript that stem from errors originally made in the equation by van Boekel (2008) used in our reference. Since the mistakes are not included in either of the reviewer's comments or in the short comments by Prof. Clegg, we clarify this issue first before responding to the reviewers' comments in detail. The details of the mistakes are shown in Table 1 below.

Table 1. Correction of Eqs. 4 and 9 in the original manuscript

Eq. #	Original (with mistake)	Corrected [a]
4	$y_H = f_H \frac{\rho_{\mathrm{sln}}}{\rho_{\mathrm{sln}} + 0.001[M_s \sum c_i - \sum c_i M_i]}$	$y_H = f_H \frac{\rho_{solvent}}{\rho_{\mathrm{sln}} + 0.001[M_s \sum c_i - \sum c_i M_i]}$
9	$pH_x - pH_c = -\lg \frac{f_H x_H}{\mathrm{c_H} y_\mathrm{H}} = -\lg \frac{0.001Ms}{\rho_{\mathrm{sln}}} = 1.74 + \lg \rho_{\mathrm{sln}}$	$pH_x - pH_c = -\lg \frac{f_H x_H}{\mathrm{c_H} y_\mathrm{H}} = -\lg \frac{0.001Ms}{\rho_{solvent}} = 1.74 + \lg \rho_{solvent}$

[a] Since Dr. Zuend (Referee 1) suggested to use more genearl equations (considering solvent other than water), the corrected equations also do not direcely appear in the revised mansucript. Instead they have been shown in a more general form as: $f_H = y_H 1000 \frac{dm^3}{m^3} \frac{M_w}{\rho_0} \frac{c_H}{x_H}$ (6) and $pH_x - pH_c = \log 10 \frac{1000 dm^3/m^3 M_s c^0}{\rho_0}$ (12) in the revised manuscript.

In the original manuscript, we discussed the effect of the density of aerosol solution on the conversion between molality-based pH and molarity-based pH, which formed the major part of the *Results and Discussion* section. However, after correction, the conversion between molarity and molality-based pH actually does not depend on the density of the solution but does so on the density of the pure solvent. Therefore the orignal discussion is not valid anymore. Consequently, we have revised the mansucript significantly. The major revisons include (1) removing the original discussion regarding comparision between pH_m and pH_c; (2) incorporating the calculation of pH on differnet scales using multiple thermodynamci models; 3) using a gas+aerosol system instead of an aerosol only system to estimate pH; 4) discussing the differnce between different scales in a more general solvent instead of water only and (5) inclusion of a sub-section to discuss the general issues regarding aerosl acidity comparision across studies. Below are our detailed responses to each of the comments.

Response to general comment:

We agree that the clarity needs to be improved. We have revised the manuscript based on these and the other two reviewers' comments. We need to point out that we do not intend to provide a fundamental and comprehensive understanding of pH in this study. Instead, we have focused on the interconversion of pH between different scales as this is an important but often overlooked issue. Therefore, other issues regarding aerosol acidity which are well understood or well-practiced in the community are not discussed in the current study.

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

Response:

We agree with this point. We did not discuss the fundamentals of pH measurement or estimation in our original manuscript because we simply focused on the scale conversion.

(1) To make the manuscript more comprehensive and clearer, we have now added a relevant description in the introduction.

Revised text:

As per the International Union of Pure and Applied Chemistry (IUPAC), pH is defined as the negative log activity of hydrogen ions (https://goldbook.iupac.org/html/P/P04524.html). It is immeasurable because its definition involves a single ion quantity, the hydrogen ion activity (Baucke, 2002). Therefore, the value of pH is not an absolute one but depends on either how it is measured or the model used to calculate it. Especially, for aerosol pH, a commonly accepted measurement method is lacking despite some recent developments (Rindelaub et al., 2016), and it is usually calculated from thermodynamic models in practice.

(2) We have also added a section to discuss the general issues related to aerosol acidity comparison besides scale conversion.

Revised text:

3.2 General issues with pH comparison

It has been shown above that proper scale conversion has to be conducted when aerosol pH is compared. However, one should bear in mind that even with the same measured data and scale, pH calculated with different thermodynamic models or with different parameters may still not be comparable. Below, we briefly describe some of the general issues that need to be considered when aerosol acidity is compared across studies along with a summary of parameters used in the published studies in Table S1.

(1) Thermodynamic models like ISORROPIA-II and E-AIM can run in forward mode and reverse mode which result in significant difference (Song et al., 2018, Hennigan et al., 2015). It is recommended to use thermodynamic models in forward mode (gas plus aerosol as input) instead of reverse mode (aerosol only as input) which is highly sensitive to measurement uncertainties (Hennigan et al., 2015).

(2) Thermodynamic model can also be run in stable (liquid only) or metastable modes (both solid and liquid) which has not been specified in many studies (Table S1). Song et al. (2018) have shown that model calculations coupled with stable or metastable state assumptions can provide reasonable estimates of aerosol water pH. However, as pointed by Song et al. (2018), the studies using standard ISORROPIA-II (without code correction) running in stable mode have predicted unrealistic pH values of around 7 and should be reevaluated.

(3) The effect of non-volatile cations such as Na^+, Ca^{2+}, Mg^{2+} and K^+ on aerosol pH may also not be ignored. Although the effect of non-volatile cations on pH may be only 0.2-0.5 pH units, their impact on predicted partitioning of a semi-volatile species can be significant due to the highly non-linear response of NH_3-NH_4^+ or HNO_3-NO_3^- partitioning to pH (Guo et al., 2017). Since E-AIM cannot explicitly treat Ca^{2+}, Mg^{2+} and K^+ (unlike ISORROPIA-II and AIOMFAC), pH estimated using E-AIM may ignore Ca^{2+}, Mg^{2+} and K^+ (as shown in Table S1) or treat them as equivalent sodium (e.g. (Hennigan et al., 2015)). Even if all non-volatile cations are treated as Na^+, the predicted thermodynamic states can be biased due to the strong non-ideality of divalent ions as well as variations in water uptake characteristics between Na^+ salts and its counterparts (e.g., Fountoukis et al., 2009).

(4) Most studies so far have estimated pH of aerosols with only inorganic compounds. However, it has been reported that pH can be affected by organic compounds in several ways. Guo et al., (2015) have shown that the pH can be increased by 0.15 to 0.23 units when aerosol water associated with organic compounds is considered. Omission of the contribution of organic acids to H^+ has been estimated to increase the pH by 0.07±0.03 by Song et al., (2018) using E-AIM-IV. It has been shown recently that accounting for non-ideal mixing can modify the pH such that a fully interactive inorganic–organic system showed a pH roughly 0.7 units higher than that predicted using an inorganic only system by AIOMFAC (Pye et al., 2018).

2. The 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 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 NH3 or HNO3, 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.

Response:

We agree that thermodynamic models constrained by gas + aerosol measurements are more accurate than aerosol only systems that are highly sensitive to measurement uncertainties as reported by Hennigan et al. (2015). We have revised the calculation of aerosol pH in current study to gas + aerosol measurements (forward mode) in the revised manuscript.

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

Response:

Thanks. All equations have now been compiled in Table 3 in the revised manuscript along with sources in the notes. For the interconversion of activity between different scales (Eq. 3 and 4), the book by Robinson and Stokes (2002) has been cited.

Revised text:

Table 3. Summary of equations for the interconversion of concertation and activity coefficient based on different standard states.

Parameter	pH_x vs. pH_m	pH_m vs. pH_c	pH_x vs. pH_c
Activity coefficient [a]	$\gamma_H = f_H \frac{x_H}{m_H M_s}$ (4)	$\gamma_H = 1000 \frac{dm^3}{m^3} \frac{c_H y_H}{m_H \rho_0}$ (5)	$f_H = y_H 1000 \frac{dm^3}{m^3} \frac{M_w}{\rho_0} \frac{c_H}{x_H}$ (6)
Concentration [b]	$x_H = \frac{m_H}{\sum \nu_i m_i + \frac{1}{M_s}}$ (7)	$c_H = \frac{m_H}{\frac{\sum \nu_i m_i M_i + 1}{\rho_{sln}}}$ (8)	$x_H = \frac{M_s c_H}{M_s \sum c_i + 0.001 \frac{m^3}{dm^3} \rho_{sln} - \sum c_i M_i}$ (9)
pH [c]	$pH_x - pH_m = -\log 10[M_s m^0]$ (10)	$pH_m - pH_c = -\log 10 \frac{c^0 1000 dm^3/m^3}{m^0 \rho_0}$ (11)	$pH_x - pH_c = \log 10 \frac{1000 dm^3/m^3 M_s c^0}{\rho_0}$ (12)

Note: [a] Source of Eqs. (4)-(5) are Robinson and Stokes (2002) and the source of Eq. (6) is Zünd (2007). The details of derivation of Eqs. (4)-(6) are shown in Robinson and Stokes (2002) and Zünd (2007). [b] Eqs. (7)-(9) are based on the definition of each parameter. [c] Eqs. (10)-(12) are derived from Eqs (4)-(6) and (7)-(9) for each standard state.

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.

Response:

We agree that the correlation between pH on the molarity scale and on the other scales is to be expected solely based on theory. However, the discussion of field data here is still helpful since it shows that the conversion is related to the property of each sample. We can demonstrate how the conversion will be affected by the property of samples. For example, we observe a different trend of *pH_m* and *pH_c* due to different properties of the aerosol (when activity coefficient is assumed as unity in the revised manuscript). Therefore, we have kept the discussion in our revised manuscript (but corrected the mistakes). But as also pointed out by the other reviewers, our original statement in the abstract is not proper regarding the role of field data in this study. It has been revised accordingly in the abstract.

Revised text:

This study attempts to address this issue by comparing $PM_{2.5}$ aerosol pH based on different scales (molarity, molality and mole fraction) on the basis of theoretical considerations followed with a set of field data from Guangzhou, China as an example.

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+ content of the aerosol might remain more or less the same.

Response:

We agree that if H^+ remains the same, pH will fluctuate with the diurnal cycle mainly due to the change of RH. However, this point is beyond the scope of the current study, and has been discussed extensively in other studies. (e.g. (Guo et al., 2015;Jia et al., 2018)) Therefore this is not discussed in current study.

Reference

Baucke, F. G.: New IUPAC recommendations on the measurement of pH – background and essentials, Anal. Bioanal. Chem., 374, 772-777, 10.1007/s00216-002-1523-4, 2002.

Fountoukis, C., Nenes, A., Sullivan, A., Weber, R., Van Reken, T., Fischer, M., Matías, E., Moya, M., Farmer, D., and Cohen, R. C.: Thermodynamic characterization of Mexico City aerosol during MILAGRO 2006, Atmos. Chem. Phys., 9, 2141-2156, 10.5194/acp-9-2141-2009, 2009.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite Jr, J. R., Carlton, A. G., Lee, S. H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211-5228, 10.5194/acp-15-5211-2015, 2015.

Guo, H., Nenes, A., and Weber, R. J.: The underappreciated role of nonvolatile cations on aerosol ammonium-sulfate molar ratios, Atmos. Chem. Phys. Discuss., 2017, 1-19, 10.5194/acp-2017-737, 2017.

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.

Jia, S., Sarkar, S., Zhang, Q., Wang, X., Wu, L., Chen, W., Huang, M., Zhou, S., Zhang, J., Yuan, L., and Yang, L.: Characterization of diurnal variations of PM2.5 acidity using an open thermodynamic system: A case study of Guangzhou, China, Chemosphere, 202, 677-685, https://doi.org/10.1016/j.chemosphere.2018.03.127, 2018.

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, 10.5194/acp-18-357-2018, 2018.

Rindelaub, J. D., Craig, R. L., Nandy, L., Bondy, A. L., Dutcher, C. S., Shepson, P. B., and Ault, A. P.: Direct Measurement of pH in Individual Particles via Raman Microspectroscopy and Variation in Acidity with Relative Humidity, The Journal of Physical Chemistry A, 120, 911-917, 10.1021/acs.jpca.5b12699, 2016.

Robinson, R. A., and Stokes, R. H.: Electrolyte solutions, Courier Corporation, 2002.

Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmos. Chem. Phys., 18, 7423-7438, 10.5194/acp-18-7423-2018, 2018.

van Boekel, M. A. J. S.: Kinetic Modeling of Reactions In Foods, CRC Press, New York, 2008.

Zünd, A.: Modelling the thermodynamics of mixed organic-inorganic aerosols to predict water activities and phase separations, ETH Zurich, 2007.