Response to Dr. Zuend

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

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 important 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) a discussion of the general issues with pH estimation of field aerosol samples.

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.

Response:

We thank Dr. Zuend for the constructive comments on our manuscript. We also thank him for agreeing with the importance of pH interconversion between different scales, which is the main focus of the current study.

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all, we would like to apologize for the mistakes made in Eqs. 4 and 9 in the original manuscript that stem from errors originally made in the equation by van Boekel (2008) used in our reference.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 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 $pH_x - pH_c = \log10\frac{1000dm^3/m^3 M_s c^0}{\rho_0}$ (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 for a generalized solvent system instead of only water 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 comments:

We have addressed Prof. Simon Clegg's comments point by point. A major revision of the manuscript has been conducted according to all comments. Especially, we have now revised the method to estimate aerosol acidity using a gas + aerosol system instead of the aerosol only system utilized in original version. We have also added an entire section (Section 3.2) in the revised manuscript to summarize the general issues for pH comparison across studies. A detailed response to each of the Reviewer's comments is listed below:

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).

   Response:

   We agree that the description here is inappropriate. We have deleted the concerned phrase in the description.

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.

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.

   Response:
   We agree with the reviewer's point that the relationship between pH_x and pH_m is from theory. The field data shown in this study is only an example of the application of the theory. The text has been revised as below.

   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. The three most widely used thermodynamic models (E-AIM-IV, ISORROPIA-II, and AIOMFAC) are employed for the comparison. It has been shown theoretically that the difference between pH_x (mole fraction based) and pH_m (molality based) is always a constant (1.74, when the solvent is water) within a thermodynamic model regardless of aerosol property.

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.

   Response:
   We agree that our original description was vague. In the revised manuscript, we have (1) added the definition of both strong and free acidity; and (2) specified the drawbacks of these parameters.

   Revised text:
   The most accurate parameter to characterize aerosol acidity is considered to be pH. The other parameters often used as proxies of aerosol acidity do not offer information on how acidic the particles are when they are present as aqueous droplets (Pathak et al., 2004). For example, strong acidity (defined as nmol of total H^+ per m^3 of air measured in water extracts of particles using the USEPA Reference Method (USEPA, 1992)) and ion charge balance are unable to

distinguish between free and undissociated H^+ (e.g., protons associated with bisulfate) (Pathak et al., 2004;Hennigan et al., 2015). Ammonium-to-sulfate ratio and cation-to-anion ratio are unable to provide any measure of the degree of aerosol acidity even qualitatively (Hennigan et al., 2015). And lastly, free acidity (defined as the actual concentration of free H^+ per m^3 of air, not including the H^+ released from bisulfate ions in aqueous extracts) represents the quantity of H^+ in a specific volume of air while neglecting the concentration of H^+ in liquid water (Pathak et al., 2004).

4. Equation (1): Define the meaning of “lg”.

   Response:
   We have revised lg to log10 to make it clearer throughout the manuscript.

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 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 $\ln[\gamma_i] = \ln[f_i^*] + \ln[\frac{x_i}{m_i M_w}]$ and f^* 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 $pH_x - pH_m = -\log10[m^0 M_w]$, 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).

   Response:
   We thank the Reviewer for pointing out this issue.
   1) The factor of 1000 in the original equation was for the conversion of kg to g. The unit of molecular mass was g/mol in the original manuscript. We have now revised the unit of molecular mass to the SI unit of kg mol^{-1} as suggested. All other units in the manuscript are SI units except molarity (mol dm^{-3}). So 1000 $\frac{dm^3}{m^3}$ will be still shown when molarity of ion is involved.

2) We agree that the original Eq.2 is only valid when water is the only solvent. We have now cited Eq. 2.59 in the PhD thesis by Zünd (2007) and Robinson and Stokes (2002) to show the conversion (1) between γ_H and f_H (Eq. 4); (2) between γ_H and y_H (Eq. 4); and (3) between f_H and y_H in a more general form as below.

Revised equations:

$$\gamma_H = f_H \frac{x_H}{m_H M_s} \tag{4}$$

$$\gamma_{\mathrm{H}} = 1000 \frac{dm^3}{m^3} \frac{c_H y_{\mathrm{H}}}{m_H \rho_0} \tag{5}$$

$$f_H = y_H 1000 \frac{dm^3}{m^3} \frac{M_w}{\rho_0} \frac{c_H}{x_H} \tag{6}$$

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

Response:

We agree with the Reviewer's point. This comment has been handled in combination with #10. We have now added Section 3.2 to discuss the general issues when comparing aerosol acidity across studies (including the difference in models, forward vs. reverse, stable vs. metastable, effect of non-volatile cations and effect of organic compounds).

Revised text:

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).

7. Equation (4): Similar to above comment. A general expression should be shown, with proper use of units.

   Response:
   Thanks. Equation 4 has been revised accordingly (Eq. 6 in the revised manuscript).

   Revised equations:

$$f_H = y_H 1000 \frac{dm^3}{m^3} \frac{M_w}{\rho_0} \frac{c_H}{x_H} \qquad (6)$$

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.

   Response:
   We assume that the Reviewer actually meant page 5 in the original manuscript. This sentence has been deleted in the revised manuscript.

9. Page 4, line 13: "This is supported by our field data". Again, this is a circular argument. The $\mathrm{pH}_x - \mathrm{pH}_m$ 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).

Response:

We assume the Reviewer actually meant page 5 in the original manuscript. We agree with the reviewer's point and have revised the text accordingly. As we clarified in the beginning of our response, other revisions have also been made and the final revised text is as below.

Revised text:

The difference of pH_x and pH_m is $\log 10 M_w m^0$ (according to Eq. 10) which is only determined by the molecular weight of the solvent. When water is the only solvent in the system (molecular weight of 0.018 kg mol^{-1}), pH_x - pH_m is fixed at 1.74 within the model regardless of aerosol property or the model (as in this study).

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 pHx, pHc and pHm 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 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.

Response:

We agree with the reviewer's point. This comment has been handled in combination with #6. We have now added Section 3.2 to discuss the general issues when comparing aerosol acidity across studies (including difference in models, forward vs. reverse, stable vs. metastable, effect of non-volatile cations and effect of organic compounds). The revised text is shown in the response to comment #6.

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.

Response:

Table 1 has been revised thoroughly. The reference state of activity and activity coefficient have been added in the definition of activity. The revised Table 1 is shown below.

Revised table:

Table 1. List of abbreviations.

Abbreviation	Definition
ac_H	activity of hydrogen ions with standard state of the hypothetical ideal aqueous solution of unit molarity and reference state of infinite dilute solution (dimensionless)
am_H	activity of hydrogen ions with standard state of the hypothetical ideal aqueous solution of unit molality and reference state of infinite dilute solution (dimensionless)
ax_H	activity of hydrogen ions with standard state of the hypothetical pure H^+ solution and reference state of infinite dilute solution (dimensionless)
c^0	unit molarity (1 mol dm^{-3} solution)
c_H	molarity of hydrogen ion (mol dm^{-3} solution)
c_i	molarity of solute species *i* (mol dm^{-3} solution)
f_H	mole fraction scale activity coefficient
m^0	unit molality (1 mol kg^{-1} solvent)
m_H	molality of hydrogen ions (mol kg^{-1} solvent)
m_i	molality of solute species *i* (mol kg^{-1})
M_i	molecular mass of solute species *i* (kg mol^{-1})
M_s	molecular weight of single solvent or averaged molecular weight for multiple solvents (kg mol^{-1})
pH_c	molarity based pH (dimensionless)
pH_m	molality based pH (dimensionless)
pH_x	mole fraction based pH (dimensionless)
x_H	mole fraction of hydrogen ions (dimensionless, mol H^+ in total moles)
y_H	molarity scale activity coefficient
γ_H	molality scale activity coefficient
ρ_0	density of pure solvent (kg m^{-3})
ρ_{sln}	density of hygroscopic aerosol solution (kg m^{-3})

Reference

USEPA, 1992. Determination of strong acidity of atmospheric fine-particles (<2.5 μm) using annular denuder technology. Atmospheric Research and Exposure Assessment Laboratory, EPA Report No. EPA/600/R-93/037, Washington, DC.

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