Response to Anonymous Referee #2

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

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.

Response:

We thank the Reviewer for the helpful comments and suggestions, and also for agreeing with the importance of pH interconversion between different scales, which is the main focus of 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all, we would like to apologize for the mistakes made in Eqs. 4 and 9 in the original manuscript that stem from errors originally made in the equation by van Boekel (2008) used in our reference.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 (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 diffence 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 comparison across studies. Below are our detailed responses to each of the comments.

1. 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.

   Response:
   We agree with the Reviewer's point. The differences between *pHx*, *pHc* and *pHm* are expected from their definitions. The field data shown in this study is actually an example to show the conversion between different scales. The following revision has been done.

   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. 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.

   Response:
   We agree with the Reviewer's point. Following the reviewer's suggestion, we have now shown the calculations with all the 3 models. We have also described the parameters that can be

obtained from the model outputs as well as how other parameters are estimated. The revised text is shown below.

Revised text:

Table S1. A summary of estimation methods of parameters for pH calculation based on different standard states.

Parameters	E-AIM-IV	ISORROPIA-II	AIOMFAC
Mole fraction			
x_H	output	Eq. (7)	output
f_H	output	1[a]	Eq. (4)
Molality			
m_H	output	output	output
γ_H	Eq. (4)	1[a]	output
Molarity			
c_H	Eq. (8) [b]	Eq. (8) [b]	Eq. (8) [b]
y_H	Eq. (6)	1[a]	Eq. (6)

Note: [a] activity coefficient is assumed to be 1; [b] the density of aerosol solution is based on the result from E-AIM-IV.

3. 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 the1:1 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.

Response:

We thank the reviewer for pointing out this important issue.

(1) We have revised the method to calculate aerosol pH from the forward mode, which is of lower uncertainty, instead of reverse mode.

(2) We acknowledge that the difference between pH_m and pH_c may not be large compared with uncertainties from measurement errors. Therefore, we have added the following text in the discussion.

Revised text:

Given that the uncertainty of pH calculation due to measurement errors can be as high as 14% (Guo et al., 2015), the difference of pH_x and pH_m can simply fall within the range of measurement errors. However, the bias between pH_x and pH_m can be considered to be a systematic one, which needs to be addressed for the sake of comprehensiveness in theoretical analysis. Moreover, even small biases in pH may imply substantial partitioning errors for semivolatile species like ammonium, nitrate, chloride, and even organic acids (Guo et al., 2017).

4. As Andreas Zuend points out, it would be nice to mention the possible differences be- tween 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)

Response:

We agree with the Reviewer's point. We have addressed this issue in the revised manuscript.

(1) Following the reviewer's suggestion, we have shown the comparison of pH calculated using different thermodynamic models in the revised manuscript as below followed by a comparison of the three models.

Table 3. Calculated concentrations, activity coefficient of H^+ and pH for the three thermodynamic models. [a]

	E-AIM-IV	ISORROPIA-II	AIOMFAC
Molar fraction			
x_H	$1.07\times10^{-4}\pm1.28\times10^{-4}$ $(2.17\times10^{-5}$–$9.49\times10^{-4})$	$3.49\times10^{-5}\pm4.80\times10^{-5}$ $(4.59\times10^{-6}$–$3.69\times10^{-4})$	$2.71\times10^{-4}\pm3.36\times10^{-4}$ $(4.56\times10^{-5}$–$2.46\times10^{-3})$
f_H	0.74±0.25 (0.43–1.97)	1 [b]	0.27±0.10 (0.15–0.79)
pH_x	4.26±0.28 (3.16–4.82)	4.63±0.36 (3.43–5.34)	4.31±0.27 (3.24–4.86)
Molality			
m_H	$7.80\times10^{-3}\pm9.52\times10^{-3}$ $(1.50\times10^{-3}$–$7.03\times10^{-2})$	$2.60\times10^{-3}\pm3.64\times10^{-3}$ $(3.18\times10^{-4}$–$2.80\times10^{-2})$	$1.98\times10^{-2}\pm2.50\times10^{-2}$ $(3.14\times10^{-3}$–$1.82\times10^{-1})$
γ_H	0.57±0.19 (0.35–1.54)	1 [b]	0.21±0.08 (0.12–0.62)
pH_m	2.52±0.28 (1.41–3.07)	2.77±0.36 (1.55–3.50)	2.56±0.27 (1.50–3.11)
Molarity			
c_H	$5.56\times10^{-3}\pm6.59\times10^{-3}$ $(1.14\times10^{-3}$–$4.89\times10^{-2})$	$1.73\times10^{-3}\pm2.35\times10^{-3}$ $(2.38\times10^{-4}$–$1.80\times10^{-2})$	$1.43\times10^{-2}\pm1.76\times10^{-2}$ $(2.48\times10^{-3}$–$1.30\times10^{-1})$
y_H	0.79±0.26 (0.45–2.04)	1 [b]	0.28±0.10 (0.16–0.75)
pH_c	2.52±0.28 (1.41–3.07)	2.94±0.35 (1.75–3.62)	2.56±0.27 (1.50–3.11)

Notes: [a] All parameters are shown as average ± standard deviation with the range in bracket except for [b] activity coefficient of ISORROPIA-II which is assumed to be 1.

The results of pH calculated based on different standard states with the three thermodynamic models are shown in Table 3. Overall, there are slight difference between pH calculated using different models. Taking pH_m as an example, the averaged pH_m calculated by ISORROPIA-II (2.77±0.36) is 0.25 pH unit higher than that calculated by E-AIM-IV (2.52±0.28), which is consistent with the result reported by Song et al. (2018) and Liu et al. (2017). The pH_m calculated by AIOMFAC (2.56±0.27) is closer to that calculated with E-AIM-IV (2.52±0.28). It is worthwhile to note that the activity of H^+ calculated by E-AIM-IV (0.57±0.19) is 2.7 times higher than that calculated by AIOMFAC (0.21±0.08) while the molality of H^+ calculated using AIOMFAC ($1.98\times10^{-2}\pm2.50\times10^{-2}$) is 2.5 times higher than that calculated by E-AIM-IV ($7.80\times10^{-3}\pm9.52\times10^{-3}$) although the resultant pH_m is similar.

The difference in the calculated pH between different studies is due to differences in both concentration and activity coefficient. For example, a unity activity coefficient of H^+ is assumed for ISORROPIA-II for pH calculation even though the non-ideal interaction of H^+ with all other ions in solution is explicitly considered by the Kusik-Meisner and Bromely formulations in ISORROPIA-II (Fountoukis and Nenes, 2007). The exact factors contributing to the difference in pH remains unclear, and is not the focus of current study. The models may differ in many ways such as their methods for calculating the activity coefficients for H^+ and other ionic species, and in estimating aerosol water contents (Song et al., 2018).

(2) We have added a full section to discuss the general issue in pH comparison between different studies in the revised manuscript.

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).

Minor comments:

1. 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.

Response:

Thanks for pointing out the issue. We have deleted the concerned phrase in the description and elsewhere in the revised manuscript.

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. 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.

Response:

We thank the reviewer pointing out the issue. The two equations have been changed accordingly. We have also explained that molarity means mol dm^{-3} solution while molality means mol kg^{-1} solvent in Table 1.

Revise equations:

$$pH_c = -\log10(a_{c_H}) = -\log10(\frac{y_H c_H}{c^o}) \qquad (2)$$

$$pH_m = -\log 10(a_{m_H}) = -\log 10(\frac{\gamma_H m_H}{m^o}) \quad (3)$$

Explanation of parameters (in Table 1):

m_H	molality of hydrogen ions (mol kg^{-1} solvent)
c_H	molarity of hydrogen ion (mol dm^{-3} solution)

3. Proper reference as suggested by Simon Clegg.

Response:

We have now added the sources of all equations as suggested by Prof. Simon Clegg in Table 2.

Revised text:

Table 2. 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.

Reference

Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O aerosols, Atmos. Chem. Phys., 7, 4639-4659, 10.5194/acp-7-4639-2007, 2007.

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.

Liu, M., Yu, S., Tian, Z., Zhenying, X., Caiqing, Y., Mei, Z., Zhijun, W., Min, H., Yusheng, W., and Tong, Z.: Fine particle pH during severe haze episodes in northern China, Geophys. Res. Lett., 44, 5213-5221, doi:10.1002/2017GL073210, 2017.

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.

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.