

Interactive comment on “Fine particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models” by Shaojie Song et al.

A. Nenes

nenes@eas.gatech.edu

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Comment on Song et al. (by A.Nenes, H.Guo, A.Russell and R.Weber)

We would like to commend Song et al. for their extensive analysis that goes deep into the model code and data. The importance of understanding aerosol pH is key to understanding of aerosol growth and impacts, as has been demonstrated in a growing body of literature. This literature, however, also exposes knowledge gaps. Following are some comments and thoughts about the analysis that in our opinion require attention, especially on the impact and importance of the H^+ activity coefficient. Addressing these points, may require considerable rewriting and refocusing of the paper, but we

C1

feel it will eventually substantially enhance the contribution.

Algorithm changes to ISORROPIA-II routines.

We would like to thank the authors for their very detailed explanation of the pH calculation issue, and the resolution provided. This clearly shows the value of having open source codes so that they are continuously used and tested by the community. The alternative approach in the standard code was used in the routines identified, because loss in precision in calculating the SQRT function (at low concentrations of aerosol precursors and when solid precipitates formed, e.g., NH_4Cl), made partitioning calculations at times inaccurate and noisy. Although the alternative approach captured partitioning, pH was clearly not, so adopting the standard calculation approach used in the subcases with higher RH values is appropriate; however, provision still needs to be shown to avoid loss of precision (e.g., Taylor expansion approximations or renormalization instead of SQRT). We will address this in the upcoming version of ISORROPIA-II.

Application of thermodynamic models when interpreting data.

We were very pleased to see that the analysis of Beijing data carried out here fully supports our prior work on how to use observational data to constrain pH, namely: *i*) avoiding usage of molar ratios and ion balances as pH proxies (Guo et al., 2015; Hennigan et al., 2015; Guo et al., 2016; Weber et al., 2016; Guo et al., 2017b), and, *ii*) the large pH errors that can result when aerosol-only concentrations from observations are used in open-system thermodynamic calculations (i.e., “reverse mode” calculations that are not subject to a global constraint of mass balance (Pilinis et al., 2000; Hennigan et al., 2015)). It should also be noted that the secondary effect of water-soluble organics on aerosol pH is also consistent with the recent work of Pye et al. (2017).

One conclusion that the authors come to is that the pH calculations are not sensitive to the assumption of metastable and stable state. As presented, this can be misinterpreted by the reader that partitioning evaluations are not valuable for constraining aerosol pH. Partitioning calculations can sufficiently constrain pH, but only when

C2

predictions of aerosol water and semivolatile partitioning (of $\text{NH}_3\text{-NH}_4^+$, $\text{HNO}_3\text{-NO}_3^-$, and HCl-Cl^- if possible) are reproduced by observations (as shown in e.g., Guo et al. (2015) and other studies) – and a sufficient fraction of the partitioned aerosol species is associated with the aqueous phase. When aerosol water measurements are lacking or too uncertain, then showing that when **aqueous phase semivolatile partitioning by itself** (i.e., provided by the metastable solution) reproduces aerosol observations, aerosol pH is sufficiently constrained. **The pH values calculated for the metastable solution, for cases where partitioning is consistent with observations, provide the most plausible estimates of acidity.** pH values for the stable solution, especially when the liquid water content becomes very small (hence aqueous-phase partitioning a secondary contribution to the total partitioning), are subject to considerably more uncertainty – even if the pH corresponding to the metastable and stable solutions agree.

Activity coefficient discussion

The authors extensively comment on the usage of $\gamma_{\text{H}^+} = 1$ in some of the calculations behind ISORROPIA-II. In fact, the assumption that $\gamma_{\text{H}^+} = 1$ is thought to be a major source of pH discrepancy between ISORROPIA and E-AIM (it's even stated in the abstract). The data presented does not really support this for the following reasons:

1. γ_{H^+} varies by ± 0.2 units over the ionic strengths considered (0-20), Figure 2b, while pH differences between the models are typically larger than 0.2 units.
2. The correlation of pH discrepancy between ISORROPIA-II (as calculated with the formula of Guo et al. (2015)) and E-AIM with γ_{H^+} *does not* indicate a causal relationship.
3. If $\gamma_{\text{H}^+} = 1$ was indeed the reason for the discrepancy, then at an ionic strength of ~ 20 , when $\gamma_{\text{H}^+} \sim 1$, the pH discrepancy between ISORROPIA and E-AIM should be zero (Figure 2b). This is not the case at all.

C3

Considering points 1, 2, 3 together, one can actually conclude that about 0.2 pH units discrepancy between ISORROPIA-II and E-AIM may arise from the assumption of $\gamma_{\text{H}^+} = 1$ for the RH (ionic strength) range considered, while the rest of the discrepancy may be related to the predicted concentration of H^+ . This may even suggest that $\gamma_{\text{H}^+} = 1$ is not a leading cause of discrepancy. In support of this, we find it very interesting that when one compares the γ_{H^+} values from E-AIM (Figure 2c) and from AIOMFAC (Figure S6), $\log(\gamma_{\text{H}^+})$ differs by about 0.6 units at an ionic strength of 20 M (E-AIM gives 0.1 and AIOMFAC gives -0.5; note the -0.6 difference in $\log(\gamma_{\text{H}^+})$ means +0.6 pH compared to E-AIM), which seems to be consistent with the 0.6 higher pH comparing ISORROPIA to E-AIM at the same ionic strength. Could it just be then that the calculation of γ_{H^+} by E-AIM is more uncertain than implied? The Beijing haze polluted period has an ionic strength close to 40 M, which brings γ_{H^+} close to 1 according to Figure S6. Assuming $\gamma_{\text{H}^+} = 1$ to diagnose pH from ISORROPIA (single point) translates to an uncertainty of less than 0.5 pH units over a large range of RH or ionic strength (Figure S6).

There is a lack of discussion on the effects of the other ionic species as sources of discrepancy between E-AIM and ISORROPIA-II, which is surprising, given that E-AIM uses the single ion activity approach, while ISORROPIA uses mean activity coefficients of ion pairs. Predictions from the two types of activity coefficient models do show important differences (e.g., Kim et al., 1993). The configuration used in ISORROPIA-II (Kusik-Meisner binary activity coefficients with the Bromley mixing rule for multicomponent aerosol) has been shown to provide stable solutions for ionic strengths that far exceed 30, the limit where Pitzer coefficients have been shown to work well (Kim et al., 1993). The latter point of course is quite relevant for the discussion raised by the authors concerning the applicability of the activity coefficient models used by ISORROPIA-II and E-AIM when applied to the high ionic strengths corresponding to RH below 70%.

Given the above, unless a thorough analysis of how all the activity coefficients,

C4

water uptake and equilibrium constants contribute to the pH differences between ISORROPIA-II and E-AIM, one cannot really state how much uncertainty in pH arises from the assumption of $\gamma_{H^+} = 1$, though it appears to be bounded and much less than the difference in the predicted pH's between the two models. Perhaps it would be better to just plot the predicted particle phase fractions ($\varepsilon(\text{NH}_4^+)$ and $\varepsilon(\text{NO}_3^-)$) as a function of pH) by each model and compare them against the data (following the approach of Guo et al., 2017a). Then one will have a better sense of the pH uncertainty (given by the range between models) for a given value of (observed) ε .

Specific (but important) comments

- The authors note early in the manuscript that the discrepancy in calculated pH when assuming $\gamma_{H^+} = 1$ can be multiple units. This is not supported by the supplementary figure (γ_{H^+} from AIOMFAC), where for an ionic strength range of 0-100, $\log \gamma_{H^+}$ (hence the contribution of assuming $\gamma_{H^+} = 1$ to pH discrepancy) varies within 1 unit. This has always been, by the way, our view – so it is nice to see this confirmed by the analysis presented!
- Also noted throughout is that pH is overestimated when assuming $\gamma_{H^+} = 1$. This is not always true as well; as noted by the supplementary figure (γ_{H^+} from AIOMFAC), pH can be underestimated or overestimated by assuming $\gamma_{H^+} = 1$, but not more than half a unit. In fact, the average pH estimated by ISORROPIA-II is *actually lower* than that reported for E-AIM (4.2 vs 5.4, for ISORROPIA-II vs E-AIM respectively) inconsistent with pH trends stated above.
- In ISORROPIA-II, the non-ideal interactions of H^+ with all the ions in solution (especially NO_3 , Cl , HSO_4 , SO_4) is explicitly considered by the Kusik-Meisner and Bromely formulations. $\gamma_{H^+} = 1$ is only invoked when the single ion activity is required. This is not sufficiently noted in the text.
- The authors understandably treat NVC (i.e. Ca, Mg, K, Na) as equivalent sodium, C5

because E-AIM cannot explicitly treat Ca, Mg and K. The impact of this assumption can lead to important differences in the predicted thermodynamic state, owing to the strong nonideality of divalent ions and different water uptake characteristics of sodium salts vs. their other counterparts (e.g., Fountoukis et al., 2009).

- What constitutes a “large/important” and “small/minor” difference in pH depends on the context in which the pH is used. Constraining “absolute” pH for ambient aerosol to within less than 0.5 units may prove to be extremely challenging (e.g., the difference in $\log \gamma_{H^+}$ between E-AIM and AIOMFAC, the effects of organics on activity and water uptake and so on); so it may most likely be necessary to use a consistent pH calculation method and thermodynamic model when comparing aerosol acidities between models and/or observations.
- The authors caution about the predictions of ISORROPIA-II in metastable mode (for RH below the mutual deliquescence point) owing to the large ionic strengths of the solutions. Although we agree the ionic strengths are high, literature supports that the activity coefficient models used in ISORROPIA-II are stable for ionic strengths above 30, a situation that is also not the case for the Pitzer method (Kim et al., 1993).

In closing, we very much appreciate the analysis and it demonstrates an increasing sophistication of which the community is both understanding and discussing the thermodynamics of aerosols and the important topic of aerosol acidity. We also hope that the comments provided here add insight that will considerably strengthen the paper, and provide ideas for future work on the important topic of aerosol acidity.

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C7

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C8