

Title: Impact of non-ideality on reconstructing spatial and temporal variations of aerosol acidity with multiphase buffer theory

- 5 We thank the referees for their valuable and constructive comments/suggestions on our manuscript. We have revised the manuscript accordingly and please find our point-to-point responses below.

Comments by Referee Yunhong Zhang:

General Comments:

- 10 *This paper is significant work to understand the total contribution of NH₃ on the acid-base equilibrium of condensed phase of atmospheric particles. Especially for the case of concentrated aqueous phase at low RH, non-ideality correction factors are explored. This paper should be published with considering the two comments.*

Detailed Comments:

- 15 *(1) when it gives the definition of pK_{a,NH₃*i}*, physical significant of pK_{a,NH₃*i should be more clear if the authors provide more description, i.e., both condensed chemical compositions and NH₃ content in gas phase determined the pH when chemical reactions in the particles change the pH of condensed phase, or other more better description easy understanding for readers.}

Responses:

- 20 Following the referee's suggestions, we've further clarified the meaning of $K_{a,NH_3}^{*,i}$ as (see Line 87-93 in the revised manuscript):

“For typical ambient conditions when AWC varies between 1 to 1000 $\mu\text{g m}^{-3}$, the $[\text{NH}_3(\text{g})]$ is usually 10^5 to 10^8 times larger than $[\text{NH}_3(\text{aq})]$, and the above equation can be simplified into:

$$K_{a,NH_3}^{*,i} = \frac{[\text{H}^+(\text{aq})][\text{NH}_3(\text{g})]}{[\text{NH}_4^+(\text{aq})]} = K_{a,NH_3} \frac{\rho_w}{H_{NH_3} R T AWC} \quad (1a)$$

- 25 And taking negative lognormal on both sides, we have pH is related to $\text{p}K_{a,NH_3}^{*,i}$ (i.e., $-\log K_{a,NH_3}^{*,i}$) as (Zheng et al., 2020):

$$\text{pH} = \text{p}K_{\text{a,NH}_3}^{*,i} + \log \frac{[\text{NH}_3(\text{g})]}{[\text{NH}_4^+(\text{aq})]}$$

The multiphase buffer capacity of $\text{NH}_3/\text{NH}_4^+$ pair reached its local maximum when $\text{pH} = \text{p}K_{\text{a,NH}_3}^{*,i}$, namely when $[\text{NH}_3(\text{g})] = [\text{NH}_4^+(\text{aq})]$. At given AWC and T , $K_{\text{a,NH}_3}^{*,i}$ is constant.”

- 5 (2). line 80 in the equation, $[\text{NH}_3(\text{g})]$ is equivalent molarity of gaseous NH_3 in solution, its unit is molar.Kg-1. In this case $K_{\text{a,NH}_3}^{*,i} = K_{\text{a,NH}_3} (1 + 1/(H_{\text{NH}_3} R T AWC))$, water density should not appear in the equation. The same is in 8a and 8b.

Responses:

Many thanks. We double checked the related part and our original equations are correct. The confusion
10 may be potentially caused by the definition of AWC. In this study, AWC is represented in the unit of (μg water) / (m^3 air), instead of the water volume mixing ratio, w_v , of (L water)/(L air). With the current units applied, the term $H_{\text{NH}_3} R T$ has the unit of unity, and ρ_w is needed to convert the AWC to w_v .

To avoid such confusions, we’ve further clarified the units in the relevant equations as (see Line 80-86 in the revised manuscript):

- 15 “The multiphase effective acid dissociation constant of NH_3 under ideal conditions, $K_{\text{a,NH}_3}^{*,i}$, depends only on AWC and temperature as (Zheng et al., 2020):

$$K_{\text{a,NH}_3}^{*,i} = \frac{[\text{H}^+(\text{aq})]([\text{NH}_3(\text{aq})] + [\text{NH}_3(\text{g})])}{[\text{NH}_4^+(\text{aq})]} = K_{\text{a,NH}_3} \left(1 + \frac{\rho_w}{H_{\text{NH}_3} R T AWC} \right)$$

where AWC is in $\mu\text{g m}^{-3}$, and is mainly determined by air particulate matter concentrations and RH. The ρ_w
20 is water density in $\mu\text{g m}^{-3}$, and AWC/ρ_w represents the aerosol water volume mixing ratio in the air in (m^3 water) / (m^3 air). $[\text{NH}_3(\text{g})]$ represents equivalent molality (in mol kg^{-1}) of gaseous NH_3 in solution (see details in Zheng et al. (2020)). The H_{NH_3} is Henry’s law constant of NH_3 in $\text{mol L}^{-1} \text{atm}^{-1}$, R is the gas constant of $0.08205 \text{ atm L mol}^{-1} \text{K}^{-1}$, and T is temperature in K.”