

Interactive comment on “Amines are likely to enhance neutral and ion-induced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia” by T. Kurtén et al.

Anonymous Referee #1

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The manuscript describes cluster thermodynamics relevant to gas phase atmospheric nucleation obtained from ab initio molecular structure calculations. In this manuscript authors further build upon their prior excellent work to provide novel and useful information to the nucleation community. The manuscript is acceptable for publication in ACP after addressing the issues highlighted below.

1. The title as well as statements in the abstract and conclusions relate to relative enhancements to the sulfuric acid-water nucleation. However, cluster energetics are only calculated for sulfuric acid-ammonia and sulfuric acid-amine systems, not for the full water-containing ternary systems. Therefore, the relative contributions of ammonia

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and amines to the sulfuric acid-water system can only be implied here. The addition of water molecules (perhaps 2-8 waters at equilibrium conditions) is very likely to change the bonding schemes shown in Fig 1-3. The relative thermodynamic values listed in Tables 2 & 4 are also likely to change somewhat for the corresponding clusters in the ternary system. In particular, the advantage of the more highly-substituted amine neutral clusters due to their higher stabilities may be offset upon addition of water because those clusters are probably less hydrophilic than e.g., H₂SO₄-NH₃ or H₂SO₄-CH₃NH₂. Please address this point in the discussion section, and add an appropriate statement to the conclusions.

2. The authors discuss how low amine concentrations on the order of 1 pptv affect the production rate of sulfuric acid-amine clusters. Even with collision rates between the two reactants of 10^4 - 10^5 cm³ s⁻¹, association reaction lifetimes would be 100's of seconds, significantly long when compared to timescales of nucleation. Actual reaction lifetimes would likely be even higher since reaction rates would not be as fast as the hard sphere collision rate, especially for the neutral clusters. Using these estimations, a significant kinetic limitation to growth can be expected under most atmospheric conditions except for highly polluted continental air or near source regions. Please revise or add statements to the discussion regarding these points.

3. Although equation 1 can be written more generally, it is presented in a form that implies chemical equilibrium. In an equilibrium case, the concentration ratios from equation 1 will still apply even if the reactant becomes highly depleted. As presented, the concentration ratios in Table 5 are at equilibrium. However, I believe the authors intended to present the product ratios as a function of $[(\text{CH}_3)_2\text{NH}]_0/[\text{NH}_3]_0$, ie, the initial the reactant ratio. They are correct in stating that if reactants are not significantly depleted, the equilibrium reactant ratio is effectively that which is calculated from equation 1. The pseudo steady state terminology applies more to a kinetic treatment of the reaction scheme rather than the thermodynamic driving forces discussed here. Please clarify the presentation of Table 5 results.

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