

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-84

Anonymous Referee #1

Referee comment on "A predictive model for salt nanoparticle formation using heterodimer stability calculations" by Sabrina Chee et al., Atmos. Chem. Phys. Discuss.,
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S. Chee and co-workers have used computational methods to study the stabilities and formation rates of acid-base clusters relevant to atmospheric new-particle formation. The study has two main parts. First, the authors investigate whether the formation free energy ("stability") of a "heterodimer" (a cluster of one acid molecule and one base molecule) can be predicted based on various single-molecule properties, including both experimental and easily computed parameters. Second, the authors then study how well this heterodimer stability correlates with particle formation rates computed with a cluster population dynamic model using quantum chemistry data (at the same level) as input. The study is interesting, well carried out, and useful to the atmospheric aerosol community. In addition to the main results, the study also has some very useful discussion connecting various molecular and/or cluster properties or property trends to the actual structures. I especially liked figures 3 and 6, and the associated discussion. I thus recommend publication in ACP subject to some fairly minor revisions.

Suggestions for revision:

-Please define what is meant by a "weak salt" e.g. in the abstract (or rephrase this).

-When the authors discuss "gas phase acidity", as well as pKa, they mean both the acidities of the studied acids, and the acidities of the conjugate acids of the bases (which are in turn measures of the "basicities" of the parent bases). Or in other words, when they discuss for example the "pKa of methylamine", they do NOT literally mean the negative base-10 logarithm of the equilibrium constant for the reaction $\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{NH}_2^- + \text{H}_3\text{O}^+$ (that would be the technical literal interpretation of the phrase), but instead that of the reaction $\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_2 + \text{H}_3\text{O}^+$. This is obvious to most chemists, but not necessarily to all physicists. I suggest the authors explicitly explain/define this notation early on in the manuscript (now this is implicitly mentioned only on page 8).

-As noted above, the study really has two quite separate parts: the prediction of heterodimer stability on one hand, and the prediction of $J_{1.5}$ based on that stability on the other hand. Also while the first is done with three different acids, the second is apparently only done for H_2SO_4 - base clusters. The abstract does not really make this clear, and

also the two topics are presented in a somewhat counterintuitive order. I would suggest some rephrasing and rewording of the abstract to make the content and structure of the study more clear.

-In section 2.1, the authors say "In order to simulate cluster formation and growth, one must calculate accurate structures and thermochemical properties of neutral sa-base clusters up to the cluster size of four sa and four base molecules". As the authors must know, the appropriate "box size limit" depends both on the system (which acid and which base) and on the conditions (concentrations and temperature). 4,4 is not some universally valid constant. See for example Besel et al, <https://pubs.acs.org/doi/abs/10.1021/acs.jpca.0c03984>, for some discussion, and on how to check if the box size is suitable (by comparing the evaporation and collision rates of the most stable of the largest included clusters). The authors should add a few sentences of discussion on this, and also check if the 4,4 box is appropriate for all the studied cases. I would expect based on the study quoted above that especially for H₂SO₄:NH₃, at the lowest concentrations (1E5 per cm³) and highest temperatures (348 K!), the box size may be (way) too small. A caveat on this should be added, and it would be good if the authors could indicate also in their figures which of their formation rates may be overestimated due to box size effects. (This should mainly affect rates that are anyway quite low, so this is not a huge problem, but it ought to be properly documented.)

-The first sentence of section 2.2 should slightly be amended to reflect the above: yes the methods can in principle be used to simulate "any conditions", but for weakly bound clusters, low concentrations and high temperatures, the set of included clusters may need to be expanded if accurate rates are desired.

-Give a few more details on the conformational sampling please: the Kubecka et al 2019 study contains quite a few different options and possible parameter (e.g. cut-off energy) values. Also, did the authors use e.g. quasi-harmonic corrections?

-Also explain a bit more about what ACDC does, e.g. the fact that collision rates correspond to hard-spheres, and then evaporation rates are computed from quantum chemical free energies using detailed balance.

-I suggest using capital letters for the abbreviations (so tma => TMA etc); e.g. "put" is easily confused with the corresponding verb when written in lower case.

-Page 11, "volatility of the constituent acid and base plays a relatively minor role in heterodimer stability". This is true as stated, but maybe to avoid misunderstandings you could note in this discussion that e.g. the low volatility of H₂SO₄ is still a big part of why this molecule is so important for atmospheric new-particle formation. (This does not contradict anything the authors state, it's just a complementary fact.)

-Please explain what is meant by "lognormal" in the context of Fig 8a.

- $W(1/2)$ in equation 2 should presumably be $W(1,2)$. Also please explain this notation in a bit more detail. E.g. $p(1,2)$ is the number concentration of what species? (Also presumably J is proportional to concentration, not the other way around!

-Please confirm that the delta-Gs are calculated from partition functions at each temperature (and not from equation 1 assuming temperature-independent delta-H and delta-S, which would introduce a completely unnecessary extra error source). Also you could note if the calculations are based on lowest free-energy minima (at 298 K, or checked at each temperature?), or if multiple minima are included.

-The heterodimer predicts theoretical J 1.5 well at cold temperatures, but additional

factors become more prominent at warmer temperatures". Isn't this just reflecting the fact that especially for the stronger bases, evaporation of clusters larger than the heterodimer are negligible for lower temperatures, so J is then determined by the heterodimer evaporation rate? While, for higher temperatures also evaporation rates of larger clusters (which correlate with, but are not directly determined by, the heterodimer ΔG) start to matter?

-Is Figure 11 only for SA:AMM, or for all bases with SA? (Based on the text probably the latter, but I'm not 100% sure.) Please note this in the caption.

-Comparing equations 3 and 5, the normalised heterodimer concentration seems to be simply $([\text{acid}][\text{base}]/c_{\text{ref}})^{0.5} \times \exp(-\Delta G/RT)$. I.e. the same as the mass balance equation but with a square root around the prefactor. This could perhaps be noted. Also, to me this seems to be maybe be somehow related to the concept of saturation ratio (perhaps it depicts the saturation of the monomers with respect to the heterodimer)? If the authors have any insight into such a connection, please feel free to speculate :-).

-In the conclusion, the authors write "The effects of temperature and concentration on heterodimer concentration were much less than that of those on $\Delta G_{\text{heterodimer}}$ ". I was under the impression that their ΔG was defined for $c_{\text{ref}} = 1 \text{ atm}$, i.e. the actual value should not depend on the monomer concentrations. Perhaps they need to reformulate this sentence?

-As the authors themselves note, the proposed approach for using heterodimer stability to predict new-particle formation rates is valid only for acid-base clusters, and for conditions where the acid and base concentrations are fairly similar. In the literature, the stabilities of heterodimer of type $(X)(\text{H}_2\text{SO}_4)$ is very often used to (in my opinion incorrectly) argue for e.g. "nucleation enhancement" by a great multitude of (usually non-basic oxidised organic) species X. For example, dicarboxylic acids, such as oxalic acid mentioned by the authors, often bind quite strongly to one H_2SO_4 molecule - but are incapable of promoting the addition of further H_2SO_4 to the cluster. In such cases, "heterodimer stability" is clearly NOT a sufficient or good indicator of particle formation efficiency. To avoid other researchers misrepresenting their results, I strongly recommend that the authors explicitly state that the proposed relation between heterodimer stability and new-particle formation holds ONLY for acid-base clusters, and NOT for the general case of H_2SO_4 clustered with an arbitrary other (non-basic) molecule.