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Atmospheric Chemistry and Physics Discussions

Interactive comment on "On the formation of sulphuric acid-amine clusters in varying atmospheric conditions and its influence on atmospheric new particle formation" *by* P. Paasonen et al.

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We would like to thank the referee for his comments. In the following we give our responses.

1. The text is verbose and the figures are complex and not always well-described. The authors could greatly enhance the manuscript's readability through a more concise and targeted discussion. Some specific examples will be given in the comments below, although this is not an exhaustive list.

The text has been reviewed, and especially the notifications by the two referees have been considered.

2. Page 11494, lines 18-19: The authors assume that ΔH and ΔS are constant over the studied temperature range for a given cluster. Is this a reasonable assumption? How much variability exists in ΔH and ΔS over the temperature range studied?

Assuming constant ΔH and ΔS is justified: in the studied temperature range the formula applied in the manuscript gives the same result for ΔG as calculating it directly from the vibrations and rotations within around 0.01 kcal/mol. We have added this information to the manuscript.

3. Page 11494, line 26: Why are the clusters $A_2D_2T_1$ and $A_2D_1T_2$ allowed but then, "as it is obvious that they are very unstable, they were set to evaporate one amine molecule instantaneously when formed"? Isn't this simply saying the same thing as in the previous sentence, where the authors list the collision types where the rate coefficient is set to zero? It is not clear what is meant by this statement.

In case of collisions listed (page 11494, lines 24-25) it is presumable that the molecule/cluster that collides with the initial (larger) cluster evaporates immediately, in other word the exact reverse of the collision process occurs instantly: thus the outcome of the collision can be estimated by not allowing the collision to occur at all. In case of collisions leading to clusters $A_2D_2T_1$ and $A_2D_1T_2$ the situation is somewhat different, as these clusters may evaporate producing something else than the initial clusters/molecules. For example, in collisions between $A_2D_1T_1$ and DMA in 99,998 % cases it is not the DMA that is evaporates, but the TMA instead. Thus, the collisions producing these clusters may change the composition of the initial clusters, and allowing the formation of these clusters (even evaporating them instantaneously) was necessary. The related explanation in the manuscript has been revised to make the point clearer.

4. Also regarding the $A_2D_2T_1$ and $A_2D_1T_2$ clusters, why weren't free energies com-

puted for these clusters? It appears that B3LYP/CBSB7, a density functional method, is used to calculate free energies. This is a fairly efficient method for determining structure and thermochemistry, and the clusters are relatively small so it should not take too much time. It would improve the manuscript to perform the thermodynamic calculations on those clusters that are not already modeled.

Naturally, if free energies for a number of more clusters would be available, the results would become more exact and it would decrease the need for assumptions. However, the real and computer time required and the related costs for calculating the free energies for clusters with 5 or more molecules forces one to make decisions in where to draw the line between calculating more and modeling the results. Actually, B3LYPP/CBSB7 is not the only nor the most time consuming step, as both the conformational sampling and the single point energy (RI-CC2/aug-cc-pV(T+d)Z) calculation take a lot of time, the latter being even more demanding than the B3LYPP/CBSB7 calculations. Typically, determining the free energies for a cluster of this size takes something like 3 weeks to over a month. We find that, for this study, the applied number of cluster free energies calculated is reasonable. Additionally, the mentioned clusters $A_2D_2T_1$ and $A_2D_1T_2$ are not the first ones in our list that we would calculate as they definitely evaporate fast (compare to other neutral clusters with more bases than acids e.g. in Ortega et al. 2012) and with the available free energies we can already calculate what the evaporation products are. Our vision of the most important clusters for which the free energies need to be calculated are mentioned in the end of Sect. 6 of the manuscript.

5. Page 11497, line 8: Specifically in this location, but also elsewhere in the manuscript, the authors spend a lot of time discussing the conversion of clusters containing TMA to DMA or vice versa. It is worth noting that Bzdek et al. (2010) examined the kinetics and thermodynamics of DMA-TMA exchange in positively charged bisulfate clusters containing 1-3 bisulfate ions. They found that for [$((CH_3)_2NH_2)_3(HSO_4)^2]^+$ exposed to TMA, the first substitution step has ΔG = -1.1 kJ/mol, the second step has ΔG = -

0.37 kJ/mol, and the third substitution step has ΔG = +7.9 kJ/mol. The authors should discuss these experimental results in their revised manuscript, especially as it relates to their model for DMA-TMA exchange.

The cited study is mentioned in the revised version of the manuscript.

6. The authors also discuss cluster stability in terms of the difference in basicity and hydrogen bonding capacity (e.g. page 11499, lines 11-15). Recent computational work by DePalma et al. (2011) has shown that amine-ammonia exchange is governed by the tradeoff between basicity and binding. Reference to this work should be made in the revised manuscript.

The cited study is mentioned in the revised version of the manuscript.

7. Page 11502, lines 12-13: The authors refer to a dashed black line in Fig. 1 as giving the collision rate. Is this what the authors really mean? Or are they referring to the solid black line in Fig. 3?

The typo has been corrected.

8. Page 11503, lines 14-15: At the lowest temperatures, the values of both K_{A2T2} and K_{A2D2} decrease as [$A_{1,tot}$] increases, and the authors then infer that J_{A2B2} is proportional to [$A_{1,tot}$]$^{<2}$. Is this conclusion based on the extent to which the K value decreases with increasing [$A_{1,tot}$]? It is not clear how the authors reached that conclusion. Since this relationship appears to be an important component of the manuscript, the authors should provide a more detailed explanation. A similar explanation should also be provided on page 11504, line 10.

The interpretation of the referee is correct: if J=K*[H_2SO_4]^2 and the value of K decreases with [H_2SO_4] the yielding result is that the [H_2SO_4] dependence of J is weaker than quadratic, which we denote as J ~[H_2SO_4]$^{<2}$. And on the contrary, if K increases with [H_2SO_4], J is proportional to [H_2SO_4]$^{>2}$. We have explained more clearly how this conclusion has been achieved.

9. The authors spend a significant amount of time discussing the effect of relative humidity on collision and evaporation rates, but Section 2.1.3 is quite short and doesn't provide much data to support the points made. The authors should consider including a supplemental figure or test calculation to illustrate how water was incorporated.

Indeed, the role of water has to be explained in detail. We have added to the Sect. 2.1.3. more detailed information on how the hydrate distribution calculations were performed and verified, and to the Sect. 3.1. more explanation of how the water molecules affect the relative stabilities of the smallest clusters. Related to the text in Sect. 3.1. we have added Fig. 1b to illustrate the effect of RH.

10. On page 11509, lines 5-9, the authors compare temperature trends in the ambient dataset to trends in the modeled dataset. The authors state that the trend in the ambient dataset is best approximated by the modeled K_{A2D2} coefficient. However, visual inspection of the figure suggests that one could draw arbitrarily several curves that may reproduce the data as well or better than K_{A2D2}.The authors should perform a statistical correlation analysis in order to demonstrate a better fit to the ambient data with the K_{A2D2} model rather than the K_{A2T2}.

It is true that by visually comparing the field data and the model lines any strict conclusions cannot be made, and we have underlined more clearly that this comparison is only made by visual estimation at the very qualitative level. A proper correlation analysis would require a significant extension of our study, and is beyond the scope of this paper. The results of this correlation analysis would be greatly dependent on the unknown dependence between amine concentrations and temperature, and could, thus, give even false information if not done carefully enough. This kind of study concentrating on the ambient data analysis should, however, be made in the future in another manuscript.

11. Figure 8 is of very poor quality, and it is quite difficult to interpret. The lines are much too thin and the resolution is poor.

The quality of Fig. 8 has been improved.

References:
Ortega, I. K., Kupiainen, O., Kurtén, T., Olenius, T., Wilkman, O., McGrath, M. J., Loukonen, V., and Vehkamäki, H.: From quantum chemical formation free energies to evaporation rates, Atmos. Chem. Phys., 12, 225–235, 2012.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 11485, 2012.