This manuscript utilizes a kinetic cluster model to simulate the formation rate of clusters containing two acids and two bases, where the acid is sulfuric acid and the base is either dimethylamine (DMA) or trimethylamine (TMA), under a variety of conditions (acid and base concentrations, relative humidity, temperature). The major focus of this paper is to elucidate the parameters that most significantly impact the coefficient K in the equation $J=K[H_2SO_4]^2$. The results indicate that K depends on amine concentrations, temperature, and relative humidity. The modeled values are then compared to values of K obtained during field measurements. K_{obs} is found to have a decreasing trend when plotted against increasing temperature, similar to modeled K_{A2D2}. The manuscript is on a topic of considerable interest and is within the scope of *Atmospheric Chemistry and Physics*. This manuscript could be suitable for publication once the points discussed below are addressed appropriately.

Comments:

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.

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?

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.

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

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 $\Delta G = -1.1$ kJ/mol, the second step has $\Delta G = -0.37$ kJ/mol, and the third substitution step has $\Delta G = +7.9$ kJ/mol. The authors should discuss

these experimental results in their revised manuscript, especially as it relates to their model for DMA-TMA exchange.

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.

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?

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.

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.

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}.

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.

References:

Bzdek, B.R., Ridge, D.P., & Johnston, M.V. (2010). Amine exchange into ammonium bisulfate and ammonium nitrate nuclei. *Atmos. Chem. Phys.,* **10**, 3495-3503.
DePalma, J.W., Bzdek, B.R., Doren, D.J., & Johnston, M.V. (2011). Structure and energetics of nanometer size clusters of sulfuric acid with ammonia and dimethylamine. *J. Phys. Chem. A,* **116**, 1030-1040.