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Discussions

Interactive comment on "Thermodynamics of the formation of sulfuric acid dimers in the binary (H_2SO_4-H_2O) and ternary (H_2SO_4-H_2O-NH_3) system" *by* A. Kürten et al.

Anonymous Referee #1

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The authors present interesting and valuable low temperature data for dimer formation in sulphuric acid-water and sulphuric acid-ammonia-water systems. The experimental data is accompanied with model calculations which contain several assumption that appear unjustified or inconsistent. The sensitivity of the conclusions and the derived thermochemical parameters (two-acid cluster and one acid-one ammonia cluster formation enthalpies and entropies) to these assumptions needs to be assessed before the paper can be accepted for publication. Below are my detailed comments to the manuscript, starting with comments related to three major issues gathered together and followed by additional comments ordered by page number of the manuscript.

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Major point 1: I find it very hard to believe that the net collision rate (combination of the collision rate and subsequent reaction rate) between two sulphuric acid molecules is higher than that between a bisulphate ion and sulphuric acid (Page 13969, lines 1-7). This situation likely results from the use of collision/reaction rates from different sources for the two processes where they have been determined differently and based on different assumptions. While both values may be of the correct order of magnitude, comparison seems to imply that at least one of them is not very accurate. The enhancement to the collision rate due to ion-dipole interaction should be larger than that due to dipole-dipole interaction (given that one of the collision partners is the same in both cases and the other is as similar as a neutral molecule and an ion can be). The reaction rate of the bisulphate ion and sulphuric acid is taken from Zhao et al (2010), where it was concluded that the clustering reaction did not proceed at the collision limit (at ∼278 K). On the other hand, the clustering reaction between two neutral sulphuric acid molecules is now assumed to proceed at the collision limit. How is this assumption justified? It seems very counter-intuitive, as the chemistry after the collision is very similar in these two cases except that the neutral cluster is less strongly bound than the charged one. It also seems inconsistent to assume that sulphuric acid reacts with the nitrate ion at the collision rate (Page 13965, line 3), but with bisulphate ion with a lower rate (Page 13966, lines 11-13). Furthermore, both the neutral-neutral and neutral-ion collision rates have uncertainties. The Chan and Mozurkevich (2001) formula for the enhancement factor is derived based on a fit to experiments with 50-100 nm particles colliding with another particle of the same size. Extrapolating the parameterization from particle sizes in the continuum regime to molecules and clusters in the free molecular regime can result in fairly large errors/uncertainties. Other studies (Marlow 1980) have also found a stronger size dependence, and also a stronger dependence on whether the colliding parties are of the same size or different size, than given by the formula of Chan and Mozurkevich (2001). On the other hand, the observations of Zhao et al. could also be explained for instance by dimer (HSO4-)(H2SO4) evaporation instead of the effective collision+reaction rate between the bisulphate ion and the sulphuric acid

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molecule being lower than the theoretical ion-dipole collision rate. Thus, before the paper can be accepted, the authors must either a) amend the assumptions so that the ion+acid collision+reaction rate is higher (or at least equal) to the corresponding rate for acid+acid and repeat all the simulations and analysis with the new values or b) provide a fundamental explanation how such a situation could arise that the combined rate is higher for the acid+acid collision than for ion-acid collision, and also show how sensitive their results are to this counterintuitive assumption.

Major point 2: The assumption that ammonia-containing dimers and trimers cannot evaporate leads to the evaporation rate of the one sulphuric acid-one ammonia cluster being a fitting parameter that very straightforwardly controls the dimer concentration. There is no guarantee that this fitting procedure gives a truthful estimate for this evaporation rate if the assumptions made are not correct. Similarly, in the binary system only the dimer evaporation rate is used as a fitting parameter while all other evaporation rates are set to zero. Before the paper can be accepted, the authors should test the sensitivity of their results for the cluster formation enthalpies and entropies to these assumptions by simulating also a system where evaporation of (at least some of the) larger clusters is allowed.

Page 13959 lines 13-15: "For the ternary system the formation of H2SO4 âĂć NH3 is very likely an essential step in the formation of sulfuric acid dimers". In atmospheric conditions the cluster mentioned is not very stable according to any of quantum chemical results available in the literature, and thus assuming that this is the essential (rate limiting ?) step does not seem justified.

Page 13961 lines 10-12: the authors should justify why is it crucial to know the evaporation rate of the dimer, but it is ok to assume evaporation rates of trimer and all larger lusters to be zero. Is this actually justified?

Page 13968, lines 4-5: "The second term is significantly smaller than the first term, so it can be neglected in the following discussion. " The authors simply assume that the

trimer evaporation is zero. What is this assumption based on? How confident are the authors of this choice? How much would it affect the results and conclusions to let also the trimers (an possible larger clusters) to evaporate?

Page 13969, lines 23-24: how sensitive is the SAWNUC model to the assumption that only dimers and sometimes trimers can evaporate. The authors should run the code with evaporation for larger cluster turned on using some literature estimates for the evaporation rates, and see how much the results change?

Page 13979, lines 17-18: "This is consistent with the assumption that cluster evaporation rates are negligible for the trimers and all larger clusters at this low temperature. " One wonders would a model with also evaporation of larger clusters allowed reproduce the data equally well or even better? I don't think we can say anything about the evaporation rates of trimers and larger clusters based on the model–experimental data comparisons presented in this paper. Similarly page 13987, line 26-28: "the signals are consistent with the assumption that cluster growth is essentially kinetically controlled for all of the observed clusters above the dimer. ", is misleading although the word conclude has not been used.

Page 13987, line 17: The model has been essentially fitted to the experimental data, so it is not fair to say that the model predict the dimer concentrations to a high accuracy. Page 13987, line 20: the thermo–chemical data is not based on solely experiments, but to a large extent on a model and its several strong assumptions

Major point 3: The effect water on the clustering should be discussed in somewhat more detail. The formation enthalpy and entropy values in the binary case for the two-sulphuric acid (H2SO)2 and in the ternary case for the one sulphuric acid-one ammonia (H2SO4)(NH3) clusters deduced from the experimental data represent averages over different water contents of these clusters, rather than those specific dry clusters. This should be stated clearly, especially pointing out that these values should not be compared directly to the quantum chemical results for the dry clusters as is done for in

Table 1 and in a statement page 13984 lines 12-13. For instance, for the level of theory used by Ortega et al. (2012), Henschel et al. (2014) have published quantum chemical values for the water-containing clusters relevant to this study. For different quantum chemical levels of theory, for example. Herb et al. (2011) and Temelso et al. (2012) have calculated values for hydrated clusters.

Additional comments:

Page 13961, lines 6-7: expression "Similarly, the monomer of sulfuric acid may contain water or ammonia. " should be replaced by something like "The term monomer refers to clusters with one suphuric acid, irrespective of whether the cluster contains also ammonia and/or water molecules or not"

Page 13961, lines 19-24: I would say that the uncertainties in the experiments are too large for narrowing down the theoretical uncertainties, as they are of the same order of magnitude. Comparison of experiments and theory rather provides a sanity check in both directions.

Page 13964, equations (1a) and (1b) and page 13965, lines 1-e , sentence concerning the calibration constant . What is the uncertainty of the sulphuric acid monomer (and dimer) concentration. In some other CLOUD-related publications a factor of 2 uncertainty has been reported. How does such an uncertainty affect the results of this paper?

Page 13965, lines 10-11: "It was assumed that the diffusivity of the dimer equals 0.06 cm2 s−1 at 298 K, and varies with temperature as (298 K/T)1.75". Are this value and temperature dependence derived for a pure dimer (H2SO)2? How reliable are they if there are some number of water and/or ammonia molecules attached to the dimer, and if the number of the attached molecules is temperature dependent?

Page 13965, line 15: dimer dissociation affect also the measured monomer concentration, not only that of the dimers. Has this been taken into account?

Page 13967, lines 5-8: "Since low temperature conditions (208 and 223 K for the binary system) are considered in this study the assumption is made that only the smallest clusters (dimer and trimer) have appreciable evaporation rates (Hanson and Eisele, 2006). " Some theoretical evaporation rate values, or other such information, would strengthen the justification of this assumption.

Page 13967, lines 10-11: it should be stated clearly which specific evaporation rate $k_{i,e}$ is: the evaporation of acid, ammonia, or some combined effective evaporation rate? What is the effect of grouping clusters with equal amount of acid molecules to representative cluster sizes, without considering that there can exist clusters with similar acid content but different number of ammonia (and/or water) molecules?

Page 13968 equation (5): this represents the equilibrium cluster distribution, which should be stated clearly, and the authors should comment why is it is justified (or is it?) to use an equilibrium cluster distribution in a nucleating/ particle forming vapour. Also related to this is the statement on Page 13971, lines 4-5 that the dimer is assumed to be in equilibrium initially. It seems that this assumption is used throughout the modeled period through equation (5)

Page 13969, lines 10-13: "Cluster growth is treated explicitly by a step-by-step addition of sulfuric acid molecules while equilibrium with water molecules is assumed due to the relatively high concentration of H2O compared to [H2SO4]." The text should be revised to state that the cluster growth is treated explicitly only concerning the addition of sulphuric acid, while water is assumed to be in equilibrium, and that the equilibrium assumption also requires a much higher evaporation rate for water than for sulphuric acid, not only a much higher concentration (collision rate) of water.

Page 13969, lines 15-16: the cluster thermodynamics reported by of Lovejoy and Curtius (2001) and Froyd and Lovejoy (2003) are only partly experimental, they are partly based on quantum chemical calculations. This should be stated.

Page 13969 line 27. The authors should explain in some detail how the Kürten et al.

(2014) model has been adapted to a binary system, since to my knowledge it has so far been only used for a one-component system, and the extension to more components is not necessarily trivial.

Page 13970, line 1: How do the two independent models differ? Are the same net collision rate coefficients and evaporation coefficient used in both models?

Page 13970, lines 21-23: Much more detail is needed concerning the modelling resulting in the data shown in Figure 1, so that the readers would, even in principle, be able to reproduce the modelling

Page 13971, line 7: can the dimers grow if no larger clusters are taken into account?

Page 13972, section 3.2: the description of the ion -induced experiments could be shorted quite a bit, as most of that material has been presented in the Rondo et al (2014) paper, and they are not essential for the story of this paper.

Page 13972, line 8: does the statement "While the monomer concentration is not affected by the GCRs, . . . " imply that the ionization does not consume monomers, or at least not significantly? Or do the authors mean that the ions do not affect the apparent measured monomer concentration?

Page 13973 26-27: "the dimer signal shows almost no enhancement during ion-induced experiments when ammonia is present in the chamber." Could this be re-formulated by saying that the dimer signal comes mainly from the neutral clusters?

Page 13974, line 24 and Figure 3 caption: It would be more illustrative to use the verb "sum" rather than "integrate" here, as the authors are probably talking about summing up the concentrations of clusters of different (discrete) sizes

Page 13974, lines 27-28: I don't think the curve in Fig 3 has leveled off at the right hand edge of the figure to the extent that one can safely conclude that factor 3 is an upper bound for the contribution of fragmentation of larger clusters to dimer concentration

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Page 13977, lines 16-17: How do the values for dH and dS compare to theoretical (quantum chemical values). The comparison could be added to Table 1. Values for the cluster formation enthalpies dH are expected to be temperature dependent: the authors should comment of this when giving singles value for the temperature ranges 208-223K (binary system) and 210-248K (ternary system).

Page 13977, line 18, lines 22-23: Is there a physical justification for the RHp dependence? A plot of the evaporation rates as a function of relative humidity would help to assess how well the assumed RH-dependence fits the data. It should also be noted that since RH is connected to temperature through the temperature dependency of the saturation vapor pressure, data measured at same RH but different temperatures cannot be used to assess solely the effect of temperature because the absolute water vapor concentration may also vary (Figure 6).

Pages 13978-13980, section 3.4: The CI-APi-TOF results presented in this section seem fairly unconnected from all the other material in the manuscript. Could this material be left out, and if not, can it be tied more to other parts of the work?

Page 13980, lines11-14: "In the presence of NH3, a fraction of the sulfuric acid will be bound to ammonia. However, we assume that the sulfuric acid monomers and dimers will still be ionized by the nitrate primary ions at the same rate as the pure compounds. " It seems inconsistent that while using different net collision rates between for sulphuric acid- bisulphate ion collision and sulphuric acid nitrate ion collision (major point 1), these ionization rates are taken to be the same.

Page 13981, lines 27-28: Again, a much more simple approach is used here than in treating the collisions between different ions and molecules differently (major point 1). How is this justified, as the ammonia content of the cluster affects its collision cross section both through effective radius and the magnitude of the London van der Waals correction, which depends on the dipole moment of the cluster.

Page 13981 line 28 -Page 13892, line 1: The author should provide justification for

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assumption "We further assume that the clusters cannot contain more bases than acids"

Page 13981, line 19: A reference also to the Almeida et al (2013) paper would be in order, as the same system is treated there using another model, and also a short description of the differences between these two models (that of the current manuscript and the model used in Almeida et al) should be added

Figure 9: it would be interesting to know what are the contributions of different routes to the cluster growth.

Page 13982, lines 22-23: in addition to the Chen et al value for the evaporation rate of the base-containing dimer, theoretical (quantum chemical) value(s) should also be given for comparison

Page 13983, lines 22-23: "Our calculated dimer concentration agrees with their measured concentration within better than a factor of two." A plot illustrating this would be good to see.

Page 13985, lines 12-18: What is the reason for considering theoretical evaporation rates of dry A3B1 and A4B1 clusters instead of clusters containing more ammonia molecules? Also hydration is likely to affect net evaporation rates. On the other hand, beyond the critical size the evaporation rate is lower than the collision frequency, so it would be useful to give the collision frequency with acid and ammonia molecules in the experimental conditions of Hanson and Eisele (2002) so the reader could more easily see what conclusions the authors wish to draw from this comparison.

References

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