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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Identification of molecular cluster evaporation rates, cluster formation enthalpies and entropies by Monte Carlo method" *by* Anna Shcherbacheva et al.

Anonymous Referee #1

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This manuscript applies Markov Chain Monte Carlo method to estimate cluster evaporation rates and cluster thermodynamic parameters such as formation enthalpies and entropies while taking collision rates from kinetic gas theory. Cluster evaporation rates were estimated from two data sets: steady-state and transient data. While the transient data can improve the estimates of the evaporation rates compared to the steady state data, neither of them can be satisfied from both magnitude and the marginal posterior distributions of the rates. Cluster formation enthalpies and entropies were then estimated from steady-state cluster concentrations at two temperatures (278 and 292 K) and the cluster evaporation rates were inversed from the cluster Gibbs free energies (determined by enthalpies and entropies). It turns out that the evaporation rates were

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Discussion paper

greatly improved in terms of variation and the probability distributions except for clusters containing both 5 sulfuric acid and 5 ammonia. Since cluster evaporation rate is an essential parameter that controls cluster growth, this parameter ought to be accurately determined in order to understand atmospheric nucleation. The scientific questions are worthy exploring and are important topics in atmospheric research. However, several major issues need to be fully resolved before the manuscript is considered for publication in this journal.

1. Section 2: the way the authors describe simulation methods is hard to understand. It seems that the authors wrote paragraphs in casual ways, in particular, when describing MCMC simulations, it is very hard to follow the logic. It is suggested that the authors use more plain languages and better logic to rearrange section 2 in order for readers to understand the methods and data sets the authors used or generated.

2. It is quite confused that throughout the paper, the authors use identification of the rates and thermodynamic enthalpies/entropies. Is it better to use for example estimate or similar words?

3. For pairwise marginal posterior distributions, either for evaporation rates or enthalpies/entropies, what criteria the authors used to create these correlations? For example, it seems that evaporation of different monomers from different clusters might be irrelevant.

4. Section 3.4: can the authors present more details of the comparison instead of just some dry descriptions? For example, the authors can add a table to summarize the knowledge up-to-date regarding the evaporation rates from both measurements and modeling so that the readers can be benefit from reading this paper.

5. Can the authors give some plausible explanation why evaporation rates estimated from transient data seem better than those from steady-state data?

6. The authors claimed that the 5A5N has low variance in free energies. However,

an order of magnitude is not small for free energies and it is substantial if this value is applied to the evaporation rates (Line 319 on p18).

7. There are several rather minor comments below:

1) P11, lines 233, do the authors mean that the lower limits of evaporation of a monomer from those clusters are far above the 10ˆ-10 as defined for complete growth?

2) P11, line 240, Figures 3-4 can actually be combined to one figure since they basically represent different parts of the same thing. There are some figures that have similar issues.

3) P15, Figure 5, no label for a, b, c, d.

4) P15, line 284, how the evaporation rates of monomers for clusters 2A display inverse linear correlations in Figures C4-C8?

5) P18, the claim that the estimated formation enthalpies vary at most by 1 kcal mol$-$1, while the variance for the formation entropies is less than 1 cal K-1 mol-1 is not right.

6) P18, line 313 and line 321, Figure 9 should not appear before figure 8.

7) There are lot of typos of molecular sulfuric acid formula throughout the manuscript and a thorough check should be made before submitting the revision. For example, H2SO2.

8) The references cited in the text are not followed the journal guidelines.

9) Line 34 on p2, subscript; line 37, miss a comma? Line 39, "," is surplus.

10) Line 54 on p3, "-" superscript? line 59, miss a comma between experiment and these? It is apparent an ill-sentence (line 65).

11) Line 104 on p4, into instead of in to?

12) Table 1, it is suggested to add a third column to indicate the number of clusters in each row.

13) Line 123 on p5, kinetic model?

14) Line 369 on p23, what is question mark for?

15) Figure D2, kkal/mol?

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