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Atmospheric
Chemistry
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Discussions

Interactive comment on "Influence of non-ideality on aerosol growth" *by* S. Compernolle et al.

Anonymous Referee #2

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The authors present an analysis on the relative importance of parameters which dictate gas-particle partitioning. Choosing alpha-pinene oxidation as the reference system from which all of the conclusions are made, the authors use a detailed chemical mechanism and treatment of aerosol formation which calls several versions of the UNIFAC model. The overlying conclusions are that, for most experiments used in this report, non ideality has a limited impact on SOA yields and composition. Similarly, when modelling aqueous systems, water uptake is activity coefficient model dependent and only shows a significant amount of variability for experiments with low amounts of volatile organic carbon. These conclusions are based on predictions from thermodynamic models currently available to the community at large and also depend on the range of functionality linked to the detailed chemical mechanism used for characterising alpha-pinene oxidation. Conclusions based on the applicability of existing non-ideal frameworks should be taken presented with an appropriate level of caution when considering

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complex systems covering a wide range of functionality given the acknowledged difficulty of available group contribution methods to capture the behaviour of multifunctional compounds.

In all, the paper provides interesting results regarding sensitivities to SOA yield predictions using thermodynamic models currently available to the atmospheric community.

I have some general comments which I feel the authors should address before publication.

General comments:

1) I think the title is slightly confusing. The term ‘aerosol growth’ implies a change in diameter. You do not analyse how particle dimensions alter but focus on mass transfer between the gas and particulate phase. The paper would benefit from modification of the title to reflect this.

2) The authors essentially highlight that existing activity coefficient models show a lot of variability when used to model the same ‘atmospherically relevant’ systems. This variability is slightly concerning and clearly justifies the need for further experimental measurements and theoretical investigations of non-ideality on a wide variety of systems. It has been found previously that parameters which have been optimised using a subset of compounds within a given class do no necessarily work when used to model systems which include combinations of functionality not included in the original studies (e.g. Topping et al 2005; Clegg et al 2001; Tong et al 2008; Topping 2008). This in general requires a wide range of new experimental data. In some respects this brings into question the validity and strength of the statements the authors make regarding the importance of non-ideality. I can fully appreciate that this study highlights the variability of the only models which are readily available to the community. This is both important and very interesting. However I think a comment should be made regarding empirical validation of these models. Firstly, whilst the authors make adequate reference to the fact that attempts have been made to optimise versions of

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UNIFAC for small subsets of functionality, there are many systems encountered in secondary aerosol formation which ultimately require experimental validation. Not only that, but the theoretical basis on which various flavours of UNIFAC (those with or without inorganic ions) are based will determine how accurate these models are. However this is not entirely apparent to the reader.

3) The authors try to bypass issues of ‘missing parameters’ within UNIFAC through implementation of the model SPARC as an input. I would suggest caution is made regarding the validity of this approach. Firstly, multiple studies have suggested that inferred interaction terms do not necessarily produce accurate results. In some instances a neglective approach has proved more accurate with respect to modelling water uptake (e.g. Topping et al 2005; Clegg et al 2001; Tong et al 2008; Topping 2008). In this study, interaction terms have been based on an untested complex theoretical model. Again, whilst the authors present this as a truly restricted avenue for improvement, ultimately these models need to be tested against reality and this should be made clear to the reader. Similarly, the validity of the SPARC method is based on its use for predicting vapour pressures.

4) On page 5 lines 127-135. you make comments and references regarding the applicability of SPARC to calculate vapour pressures and thus infer activity coefficients. On line 130 the authors make the comment that ‘SPARC produces vapour pressures that compare fairly well with experimental values’. What does ‘fairly well’ mean? Given this is a crucial parameter for predicting gas-particle partitioning I would think that more concrete statistics are required. Whilst the authors present overall statistics in table 2, this statement makes the whole paragraph confusing. I would suggest removing ‘fairly well’. This is important because the authors then go on to state that the activity coefficient model is based on similar principles. Only at this point is the reader presented with a limitation to SPARC, which is the lack of data for peroxy acids and peroxy acyl nitrate. Also, in the following paragraph the authors state that SPARC is mainly tested for infinite dilution data.

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Does this mean we cannot trust conclusions or model predictions made for moderately concentrated aerosols? In other words, doesn’t this mean that any predictions made below an RH of say 95% is untested? This also has implications for the strength of the conclusions made.

References:

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