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Interactive comment on “SIMPOL.1: A simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds” by J. F. Pankow and W. E. Asher

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Responses to Reviewers of ACPD-2007-0285, Pankow and Asher: SIMPOL.1: A Simple Group Contribution Method for Predicting Vapor Pressures and Enthalpies of Vaporization of Multifunctional Organic Compounds

Reviewer #1:

Comment 1: Even though the number of compounds used in the basis and test sets is large, very few of them have vapour pressures that are low enough to (at least as pure compounds) partition in the condensed phase in the atmosphere. The lowest

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data points are at $1\text{e-}8$ atm, whereas I would think that the condensable vapours in the atmosphere might have vapour pressures as low as $1\text{e-}14$ atm.

Response: We agree completely with Reviewer #1 in this assessment but we are limited by the paucity of data for compounds with extremely low volatility. It is not so much that we are unwilling to add more compounds to the database for the fitting as we were unable to identify suitable species. However, it is also true that more compounds does not necessarily guarantee increased accuracy of the fit at low vapor pressures. The problem is two-fold: firstly, accurate determination of vapor pressures at those levels is exceedingly difficult so there are direct experimental errors in the vapor pressures. Secondly, most species with such low volatility will be solids at atmospheric temperatures. This means the sublimation vapor pressures must be converted into sub-cooled liquid vapor pressures, requiring the latent heat of fusion also be known. This adds another factor through which experimental error creeps in. We do not expect this will be the final version of the SIMPOL method, hence the designation SIMPOL.1. Clearly vapor pressure estimation is a major problem in modeling atmospheric aerosols and there will be additional experimental data to work with. Finally, it should be noted that although the lower range on the figures is $1\text{e-}8$ atm, this is the lowest vapor pressure for all compounds at a temperature of 333.15 K. The basis set contains many data points with vapor pressures as low as $1\text{e-}14$ atm, although these are at lower temperatures. In order to demonstrate this, we have added a figure to the manuscript, Figure 7b, that shows vapor pressures of all compounds at all temperatures. This new figure shows the full range of the dataset. We have also added in a brief discussion to section 3.1 noting that there are on order of 35 data points for compounds with vapor pressures lower than shown on the figure for the basis set. For the combined basis and test set, that number rises to 56. In the conclusions, we mention the need for increased empirical data on vapor pressures for compounds with low volatilities.

Comment 2: Also, from an atmospheric point of view it seems a little bit odd that most of the results (on e.g. the success of the prediction method) shown in the fig-

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ures has been calculated at 333.15 K. I understand that this is about at the middle of the temperature range used in the optimization, but it is problematic, since the atmospheric temperatures correspond to the lower end of the studied range (similarly with the vapour pressures). Even though the increase in the uncertainty with decreasing temperature is demonstrated in Figs. 10 and 11, some more discussion on this would be appropriate, e.g. whether the only reason for the uncertainties is the experimental difficulties;

Response: We agree that 333.15 K is a bit high for atmospheric work, but we wanted to show data for all compounds on the figure. 333.15 K is the lower for which we have vapor pressure data for all species. We did explain this point in the text of the original manuscript and have reworded this discussion in section 3.1. Figure 7b, discussed in the response to Rev. 1, Comment 1, also will clear up this point. In order to resolve the final issue raised, we have added an explanation at the end of Section 3.3 for what we feel are the most likely causes of the increase in error of the fit with decreasing volatility.

Comment 3: On p. 11853 a comparison is made between literature data on measured vapour pressure of adipic acid and the SIMPOL.1 prediction. The solid state measurement of Tao and McMurry (1989) has been used together with the fusion enthalpy to get an estimate for the liquid phase vapour pressure. Are the authors aware of recent studies by Cappa et al. (2007) and Koponen et al. (2007)?

Response: We were unaware of these studies since they were published after we had submitted the manuscript and finished the calculations for SIMPOL.1. We have rectified this by substituting vapor pressures measured by Cappa et al. (2007) for compounds already in the fit and adding two other branched di-acids whose unpublished data were supplied directly to us by Prof. Cappa. The manuscript has been revised accordingly and all calculations were redone to include the new data for the di-acids. We did not include the data from Koponen et al. since including multiple empirical data sets for a single compound complicates estimation of the fitting criterion in that it is not clear how

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to weight the different least-squares value for the different parameterizations.

(Note, the Minor Comments from Reviewer #1 begin at Number 3, we have not omitted responding to Minor Comments 1 and 2)

Minor comment #3: It would be nice if the authors could comment shortly how the basis and test sets have been chosen;

Response: Done, added sentence to beginning of Section 3.2 stating that the test set of compounds was chosen to span the range of functionalities and vapor pressures contained in the basis set. However, in some cases (e.g., peroxy-carbonyls), this was impossible due to lack of experimental data.

Minor Comment #4: What about multicomponent mixtures?

Response: We do not address multicomponent mixtures as most aerosol formation models assume system vapor pressures can be estimated from activities and pure liquid vapor pressures. Speculation on the applicability of SIMPOL.1 to mixtures is well beyond the scope of the paper.

Minor Comment #5: I am not sure whether it is necessary to show all Eqs. 4-6 and 10-18.

Response: We have reduced the number of equations following the advice of the reviewer.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 11839, 2007.

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