**Atmospheric
Chemistry
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Discussions**

Interactive
Comment

Interactive comment on "A group contribution method for estimating the vapour pressures of α-pinene oxidation products" *by* M. Capouet and J. F. Müller

M. Capouet and J. F. Müller

We are grateful to the referees for their comments on this work. Each discussion point is addressed in the same order as in their reports. A revised manuscript taking the referees' suggestions into account is submitted.

Referee 1

Major points

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Page 11255, line 6 (Eq. 3): *The referee requests a comment on the impact of the accuracy of the fusion enthalpy change term in Eq. 3.*

The values of the entropy change in Eq. 3 for the diols and dicarboxylic acids are deduced from the measurements of the enthalpy changes and triple point temperatures ($\Delta S_{fus} = \Delta H_{fus}/T_t$.) compiled on the NIST website. The experimental accuracies reported by the studies are at most 2%. Note that Eq. 3, commonly used to estimate the vapour pressure of subcooled liquids, is a simplified form of the exact equation described in Prausnitz (1969):

$$\ln(p_L) = \ln(p_s) - \Delta S_{fus}/R(1-T_t/T) - \Delta Cp/R\,((T_t-T)/T) + \Delta Cp/R\ln(T_t/T),$$

where ΔCp is the difference of heat capacity between the liquid and the solid state. The use of the normal melting point instead of the triple point introduces little difference. Moreover, when T and T_t are not far apart as in the case of the diols, the two last terms tend to cancel each other and the Prausnitz's equation reduces to Eq. 3. However, the melting points of the C3-C9 α,ω-dicarboxylic acids are much higher, around 400 K. The lack of experimental data for ΔCp implies a larger uncertainty for p_L in this case. If we assume a ΔCp of 100 J mol.$^{-1}$ K^{-1} for the carboxylic acids on the basis of the data available from the NIST website, and an experimental error of 50%, Eq. 3 could overestimate the vapour pressures of dicarboxylic acids by a factor 3 on average. A comment on the uncertainties related to the simplification of the Prausnitz's equation and the entropy of fusion is added in the manuscript.

Page 11256, line 6 (Eq. 4): *The referee finds the discussion of Eq. 4 not always clear.*
We think that this lack of clarity is due to an error of typos in line 24. The sentence: "the group contribution method of Marrero and Gani (2001) is used to calculate the boiling point , the critical temperature and the critical pressure of the compound **i**. $p°_{L,\mathbf{i}}(T)$ is obtained using the Lee and Kesler formulation" has to be replaced by "the group contribution method of Marrero and Gani (2001) is used to calculate the boiling point , the critical temperature and the critical pressure of the compound **hc**. $p°_{L,\mathbf{hc}}(T)$ is obtained using the Lee and Kesler formulation".

The first pressure term ($p°_{L,hc}$(T)) representing the vapour pressure of the alkane parent compound "hc" is obtained directly from the experimental measurements in most situations. When no data are available for "hc", a prediction method is required. We suggest to use the method of Marrero and Gani (2001) and the Lee and Kesler formulation which give good performances for alkanes.

The $p°_{L,hc}$(T) data used for the derivation of the parameters "τ" are experimental measurements except in the case of pinonaldehyde and caronaldehyde. The vapour pressures of the alkane parents for these two compounds were estimated using the Marrero and Gani / Lee and Kesler methods. The impact of this prediction method on the determination of the group contributions in this work is therefore very limited. A comment on that point is included in the revised manuscript.

Page 11256, line 27:*The referee requests a clarification regarding the definitions of "primary", "secondary" and "tertiary" degrees of substitution.*
The term "degree of substitution" used in Table 2 and further (e.g. l.7, page 11263) in the context of the hydroxy and nitrate functionalities refers to the number of alkyl substitutions (C-C) of the carbon(s) bearing the oxygenated functionalities, as stated in the text (line 26, page 11256). This definition is also applied to the cyclic compounds. As suggested by the referee, an illustration of this definition is given in Fig. 2 of the revised manuscript. In a more general context, substituted species (e.g. l.14, page 11254) represent non linear carbon chain species.

Page 11257, lines 11-13: *The referee questions the impact of the approximation on the temperature dependence of the secondary and tertiary nitrate contributions.He/she suggests an evaluation of this impact with respect to the temperature dependence of the secondary and tertiary diols.*
Assuming the temperature dependence of the secondary and tertiary hydroxy contributions to be the same as for the primary contributions would have a large effect on the prediction of vapour pressures for the alcohols. At 320K, the standard error on the estimated vapour pressures of the secondary and tertiary monoalcohols would in-

crease from 0.29 to 0.75 and from 0.06 to 1.03, respectively. These effects would be even higher in the case of the diols. The picture is somewhat different for the organic nitrates because they show a small dependence of the vapour pressure with temperature. If we assumed a similar behaviour for the temperature dependence of the nitrate and hydroxy contributions (i.e. a temperature dependence coefficient reduced by a factor of 1.6 for the tertiary functionality as compared to the primary functionality), the vapour pressure of the organic nitrates would not change significantly. For example, $p°_L$ for a C9 linear dinitrate with two tertiary functionalities would change from 2.9E-02 torr (temperature dependence as in Table 2) to 2.2E-02 torr (τ_{ONO2t} = -1.2793 + 0.0038*(T-298)) at 320 K.

Page 11257, lines 24-26: The structure of the parent compound of pinic acid is indeed not correct in Fig. 2. The structure is corrected in the revised version.

Page 11263, lines 25-28: Interactions between different functionalities in heterofunctional compounds are indeed quite likely. However, due to the lack of (precise) data, these interactions cannot be quantified. This is reflected by the higher standard error obtained for the tri-O-acids.

<u>Minor points</u>

Page 11252, lines 6: The text is amended accordingly.

Page 11259, lines 11-12: A few additional plots illustrating the temperature-dependent vapour pressures of differently substituted substances predicted by the new method and by the UNIFAC method are introduced in the new version. In general, the temperature dependences predicted by both methods are similar.

Page 11260, lines 22-28: *The referee notes that the sigma values could be significantly improved if the J function was made more compound-class specific.*
The contributions are assumed to be independent on the structure of the compounds, except for the degree of substitution of the alpha-carbon bearing the nitrate and hydroxy

functionalities. Therefore, the minimization function is applied on the complete data set without any distinction between e.g. monofunctional, difunctional or heterofunctional structures. We acknowledge that the parameterization could be possibly improved by increasing the number of contributions. However, to date, the lack of data for many chemical families makes difficult to constrain the influence of many structural effects on the vapour pressure.

Page 11262, line 3: The text is corrected accordingly.

Page 11262, line 13-14: A figure showing the adduct of pinic acid /pinonic acid and the dimer of pinic acid is included in the revised manuscript.

Page 11272, Fig. 1: *The referee finds Fig. 1 unclear and proposes to use different symbols to represent off-line compounds.*
We have preferred to distribute the vapour pressure data of linear and isomer compounds in two separated figures in the new version. The vapour pressures of non-linear compounds are given in the legend of Fig. 2 of the revised manuscript so that the different compounds can be easily identified on the figure.

Page 11273 Fig.2: The structure is corrected in the revised version.

Page 11276, Fig.5: *The referee asks a clarification on the error of the fusion entropy term of the subcooled vapour pressure of pinic acid.*
The experimental error on the solid vapour pressure of pinic acid is estimated to 50%. The uncertainty due to the neglected terms of ΔCp in Eq. 3 is smaller than for the α,ω-dicarboxylic acids, because of the low melting point of pinic acid (343K). At 290K, the overall error on the estimated subcooled vapour pressure reaches a factor 2 essentially because of the lack of data for ΔS$_{fus}$. Error bars are given for pinic acid and pinonaldehyde in Fig.5.

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Referee 2

Specific comments

The revised manuscript is amended according to the suggestions of referee 2.

Referee 3

General comments

The referee finds that, although the new method relies on a more complex parameterization, it does not perform considerably better than the UNIFAC method. He/she suggests to evaluate the quality of the experimental data used in this study, and also to use additional sources of data.
We think that a major improvement of our method with respect to UNIFAC is its applicability to a larger number of chemical families. The method developed in this work includes 10 group contributions to represent 7 chemical functionalities (ketone, aldehyde, nitrate, hydroperoxy, hydroxy, carboxy and PAN) while UNIFAC includes 5 groups contributions to represent 4 chemical functionalities (hydroxy, ketone, aldehyde and carboxy). UNIFAC and the new method are therefore on the same order of complexity.

We agree that a more detailed comment on the quality of the data used in this study is required. As stated in the manuscript, the relative uncertainty of the measurements, when known, ranges from 25% to 50%. However, the lower volatility of the diols and dicarboxylic acids requires extrapolations of the measurements to the ambient temperatures, or to the subcooled state: ESDU (2001) provides vapour pressure data for diols under the form of the Wagner equation:

ln (p$^{\circ}{}_L$) = ln(P$_c$) + (a*Q + b*Q$^{1.5}$ + c*Q$^{2.5}$ + d*Q^5)$/(T/T_c)$,

with Q=1-T/T$_c$. T$_c$ and P$_c$ are the critical temperature and pressure, respectively. The parameters a,b,c,d are determined by a constrained fit to the data. The Wagner equa-

tion is more accurate than other usual fits (equations of Clapeyron, Antoine or Riedel) because of its largest number of correlated parameters, and it is particularly recommended for extrapolation to lower temperatures (Poling et al., 2001). A comparison study has been performed on the vapour pressure data of the diols provided by three sources: Yaws (1994), Daubert and Danner (1989) and ESDU (2001). The comparison shows that in the temperature range of [290K-320K], the interpolation methods leads to differences reaching a factor of 2 on average. The Wagner equations have been preferred in this work because of their better accuracy underlined by Poling et al.(2001). The most recent measurements of solid vapour pressures for α,ω-dicarboxylic acids between 290 and 320K (Bilde et al.,2003) have been used in this study. As answered in a question raised by referee 1, the lack of data for heat capacities precludes the accurate conversion of these data into subcooled vapour pressures. Therefore, Eq. 3 applied on dicarboxylic acids might introduce an overestimation. Although the subcooled vapour pressures of $C_{\geq 7}$ diols were estimated with the same equation, their related uncertainty is small (10%) because of their higher volatility.

The performance of this new method compared to UNIFAC has been discussed and illustrated by comparisons between the vapour pressures estimated using both methods and the data of the complete set used in this study in Table 2, and in Fig. 5 and 6. They show a better performance of the new method for the dicarbonyls. Estimations given by UNIFAC and the new method for the diols and dicarboxylic acids can be considered as comparable in view of the large uncertainty on the data. However, the predictions for the very substituted compounds in these chemical classes are conclusively improved when using the new method. This is illustrated by additional figures in the new manuscript representing the vapour pressure as function of the temperature for a selection of compounds. The performances of both methods remain poor for the tri-O-acids. To date, the treatment of these compounds by group contribution methods remains crude due to the lack of data.

The other compilations of vapour pressure data suggested by the referee would indeed

be potentially helpful, although we don't believe that they will lead to a significant improvement of the parameterization for the critical chemical families suffering a lack of data. We thank the referee for the suggestion, which we will certainly consider in future versions of our prediction method. Note that the data set used in this study includes >100 compounds, to be compared with UNIFAC based on 76 compounds.

Specific comments

Page 11251, line 14: *The referee suggests to use a better terminology for "alkanoic compound".*
Following the suggestion of referee 2, the term "alkanoic compound" is replaced by "alkane" in the revised version.

Page 11254, line 14: Following the suggestion of the referee, "1,n-dicarboxylic acid" is replaced by "α,ω-dicarboxylic acids ". The terminology is also corrected accordingly for the diols and dinitrates.

Page 11255, line 24: $p^{\circ}_{L,i}(T)$ has to be replaced indeed by $p^{\circ}_{L,hc}(T)$.

Page 11256, lines 11-12: The text is amended accordingly.

Page 11257, lines 16-19: *The referee requests additional explanations concerning the low vapour pressures of the even carbon number α,ω-dicarboxylic acids.*
Fig. 1 represents subcooled vapour pressures at 298K. The dependence of the vapour pressures of the α,ω-dicarboxylic acids to the parity of the carbon number is believed to originate from the increased stability of their conformation in the solid state. This pattern is indeed not observed in their liquid state, at temperatures higher than 400 K. At 298K, Fig. 1 shows that the subcooled vapour pressure of suberic acid (C8) is lower than that of azelaic acid (C9), suggesting that the dependence of the vapour pressure with the carbon number parity is also found for subcooled particles. This anomaly is likely to be a result of the large uncertainties on the subcooled vapour pressures. A comment on this point is incorporated in the new manuscript.

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Page 11262, lines 2-17: *The referee remarks that the degree of dimerization depends on the gas phase concentration of the monomer.*
We acknowledge the fact that the concentration of pinic acid is much lower than that of acetic acid in vapours in equilibrium with the condensed phase at ambient temperatures. However, the much lower concentration of pinic acid is more than compensated by the much higher pinic acid dimer stability (some 120 KJ/mol), on account of the 4 H-bonds involved, as compared to only 2 for acetic acid dimer. Preliminary calculations made by the group of Peeters (University of Leuven, personal communication) suggest that the kinetic equilibrium for the dimerization of pinic acid favours the formation of the dimer even at monomer concentrations of the order of 1E-06 torr.

Fig.1: *The referee finds that the figure caption as well as the text of the manuscript do not explicitly state whether experimental or calculated data are presented in this Figure.*
The figure and the text have been revised to provide a clearer description of the data.

Fig.2: The structure of the parent compound of pinic acid is indeed not correct in Fig. 2. The structure is corrected in the revised version.

Fig.5: *The figure does not bring a conclusive comparison according to the referee.*
This figure presents vapour pressure estimations of alpha-pinene products using the new method. Species-specific estimations calculated for these products are also represented for comparison. Since UNIFAC has been proved to perform better than a wide set of other current methods (Asher et al, 2002), we see little interest to compare the new method with these other methods.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 11249, 2005.