**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Technical Note: Estimating fusion properties for polyacids" *by* S. Compernolle et al.

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1 Answers for referee 1

We thank referee 1 for critically reading our manuscript and proposing changes for improvements. Our answers to his comments are given below.

1.1 General comments

The authors test several estimation methods for DH(fus) DS(fus) and T(fus) against a set of experimental data for dicarboxylic acids. They assess the effectiveness of the

estimation methods and then create a new model for the first two of these properties. I am unable to recommend this paper for publication in Atmospheric Chemistry and Physics for the following reasons:-

1) The experimental dataset is too limited. It consists of 24 structurally very closely related compounds from 3 sets of data, 2 of which were provided by the same group using the same methods.

2) The scope of the new correlation is very limited. It is limited to C3- C10dicarboxylic acids substituted with either saturated hydrocarbon rings, methyl groups or carbonyl and/or alcohol groups. Adding, for example, mono acids would certainly expand the applicability and allow a much wider range of input data, as would adding suitable substituted mono acids.

We have extended our dataset. Apart from extra dicarboxylic acids (with or without other functionalities), we have now included also monocarboxylic keto- and hydroxy acids and compounds with up to four acid functionalities. Note that we did not include monocarboxylic acids without other functional groups, as (i) their melting point is generally below or close to room temperature (for the molecule size we consider: up to ten carbon atoms) making a solid-to-subcooled liquid correction of vapour pressure less stringent, (ii) they are not likely to be important SOA contributors, (iii) they are probably adequately described by existing estimation methods. Whereas our dataset previously consisted of 24 $(T_{\text{fus}}, \Delta H_{\text{fus}})$ data point couples (Table 1 in the discussion paper) and 9 T_{fus} data points (Table 2 in the discussion paper, only used for evaluation), now our dataset for fitting includes 33 $(T_{\text{fus}}, \Delta H_{\text{fus}})$ data point couples and 53 T_{fus} data points.

We also changed our fitting approach. Whereas we previously took only $(T_{\text{fus}}, \Delta H_{\text{fus}})$ data point couples into account for the fitting, and used the isolated T_{fus} points only for evaluation of the model, now all data is used for fitting and evaluation. In this way we make a maximal use of our data to constrain our model.

Moreover, we searched for data of several references per molecule. In case all data

agreed satisfactorily for a molecule, only data of one reference was taken into account. In a few instances, quite different T_{fus} data points or $T_{\text{fus}}, \Delta H_{\text{fus}}$ data point couples were found for a compound with the same, non-stereospecific, structural formula. Sometimes this could clearly be ascribed to the fact that the compounds were different stereo-isomers, but of course also experimental uncertainty could play a role. These data points were then all taken into account. In this way, the dependence on the choice of experimental result is minimised. As the method has now a wider scope, we extended it with one extra variable: the number of carboxylic acid functionalities n_{COOH}.

We hope we have addressed with this the concerns of the referee on the size of the dataset (point 1) and the scope of the method (point 2).

3) The model is purely empirical- there is little attempt to analyze the experimental data and relate the modeling work to any scientific insights about (for instance) crystal packing in the solid phase or the role of molecular symmetry in determining the entropy of the liquid phase.

The method is indeed empirical, although the chosen variables are very likely to be important in the determination of the fusion properties. See also our answer on question 2 of referee 2. The variable τ plays a similar role as the carbon groups CH_n in more detailed group-contribution methods. This makes our method similar to a standard group contribution method. We note that empirical group-contribution methods are widely used to determine thermodynamic properties. For example, the methods of Marrero-Gani, Joback-Reid, mentioned in the discussion paper, to calculate $T_{\text{fus}}, \Delta H_{\text{fus}}$, the SIMPOL method (Pankow and Asher, 2008) to calculate liquid vapour pressure, the UNIFAC method (Fredenslund et al., 1975; Hansen et al., 1991) to calculate activity coefficients, etc. These last two methods are used frequently to estimate aerosol properties.

The referee mentions molecular symmetry as potentially important in determining the entropy of the liquid phase. This concept was used by Yalkowsky and cowork-

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ers, e.g. Dannenfelser and Yalkowsky (1996) and used in the methods of Zhao and Yalkowsky (1999) and Jain *et al.* (2004) investigated in the discussion paper. Possibly the referee refers to this. We note that most molecules in our data set are flexible, i.e. they have more than two rotatable bonds, or $\tau \geq 1$, and thus are counted, according to e.g. Walters and Yalkowsky (1996), as assymetrical and assigned the minimal molecular symmetry number of one. So for most molecules in our data set the concept of moleculary symmetry, at least as defined by Yalkowsky and coworkers, is not important.

As suggested by the referee, we tried this definition of molecular symmetry number as a variable, and also a modified one where flexibility does not reduce the molecular symmetry number. In both cases, adding this variable did not improve significantly the correlation. We mention this now in the text.

The referee mentions also crystal packing. Crystal packing will indeed be important in determining fusion properties. One known example, discussed in Thalladi (2000) and incorporated in our method, is the particularly stable conformation attained by linear chain diacids with even carbon number. However, it is very difficult to take the effect of crystal packing into account for the nonlinear molecules in our dataset, as we mostly don't have their crystal packing information. Crystal packings and their energies can, at least in principle, be calculated by quantum chemical methods, but this is beyond the scope of this work: a method for quickly estimating the fusion properties of functionalized acids, based on molecular information only, that is better than existing methods.

Again, we certainly do not suggest that crystal packing is not important in the determination of fusion properties. The fact that fusion properties are in general more difficult to predict than vaporisation properties (vapour pressure, enthalpy of vaporisation) is probably to a large extent due to the unaccounted for effects of crystal packing.

This work would have been fine if it had been presented in conjunction with other results (eg. additional experimental data) or alternatively the authors could have waited until

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further experimental data were available and then presented a model which covered a much more structurally diverse group of dicarboxylic acids from additional groups of researchers.

We cannot agree with this point. 'Waiting until further experimental data becomes available' would mean a hold on scientific progress. In our case, an improved fusion property estimation method was necessary for the development of our method EVAPORATION to calculate vapour pressures of liquids (Compernolle et al., 2011). We needed to convert sublimation pressures to subcooled liquid vapour pressures for a number of molecules in our database. For several functionalized acids -an important target of our method but for which data is scarce- the necessary fusion data was not available and existing fusion property estimation methods were not reliable. Other research groups could face a similar obstacle. Instead of simply omitting this vital sublimation data, converting it to wrong subcooled liquid vapour pressures with an existing method, or waiting until further experimental data becomes available, we wanted to have a method that gives the best estimation based on our current knowledge. If more data becomes available, new and better models can still be developed.

In its present form the paper doesn't have sufficient scientific merit to warrant publication. I do however see a lot of use for being able to estimate the necessary parameters for sub-cooled liquid corrections, as it will allow us to use certain datasets which currently only have solid data. I certainly recommend addressing the points raised here.

We are glad that the referee recognizes the need for a model providing sub-cooled liquid corrections. We hope that by extending our dataset and the scope of our method, he/she will find the revised paper acceptable.

1.2 Specific comments

If the paper is to be published then the following significant points should be addressed:

- Page7537, line 25:- "the difference between solid and liquid heat capacity" – "at T(fus)" should be added. Note that at T(fus) the heat capacity if infinite so Cp (solid) and Cp(liq) at T(fus) have to be obtained by extrapolation from temperatures below and above T(fus) respectively.

A more extensive discussion on $\Delta C_{p,ls}$ is now included. Following sentences or sentence parts are added:

"$\Delta C_{p,ls}$ is taken at the fusion point".

"Note that $C_{p,s}$, $C_{p,l}$ at T_{fus} become infinite so they have to be obtained by extrapolation from temperatures below and above T_{fus} respectively."

Page7538, lines 16-22:- What are the authors trying to do in this section? How are the standard deviations in equations 3-5 calculated and what do they mean?

For linear diacids, C3 - C10, T_{fus} and ΔH_{fus} fusion data from several reference sources are available. Their comparison provides an indication as to how much variation there is on the measurements for fusion properties. The standard deviations were calculated according to the formula (here for ΔH_{fus}):

$$\sigma_i^2 = \sum_k \left(\Delta H_{\mathsf{fus},i,k} - \overline{\Delta H}_{\mathsf{fus},i} \right)^2$$

$$\mathsf{STD}\left(\Delta H_{\mathsf{fus}} \right) = \sqrt{\frac{1}{N} \sum_i \sigma_i^2}$$

where i runs over the linear diacids (C3 to C10) and k over different reference sources per linear diacid. $\overline{\Delta H}_{\mathsf{fus},i}$ is the mean over the different reference sources for diacid i. N is the total number of data points. A similar formula was employed for the STD for $\Delta S_{\mathsf{fus}}, T_{\mathsf{fus}}$.

Note that we accidentally interchanged the values for the STD of ΔS_{fus} and T_{fus}. It should have been $\mathsf{STD}(\Delta S_{\mathsf{fus}}) = 4.1 \mathsf{J} \, (\mathsf{K\,mol})^{-1}$ and $\mathsf{STD}(T_{\mathsf{fus}}) = 2.8 \, \mathsf{K}$.

As these STD's are not essential for the rest of the manuscript, we chose to not retain these in the revised paper.

Lines 21-22:- How do the authors calculate that these experimental errors correspond to an uncertainty of 0.36 in log(P(l)/P(s)). Surely this quantity depends upon the absolute values of DH(fus), DS(fus) and T(fus) as well as the error in them, so which compound was used in this example? This whole section needs to be significantly clarified.

We acknowledge that this section was too vague. The following procedure was used to calculate the uncertainty in $\log_{10}\left(\frac{p_l^0}{p_s^0}\right)$.

In case $\Delta C_{p,ls} = 0$ can be assumed, $\log_{10}\left(\frac{p_l^0}{p_s^0}\right)$ at 298 K is given by

$$\log_{10}\left(\frac{p_l^0}{p_s^0}\right) \;=\; \frac{\Delta H_{\mathsf{fus}}}{R\ln(10)\,(298\,\mathsf{K})} - \frac{\Delta S_{\mathsf{fus}}}{R\ln(10)}$$

The uncertainty was then calculated according to

$$\sqrt{\left(\frac{\mathrm{STD}\,(\Delta H_{\mathsf{fus}})}{\ln(10)R\,(298\,\mathsf{K})}\right)^2 + \left(\frac{\mathrm{STD}\,(\Delta S_{\mathsf{fus}})}{\ln(10)R}\right)^2}$$

where $\mathrm{STD}\,(\Delta H_{\mathsf{fus}})$, $\mathrm{STD}\,(\Delta S_{\mathsf{fus}})$ were given at the previous point. We do no longer mention this uncertainty in the revised manuscript.

Page7538,lines 20:- The authors bring up two new sources of data on dicarboxylic acids that are not included in Table 1, nor in assessing and improving the estimation methods. Could the authors please explain this.

We judged the data from Cingolani (1974) and Hansen (2004) to be sufficiently close to the data already taken into account (from Booth (2010) and Roux (2005)), and hence that it was not necessary to take this data also into account, or to present it in Table 1. In the new table S1 of the Supplementary Material, all these references and

more are now presented. For the linear diacids, and most other compounds in our data set, we still use one reference source for the actual fitting and evaluation of the model. Another possibility would have been to take all available data from the different reference sources into account. But then it would have been necessary to include a weighting factor, such that a molecule for which a lot of data is available (such as the diacids) would not dominate the fitting. We judged this whole procedure unnecessary, especially as the model error is significantly larger than the experimental error. Now we took multiple reference sources into account only if important differences exist between them, and it is unclear which one is the most reliable.

Page7538 ,lines 22:- it is not clear why the authors have derived the property w problems with the oxalic acid T(fus), which could be done in other ways (eg. Plotting out T(fus) against carbon number). Can this property help to explain the variation in T(fus) and perhaps DH(fus) and DS(fus) with molecular structure via considerations of crystal packing? In the paper as it stands there is no reason to derive w.

We have now defined ω_{ls} earlier on in the text, as $\omega_{ls} = \log_{10}\frac{p_l^0}{p_s^0}$. It is an important quantity as it represents the correction from solid to subcooled liquid. In case $\Delta C_{p,ls} = 0$, it coincides with the definition employed in the discussion paper.

Page 7539, Would it be possible to estimate the DH(fus)for oxalic using the solid and liquid vapour pressures of soonsin et al 2010? Although there is (a lot of) disagreement about the solid VP values, the differences between the solid and liquid VP seem more consistent between the techniques, so it might be possible to back out the properties required for the sub-cooled correction.

Yes, but it would require relying on the assumption that the activity coefficient of oxalic acid in water is adequately described by UNIFAC-Peng, which could not be demonstrated by Soonsin (2010) because of lack of data, as opposed to malonic, succinic and glutaric acid.

In general, ΔH_{fus} could be found by saturation concentration data (see e.g. Prausnitz,

1999)

$$- \ln \left(x_{\text{sat}} \gamma_{\text{sat}} \right) \quad \approx \quad \frac{\Delta H_{\text{fus}} \left(T_{\text{fus}} \right)}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{fus}}} \right) - \frac{\Delta C_{p,ls}}{R} \left(\frac{T_{\text{fus}}}{T} - 1 - \ln \frac{T_{\text{fus}}}{T} \right) \quad (1)$$

Knowledge of $x_{\text{sat}}, T_{\text{fus}}$, and approximations for γ_{sat} (e.g. UNIFAC-Peng) and $\Delta C_{p,ls}$ (e.g. from 0 to ΔS_{fus}) would allow to derive $\Delta H_{\text{fus}} \left(T_{\text{fus}} \right)$. We have done a check for the linear diacids C3-C9, where both $\Delta H_{\text{fus}}(T_{\text{fus}})$ and x_{sat} are known. We found however that for the longer chains, γ_{sat} has to be much higher than predicted by UNIFAC-Peng (for reasonable approximations of $\Delta C_{p,ls}$). So we concluded that this method is not accurate enough to provide additional fusion data. We did however include this work in a separate section, as knowledge on γ_{sat} is certainly relevant.

Page7540, Eq. 10, also Page 7541, Eq. 11-14:- This is inappropriate use of the term standard deviation. Standard deviation is the measure of the scatter around a mean value. For a correlation the equivalent statistic is the standard error of estimate (SEE)(see Kachigan 1991, chapter 4) which takes a form similar to Eq. 10 except that the summation is divided by the number of degrees of freedom (not by N-1). This raises the issue of how many degrees of freedom to use in a multiple regression. Rather than using SEE or an equivalent statistic it is more usual to quote R2 (also known as coefficient of determination) and to compare values between different correlations. where y(est) and y(exp) are the predicted y values (from the correlation) and experimental y values respectively and y(m) is the mean of the experimental y values. Rather than quoting the PRESS statistic a cross validation R2can then be quoted (using the above formula) calculated from the leave-one-out validation for the regression model.

We use now the concepts mean deviation (MD), mean absolute deviation (MAD) and predicted MD, MAD, similar as in Compernolle et al. (2011), and in addition, R^2 and cross-validated R^2 as suggested by the referee.

Page7541, Section 4:-A plot of y(est) vs. y(exp) for DH(fus) and DS(fus) by the new correlations with some discussion about the distribution of residuals (particularly any

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outliers) should be included.

We include now plots, estimated vs. experimental, for $T_{\text{fus}}, \Delta H_{\text{fus}}, \Delta S_{\text{fus}}$, with some discussion.

Page 7543, Section 5:- Can the authors discuss the significance of the w values calculated for the compounds in Table 6. What is the significance of pinic acid having the lowest value and 4-oxo-pimelic acid having the highest??

The ω_{ls} values are a measure for the correction factor needed to convert sublimation pressure to subcooled liquid vapour pressure. This is now explained in more detail in the text. Table 6 of the discussion paper is no longer present in the revised paper, but instead plots of experimental vs. modelled ω_{ls} are presented.

Page 7543, Section 6:- Conclusions:- Authors should make it clear what are the structural limitations of the set of compounds whose properties could be estimated from these new correlations ie:- C3-C10diacids substituted with any combination of methyls/saturated rings/alcohol/ketone groups?

We included the sentence: "A simple method is developed to estimate the fusion properties of C2-C10 saturated acids, with one or more other functional groups: hydroxyl, carbonyl and/or acid."

Table 6, can the authors add their estimate for the sub-cooled liquid vapour pressure for these compounds, I believe the solid state data is present in the literature.

Table 6 is no longer present in the revised manuscript. Also, given the considerable uncertainty on solid vapour pressures of diacids, we think it is best to keep the focus on the solid-to-liquid conversion in this manuscript.

- Page7536,line 21:- "Vapor pressures of polyacids have been measured since decades..." I think the authors mean "over several decades"

Sentence has been changed.

Page7536,line 25:- "Unfortunately, pure diacids are solid at ambient temperatures..." I strongly suspect that some will be found that are not- would suggest inserting "most" after unfortunately.

"most" included.

Page 7537,lines 4/5:- suggest rewording to "In such cases, the activity coefficient is also needed..."

Sentence has been changed.

Page7538, line 3:- It might be worth saying there are 3 common ways of getting round the lack of delCp data eg, delCp = 0, 0.5delS(fus) or delS(fus)

We include now a more extensive discussion on $\Delta C_{p,ls}$, where this point is included.

Page7538 line 9:- Joback tends to give bad Tb data too, and M&Y (like most methods) tends to do badly with diacid vapour pressure,

This is correct. I added on page 7537, after line 19: "Booth (2010, 2011) measured sublimation pressures of several diacids, converted them to subcooled liquid vapour pressures, and compared them then to several methods that estimate liquid vapour pressure from molecular structure. The conclusion was that none of these methods performed well."

Page 7538,lines14/15:- suggest rewording to "In those cases where solid-solid transitions were present the sum over all transitions was taken."

Sentence has been changed.

Page 7538, Eq 3 and 4- superscript "-1" at the end of each equation.

We have put R^2 now instead of STD, so units are no longer necessary.

Page7540, line 4, should this read "..., are *not* formally delH(fus) group contribution methods," otherwise I can't really follow the sentence

Zhao (1999) and Jain (2004) treat ΔH_{fus} as a sum over functional groups, which is why one could consider it a ΔH_{fus} group contribution method. But they are not fitted to ΔH_{fus} data. Instead $\Delta H_{\text{fus}}^{\text{est}}/\Delta S_{\text{fus}}^{\text{est}}$ is fitted to T_{fus}, where $\Delta S_{\text{fus}}^{\text{est}}$ is also estimated. So these methods are more applicable to estimation fusion points than fusion enthalpies.

To make the sentence clearer, the sentence is changed into:

"The T_{fus} estimation method of Zhao (1999) (ZY) is a composite method: ΔS_{fus} is fixed by the MY method ($\Delta S_{\text{fus}}^{\text{MY}}$) and ΔH_{fus} is written as a sum of group contributions $\sum_i n_i g_i$, with the contributions g_i determined by fitting $\left(\sum_i n_i g_i\right)/\Delta S_{\text{fus}}^{\text{MY}}$ to experimental T_{fus}. The more recent variant Jain (2004) (JYY) is derived along the same lines, but with ΔS_{fus} fixed by the JYY method."

Page 7543,line 1:- compare Table 5 with Table 4 (not Table 3).

These tables are no longer present. Instead, the errors of the literature methods and the newly developed method are put on plots of estimated vs. experimental data.

Also DH(fus) units in Table 4 are KJ.mol-1 while in Table 5 they are in J.mol-1. Consistent use of the same units would aid comparison between tables.

This table is no longer present. The unit of kJ mol-1 is now used consistently.

Page 7543, line 4 :- to improve clarity replace "these methods" with "the Section 3 methods."

"these methods" replaced with "the methods described in Section 3".

2 Answers for referee 2

We thank referee 2 for carefully reading our manuscript and suggesting improvements. Our answers to his comments are given below.

2.1 General comments

1. The dataset is limited. The number of compounds could be implemented with some monocarboxylic and tricarboxylic acids. Moreover, the authors use one single reference per compound and property (Table 1). Please justify this choice, or implement with other datasets. One could otherwise consider the good performance of the model as purely accidental, based on similar compounds and on one, specific experimental result.

See the answer on the first two general comments of referee 1.

2. The model, for the general reader, may appear arbitrary in its construction. What are the reasons for choosing that set of variables (tau, n_OH, and n_CO): physico-chemical or purely statistical? Did the authors try different combination of variables and took at the end the best choice justified by a satisfactory statistical PRESS approach?

We tried a few combinations of variables. We already mentioned in the discussion paper the testing, and rejection, of carbon number and cyclicity as a variable. Together with the variables presented in the discussion paper, these were the only variables tested for the discussion paper. Hence it is not that we tried a large number of arbitrary variables and kept only the best. The chosen variables are certainly not arbitrary. To limit the number of variables, the same variables were chosen for the estimation of ΔS_{fus} and ΔH_{fus}.

- $n_{\text{OH}}, n_{\text{CO}}$: As chemical interactions are important both in the liquid and the solid

phase, chemical functional groups (OH, C=O, C(=O)OH) are likely to be important variables. As the dataset of the discussion paper consisted almost exclusively of diacids, n_{COOH} was at that point not taken as a separate variable. Now, with the inclusion of mono-, tri- and tetraacids, it is. Note that several group contribution methods for $T_{\text{fus}}, \Delta H_{\text{fus}}$ (see e.g. the methods of Joback and Gani, mentioned in the discussion paper) and ΔS_{fus} (Kolska et al., 2005) exist in the literature, underpinning the importance of functional groups for fusion properties.

- τ : This is a measure of the flexibility of the molecule and has been used before to estimate ΔS_{fus}. For ΔH_{fus}, it plays a similar role as the carbon groups (CH$_n$) in more detailed group contribution methods: $n_{\text{CH}_2} + n_{\text{CH}} + n_{\text{C}}$ is the contribution of the noncyclic carbon groups to τ, and this will in most cases be the dominant part.

- i_{even}: The particularly high $\Delta H_{\text{fus}}, \Delta S_{\text{fus}}$ of linear diacids with an even number of carbon atoms can be explained by the stable crystal structure for these compounds (Thalladi, 2000). The choice of this variable is hence motivated by physico-chemical considerations.

3. Table 6 should be extended to all the other suitable compounds and properties and include the experimental and producer's values for comparison (where available). It may be merged with Table 1 and/or 2, for instance.

We have now included all experimental $T_{\text{fus}}, \Delta H_{\text{fus}}$ in one table, together with the SMILES notation for each compound, and the estimated $T_{\text{fus}}, \Delta H_{\text{fus}}$. Due to the large size of this table, the table is included in the Supplementary Material instead of in the main manuscript. ω_{ls}, both experimental and estimated (assuming $\Delta C_{p,ls} = 0$), is also included in the Supplementary Material.

4. There is a lack of graphical visualization of the results (6 tables and no figure). For instance, one graph with estimations versus experimental results would be desirable.

We include now plots of $T_{\text{fus}}, \Delta H_{\text{fus}}, \Delta S_{\text{fus}}, \omega$, modelled vs. experimental, for the various literature models and our own model. The mean deviation and mean absolute deviation are given on the figures themselves. Table 4 and 6 of the discussion paper are then skipped.

2.2 Specific comments

Suggested Title: "Technical Note: Estimating fusion properties of a series of poly-acids".

As we enlarged the scope, the title now is "Technical Note: Estimating fusion properties of functionalised acids." We do not think "a series of" would improve on the title.

Introduction. The authors do not mention experimental methods. The reader cannot distinguish high T methods from ambient T, or bulk from particles.

We mention now the different experimental methods used to measure the vapour pressure of diacids, if it is at high T or ambient T, and if bulk or aerosol samples are used.

7536, 2. The statement is too strong. There is experimental evidence, and theoretical support, that multi-component OA is likely to be liquid, or partially liquid.

Changed the sentence into:

"Multicomponent organic aerosol (OA) is likely to be liquid, or partially liquid."

7536, 25. Reformulate. I would mention the possibility of solid stable/liquid metastable state of those compounds in a condensed phase.

We changed the sentence into:

"Unfortunately, most pure diacids are stable as solid at ambient temperature, although a liquid metastable state can also occur.

7537, 2. "Very prone to error". This is in principle true, but actually there are also examples of amazing agreement. Succinic acid (you cite Ribeiro and DaSilva, 2001) is one example. Reformulate.

We changed the sentence into:

"To obtain the liquid vapor pressure, one could extrapolate from measurements above the melting point T_{fus}. As T_{fus} can be a few hundred Kelvin above the temperature of interest, this approach is prone to error, although there are also examples of excellent agreement, e.g. for succinic acid (Riipinen 2006)."

7537, Eq1 - and 7538, line 4. The authors do not talk about DeltaC_p. This is critical to get the correct liquid state vapor pressure form the solid state, since DeltaC_p can vary from zero up to DeltaS. Can the authors say something (briefly) on the best choice of DeltaC_p based on their estimate of the other fusion properties?

We included now an extensive discussion on $\Delta C_{p,ls}$ and the impact of the different assumptions for this quantity. However, it is difficult to conclude on the basis of only $T_{\text{fus}}, \Delta H_{\text{fus}}$ data which assumption is the best.

7538 Eq3,4,5. How did you calculate the STD? Please reformulate lines 19-22.

This question was already answered for referee 1.

Section 5. Too short. Expand or move it before.

This section is removed in the revised paper.

Table 2. Please add a column with producer's values: they are often used for back of the envelope calculations, but can differ substantially among different experimental methods.

In Table S1, we included also data from the producent Sigma Aldrich. We hope this meets his concerns.

2.3 Minor/Technical comments.

7539, 3. Roughly speaking(?)

This sentence is no longer present in the revised manuscript.

7541, 14. As is well known (?)

"As is well known" is scrapped.

7543, 1. Table 3? You probably mean Table 4.

Indeed. These tables are no longer present in the revised manuscript. The data on the errors is put on plots of estimated vs. experimental fusion properties.

7543, 3. This should of course not be a surprise(?)

We formulate it now as:

"This can at least in part be ascribed to the fact that much experimental data used to develop this model is more recent than the methods described in Section 3. "

7543, 10. no way (?)

As we now include also data when only the fusion temperature is known, this sentence is no longer present in the revised manuscript.

References

Compernolle, S., Ceulemans, K., and Müller, J.-F.: EVAPORATION: a new vapor pressure estimation method for organic molecules including non-additivity and intramolecular interactions, Atmos. Chem. Phys. Discuss., 11, 13 229–13 278, 2011.

Dannenfelser, R.-M. and Yalkowsky, S. H.: Estimation of Entropy of Melting from Molecular Structure: A Non-Group Contribution Method, Ind. Eng. Chem. Res., 35, 1483–1486, 1996.

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Fredenslund, A., Jones, R. L., and Prausnitz, J. M.: Group-Contribution Estimation Of Activity-Coefficients In Nonideal Liquid-Mixtures, AIChE J., 21, 1086–1099, 1975.

Hansen, H. K., Rasmussen, P., Fredenslund, A., Schiller, M., and Gmehling, J.: Vapor-Liquid-Equilibria By Unifac Group Contribution .5. Revision And Extension, Ind. Eng. Chem. Res., 30, 2352–2355, 1991.

Kolska, Z., Ruzicka, V., and Gani, R.: Estimation of the Enthalpy of Vaporization and the Entropy of Vaporization for Pure Organic Compounds at 298.15 K and at Normal Boiling Temperature by a Group Contribution Method, Ind. Eng. Chem. Res., 44, 8436–8454, 2005.

Pankow, J. F. and Asher, W. E.: SIMPOL.1: a simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds, Atmos. Chem. Phys., 8, 2773–2796, 2008.

Walters, W. P. and Yalkowsky, S. H.: ESCHERA Computer Program for the Determination of External Rotational Symmetry Numbers from Molecular Topology, Journal of Chemical Information and Computer Sciences, 36, 1015–1017, 1996.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 7535, 2011.