

Estimating fusion properties for functionalised acids

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Abstract. Multicomponent organic aerosol (OA) is likely to be liquid, or partially liquid. Hence, to describe the partitioning of these components, their liquid vapour pressure is desired. Functionalised acids (e.g. diacids) can be a significant part of OA. But often measurements are available only for solid state vapour pressure, which can differ by orders of magnitude from their liquid counterparts. To convert such a sublimation pressure to a subcooled liquid vapour pressure, fusion properties (two out of these three quantities: fusion enthalpy, fusion entropy, fusion temperature) are required. Unfortunately, experimental knowledge of fusion properties is sometimes missing in part or completely, hence an estimation method is required. Several fusion data estimation methods are tested here against experimental data of functionalised acids, and a simple estimation method is developed, specifically for this family of compounds, with a significantly smaller estimation error than the literature methods.

1 Introduction

Diacids can be a significant part of OA, according to both field measurements and smog chamber experiments (Limbeck et al., 2001; Baboukas et al., 2000; Claeys et al., 2007; Yu et al., 1999). Due to the multicomponent nature of OA it is often glassy or liquid-like at ambient temperature even if the individual components are crystalline solids when in pure state, as was recently demonstrated for a mixture of diacids (Cappa et al., 2008b). To describe the partitioning of a compound to the aerosol, its liquid vapour pressure is required. Vapour pressures of polyacids have been measured over sev-

eral decades (Bradley and Cotson, 1953; Arshadi, 1974) but recently work in this area has intensified, with several publications in the last two years (Booth et al., 2010, 2011; Frosch et al., 2010; Soonsin et al., 2010; Pope et al., 2010).

Unfortunately, most pure diacids are stable as solid at ambient temperature, although a liquid metastable state can also occur. To obtain the liquid vapour 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 et al., 2006). Some groups have measured, at ambient temperature, the vapour pressure of the liquid diacid in water/diacid droplet particles, using the electrodynamic balance (EDB) (Zardini et al., 2006; Pope et al., 2010; Soonsin et al., 2010) or the tandem differential mobility analyzer (TDMA) techniques (Riipinen et al., 2007; Koponen et al., 2007). In such cases, the activity coefficient is also needed in order to determine the vapour pressure of the pure diacid, which can be calculated using empirical methods (Peng et al., 2001; Hansen et al., 1991). Other groups have measured, at ambient temperature (or for Ribeiro da Silva et al. (2000, 2001), at least below T_{fus}), the vapour pressure of the solid using temperature programmed desorption (Cappa et al., 2007, 2008a), TDMA (Frosch et al., 2010; Salo et al., 2010; Bilde and Pandis, 2001; Bilde et al., 2003) or EDB (Soonsin et al., 2010) on aerosol particles and Knudsen effusion on bulk samples (Ribeiro da Silva et al., 2000, 2001; Booth et al., 2010, 2011). However, there can be orders of magnitude difference between measurements of different groups for the same compound (e.g. for sebacic acid, 3 orders of magnitude between Cappa et al., 2007 and Salo et al., 2010), way above the reported experimental errors (typically 30–50 %). It has been speculated that this might be due to the experimental technique employed (Cappa et al., 2007; Pope et al., 2010) or to



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the physical nature of the diacids (Zardini et al., 2006; Soon-sin et al., 2010; Salo et al., 2010) (presence of defects; partially or completely liquid/amorphous character). Soon-sin et al. (2010) have measured subcooled liquid vapour pressures of mixtures with only a very small water content, and vapour pressures of the saturated solution, which allows the derivation of the vapour pressure of the pure liquid and solid, respectively.

Booth et al. (2010, 2011) measured sublimation pressures of several diacids, converted them to subcooled liquid vapour pressures using fusion data, and then compared them to several methods that estimate liquid vapour pressure from molecular structure. The conclusion was that none of these methods performed well.

Even if a given experimental sublimation pressure can be considered accurate, one still needs fusion data (fusion temperature T_{fus} , enthalpy ΔH_{fus} and entropy ΔS_{fus}) to obtain a subcooled liquid vapour pressure (Prausnitz et al., 1999), but it occurs often that fusion data is unavailable, or only the fusion temperature is known (Ribeiro da Silva et al., 2000; Monster et al., 2004; Frosch et al., 2010). General estimation methods for T_{fus} , ΔH_{fus} (Joback and Reid, 1987; Marrero and Gani, 2001; Zhao and Yalkowsky, 1999) or ΔS_{fus} (Myrdal and Yalkowsky, 1997; Jain et al., 2004a) give significant errors for functionalised acids, as we will show below. Therefore, a simple method is developed in this work to estimate the fusion properties of C_2 – C_{10} saturated acids, with one or more other functional groups: hydroxyl, carbonyl and/or acid. This method is then compared with methods of the literature.

2 Literature data

In Table S1 of the Supplement, we present experimental fusion data for functionalised acids. Important data sources were Linstrom and Mallard (NIST), Acree and Chickos (2010), Booth et al. (2010, 2011), Lide (2000) and Aldrich (1990). In those cases where solid-solid transitions were present the sum over all fusion data was taken:

$$\Delta H_{\text{fus,tot}} = \sum_i \Delta H_{\text{trans},i} \quad (1)$$

$$T_{\text{fus,tot}} = \frac{\Delta H_{\text{fus,tot}}}{\Delta S_{\text{fus,tot}}} \quad (2)$$

In many cases, only T_{fus} was available, not ΔH_{fus} . For example, ΔH_{fus} was measured for only a small minority of the compounds in our dataset with one acid functionality. This is an obvious obstacle to model development.

Whenever possible, we included per compound multiple reference sources. If different sources agreed, only one was taken into account, and prevalence was given to the case where both T_{fus} and ΔH_{fus} are available. In a few instances, quite different T_{fus} data points or T_{fus} , ΔH_{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.

For oxalic acid, T_{fus} reported by Booth et al. (2010) conflicts with the transition data reported by NIST and Thaladi et al. (2000). It is possible that Booth et al. (2010) found a solid-solid transition point rather than a fusion point (A. M. Booth, personal communication, 2010). However, interpretation of experimental data is hampered due to uncertainty regarding the precise structure of the solid oxalic acid (Soon-sin et al., 2010). Therefore, we exclude oxalic acid in our comparison analysis of experimental with modeled data.

3 Solid to liquid conversion: impact of heat capacity difference

A subcooled liquid vapour pressure p_l^0 is not directly experimentally accessible, unless a metastable liquid state can be prepared. We are interested in the factor necessary to convert sublimation pressure to subcooled liquid vapour pressure,

$$\omega_{ls}(T) \equiv \log_{10} \frac{p_l^0(T)}{p_s^0(T)} = \frac{\Delta H_{\text{fus}}(T)}{\ln(10)RT} - \frac{\Delta S_{\text{fus}}(T)}{\ln(10)R} \quad (3)$$

with $\Delta H_{\text{fus}}(T)$, $\Delta S_{\text{fus}}(T)$ ¹ the enthalpy, entropy difference between subcooled liquid and solid state respectively at temperature T . These can be found from knowledge of the fusion data at the triple point T_{tr} , $\Delta H_{\text{fus}}(T_{\text{tr}})$, $\Delta S_{\text{fus}}(T_{\text{tr}}) = \frac{\Delta H_{\text{fus}}(T_{\text{tr}})}{T_{\text{tr}}}$, and the heat capacity C_p of both solid and subcooled liquid in the temperature region $[T, T_{\text{tr}}]$ (e.g. Prausnitz et al., 1999).

$$\Delta H_{\text{fus}}(T) = \Delta H_{\text{fus}}(T_{\text{tr}}) + \int_{T_{\text{tr}}}^T (C_{p,l}(T') - C_{p,s}(T')) dT' \quad (4)$$

$$\Delta S_{\text{fus}}(T) = \Delta S_{\text{fus}}(T_{\text{tr}}) + \int_{T_{\text{tr}}}^T \frac{(C_{p,l}(T') - C_{p,s}(T'))}{T} dT' \quad (5)$$

T_{tr} is generally unavailable for the compounds of our interest, but replacement with the fusion temperature T_{fus} incurs little error (Prausnitz et al., 1999). As $C_{p,l}(T)$ is not accessible below the triple point, one possible solution is to extrapolate it. Another common approximation is to assume that the

¹Note that we indicate the temperature dependence of ΔH_{fus} , ΔS_{fus} only in this section. In the other sections it is always assumed that they are taken at T_{fus} .

difference $\Delta C_{p,ls} = C_{p,l} - C_{p,s}$ is temperature-independent:

$$\Delta H_{\text{fus}}(T) \approx \Delta H_{\text{fus}}(T_{\text{fus}}) + \Delta C_{p,ls}(T - T_{\text{fus}}) \quad (6)$$

$$\Delta S_{\text{fus}}(T) \approx \Delta S_{\text{fus}}(T_{\text{fus}}) + \Delta C_{p,ls} \ln \frac{T}{T_{\text{fus}}} \quad (7)$$

where $\Delta C_{p,ls}$ 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 (see e.g. Neau et al., 1997). In our case, the temperature of interest can be hundreds of Kelvin below the fusion point, but as $C_{p,l}(T)$ below T_{fus} is inaccessible, it is difficult to assess the error incurred by approximations (6) and (7).

Unfortunately, for the compounds of our interest, a measured $\Delta C_{p,ls}$ is typically unavailable. Common approximations are (Grant et al., 1984)

$$\Delta C_{p,ls} T \ll \Delta H_{\text{fus}}(T_{\text{fus}}) - \Delta C_{p,ls} T_{\text{fus}} \Rightarrow \Delta C_{p,ls} \approx 0 \quad (8)$$

$$\Delta C_{p,ls} T \gg \Delta H_{\text{fus}}(T_{\text{fus}}) - \Delta C_{p,ls} T_{\text{fus}} \Rightarrow \Delta C_{p,ls} \approx \Delta S_{\text{fus}}(T_{\text{fus}}) \quad (9)$$

Also the intermediate approximation, $\Delta C_{p,ls} \approx 0.5 \Delta S_{\text{fus}}(T_{\text{fus}})$ can be taken (Tsonopoulos, 1970). In Fig. 1 the sensitivity of $\omega_{ls}(T)$ on the two extreme approximations for $\Delta C_{p,ls}$ (Eqs. 8 and 9) is explored. $\log_{10} \frac{p_l^0}{p_s^0}$ at 298 K differs for glutaric acid only by 0.08 (a factor 1.2 for $\frac{p_l^0}{p_s^0}$) between both assumptions, by 0.38 for succinic acid (a factor 2.4) and by 0.91 for tartaric acid (a factor 8.2). While for a compound such as tartaric acid the choice for $\Delta C_{p,ls}$ is certainly relevant, for most compounds in our dataset where both T_{fus} , ΔS_{fus} are known, $\log_{10} \frac{p_l^0}{p_s^0}$ differs by 0.3 or less between both extreme assumptions. This is often within the uncertainty on $\log_{10} p_s^0$.

Chickos (2003) present a group contribution method to estimate $C_{p,l}$, $C_{p,s}$ at 298.15 K. As we assume that $\Delta C_{p,ls}$ is temperature-independent, we could set

$$\Delta C_{p,ls} \approx \Delta C_{p,ls}(298.15\text{K}) \approx C_{p,l}^{\text{Chickos}}(298.15\text{K}) - C_{p,s}^{\text{Chickos}}(298.15\text{K}) \quad (10)$$

Chickos (2003) themselves however recommend using

$$\Delta C_{p,ls} \approx \left(10.58 \frac{\text{J}}{\text{molK}} + 0.26 C_{p,l}^{\text{Chickos}}(298.15\text{K}) \right) - \left(0.75 \frac{\text{J}}{\text{molK}} + 0.15 C_{p,s}^{\text{Chickos}}(298.15\text{K}) \right) \quad (11)$$

In Fig. 2 both approximations (called Chickos 1 and 2) are compared vs. the approximation $\Delta C_{p,ls} = \Delta S_{\text{fus}}(T_{\text{fus}})$. The

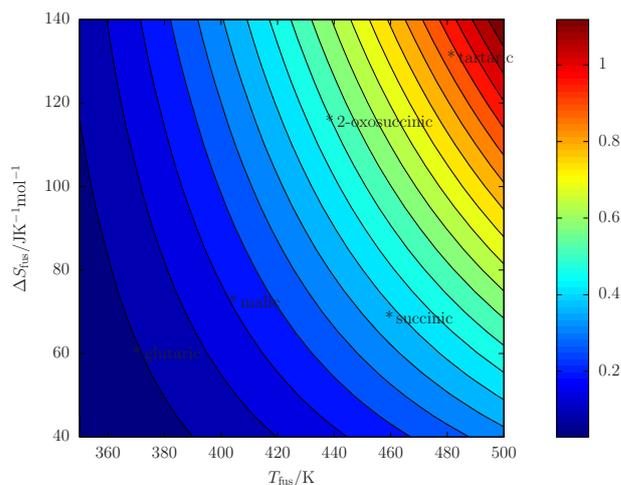


Fig. 1. $\omega_{ls}(\Delta C_{p,ls} = 0) - \omega_{ls}(\Delta C_{p,ls} = \Delta S_{\text{fus}}(T_{\text{fus}}))$ at 298 K vs. T_{fus} and $\Delta S_{\text{fus}}(T_{\text{fus}})$. The position of some diacids is indicated.

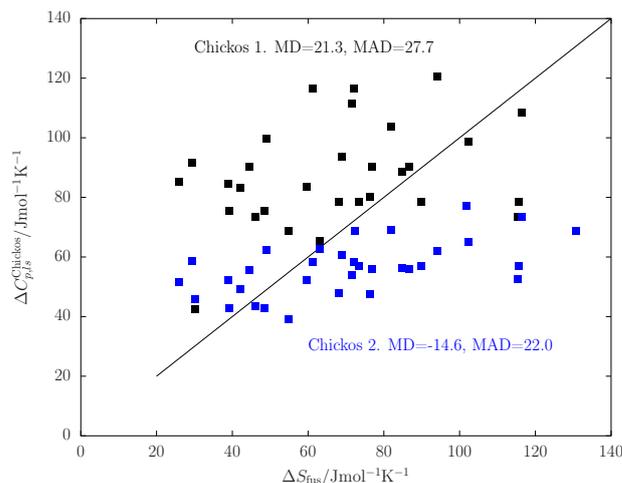


Fig. 2. $\Delta C_{p,ls}$ as estimated by the method of Chickos (2003) (Chickos 1 (black) and 2 (blue): see text for explanation) vs. $\Delta C_{p,ls}$ as approximated by $\Delta S_{\text{fus}}(T_{\text{fus}})$ for the compounds in our data set. The 1:1 diagonal is indicated (black line). The mean deviation and mean absolute deviation are also given.

mean deviation (MD) and mean absolute deviation (MAD), defined as

$$\text{MD} = \frac{1}{N} \sum_i (f_i^{\text{est}} - f_i^{\text{exp}}) \quad (12)$$

$$\text{MAD} = \frac{1}{N} \sum_i |f_i^{\text{est}} - f_i^{\text{exp}}| \quad (13)$$

where f_i^{exp} is an experimental measurement and f_i^{est} an estimation, are also given. It is clear that large discrepancies exist, both in terms of MD and MAD, between on

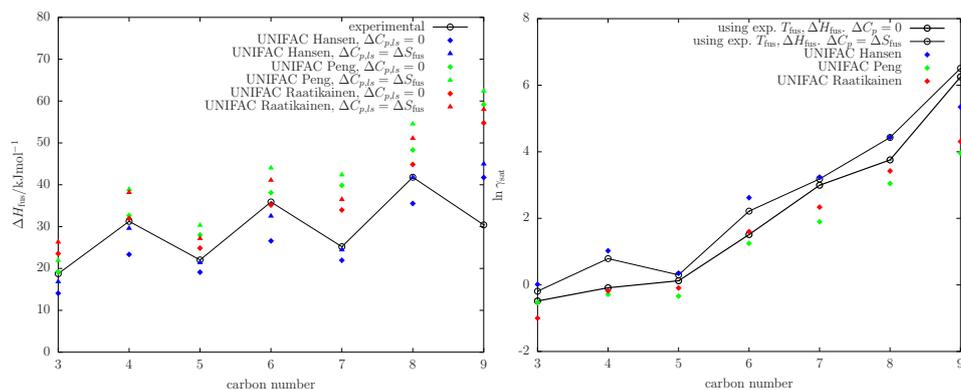


Fig. 3. Left: ΔH_{fus} for linear diacids (C3–C9), experimental or estimated from experimental T_{fus} , x_{sat} and estimated γ_{sat} (at 298 K). Right: $\ln \gamma_{\text{sat}}$ for the same linear diacids, calculated from experimental T_{fus} , ΔH_{fus} data and the two limiting assumptions for $\Delta C_{p,ls}$ (0 to ΔS_{fus}), or estimated from several UNIFAC methods.

the one hand the two assumptions involving the method of Chickos (2003), and on the other hand, the assumption of $\Delta C_{p,ls} = \Delta S_{\text{fus}}(T_{\text{fus}})$. Equation (10) predicts $\Delta C_{p,ls}$ larger than $\Delta S_{\text{fus}}(T_{\text{fus}})$ in most cases, while, under the assumption of a temperature-independent $\Delta C_{p,ls}$, this should not be possible. Hence Eq. (10) seems an invalid approximation for $\Delta C_{p,ls}$.

4 Use of solubility to estimate fusion properties

The vapour pressure of a compound at saturation is equal to its sublimation pressure as a pure solid (e.g. Prausnitz et al., 1999):

$$p_s^0 = \gamma_{\text{sat}} x_{\text{sat}} p_l^0 \quad (14)$$

with x_{sat} the saturation mole fraction of the compound and γ_{sat} the activity coefficient. Combination of Eqs. (3), (6), (7) results in

$$\ln(x_{\text{sat}} \gamma_{\text{sat}}) = \frac{\Delta H_{\text{fus}}}{R} \left(\frac{1}{T_{\text{fus}}} - \frac{1}{T} \right) - \frac{\Delta C_{p,ls}}{R} \left(1 - \frac{T_{\text{fus}}}{T} - \ln \left(\frac{T}{T_{\text{fus}}} \right) \right) \quad (15)$$

Suppose, as is frequently the case, that T_{fus} is known but ΔH_{fus} is not. Then ΔH_{fus} can be estimated from an experimental x_{sat} (e.g. in water), an estimated γ_{sat} (e.g. by UNIFAC: UNIQUAC Functional groups Activity Coefficients) and an approximation for $\Delta C_{p,ls}$ (from 0 to ΔS_{fus} , see Sect. 3). Figure 3 compares experimental ΔH_{fus} to ΔH_{fus} calculated from Eq. (15) for linear diacids with 3–9 carbon atoms.

Saturation concentrations in water at 298.15 K were taken from Apelblat and Manzurola (1987, 1990); Lide (2000). γ_{sat} was calculated by different parameterisations for UNIFAC: the original one from Fredenslund et al. (1975); Hansen

et al. (1991) (UNIFAC-Hansen), and the more recent ones from Peng et al. (2001) (UNIFAC-Peng) and Raatikainen and Laaksonen (2005) (UNIFAC-Raatikainen). The parameterisation of UNIFAC-Hansen was developed from data mainly for simple monofunctional compounds. UNIFAC-Peng and UNIFAC-Raatikainen on the other hand, were specifically developed to describe the non-ideality of mixtures of water with diacids and multifunctional acids and should be more appropriate than UNIFAC-Hansen. UNIFAC-Peng is based on the water activity of such mixtures, while for UNIFAC-Raatikainen also solubility data was used.

From Fig. 3 it is clear that both UNIFAC-Peng and UNIFAC-Raatikainen overestimate ΔH_{fus} for the larger diacids (7–9 carbon atoms). These diacids were not included in the dataset for the derivation of the UNIFAC-Peng and UNIFAC-Raatikainen parameters. For 3–6 carbon atoms, the agreement of both methods with experiment is best if $\Delta C_{p,ls} = 0$ is assumed. This can partly be understood because Raatikainen and Laaksonen (2005) derived the parameters for UNIFAC-Raatikainen, using solubility data and Eq. (15) with the assumption $\Delta C_{p,ls} = 0$. Interestingly, UNIFAC-Hansen, combined with the assumption of $\Delta C_{p,ls} = \Delta S_{\text{fus}}$, has the best overall agreement. All three methods overestimate ΔH_{fus} for azelaic acid (9 carbon atoms). Also shown in Fig. 3 is the estimation of γ_{sat} from the experimental T_{fus} , ΔH_{fus} data and the two limiting assumptions for $\Delta C_{p,ls}$ (0 to ΔS_{fus}). The true activity coefficient should be between both limits. The underestimation of γ_{sat} by UNIFAC-Peng and UNIFAC-Raatikainen for diacids with 7–9 carbon atoms is clear.

Given the uncertainty on ΔH_{fus} estimation with this approach, both due to the activity coefficient modelling and the assumption for $\Delta C_{p,ls}$, we decided not to pursue this route to obtain additional ΔH_{fus} data.

5 Development of a new estimation method

The fusion data of linear diacids follow an even-odd alternation (Roux et al., 2005; Thalladi et al., 2000) in function of carbon number. Thalladi et al. (2000) could explain this behaviour through analysis of the crystal structure of linear diacids, which is particularly stable for even-numbered chains. Using the linear diacid data from Booth et al. (2010); Roux et al. (2005), excluding oxalic acid, one obtains

$$\begin{array}{l} \text{\#CH}_2 \quad \text{odd:} \\ \frac{\Delta H_{\text{fus}}(T_{\text{fus}})}{\text{kJ mol}^{-1}} = 16.464 + 1.909 \cdot \text{\#CH}_2, R^2 = 0.984 \end{array} \quad (16)$$

$$\frac{\Delta S_{\text{fus}}(T_{\text{fus}})}{\text{JK}^{-1} \text{ mol}^{-1}} = 40.91 + 5.81 \cdot \text{\#CH}_2, R^2 = 0.995 \quad (17)$$

$$\begin{array}{l} \text{\#CH}_2 \quad \text{even:} \\ \frac{\Delta H_{\text{fus}}(T_{\text{fus}})}{\text{kJ mol}^{-1}} = 25.704 + 2.657 \cdot \text{\#CH}_2, R^2 = 0.998 \end{array} \quad (18)$$

$$\frac{\Delta S_{\text{fus}}(T_{\text{fus}})}{\text{JK}^{-1} \text{ mol}^{-1}} = 52.45 + 8.11 \cdot \text{\#CH}_2, R^2 = 0.999 \quad (19)$$

where \#CH_2 denotes the number of methylene groups and R^2 the coefficient of determination. Using correlations (18) and (21), a T_{fus} of 490 K would be predicted for oxalic acid, even higher than the fusion point reported by NIST and Thalladi et al. (2000). This gives further argument that the fusion point reported by Booth et al. (2010) could be a solid-solid transition point.

No such clear correlation of fusion enthalpy or entropy with carbon number exists for the nonlinear functionalised acids. For example, the cyclic diacid 1,3-cyclohexane dicarboxylic diacid has a lower $\Delta H_{\text{fus}}(T_{\text{fus}})$ and $\Delta S_{\text{fus}}(T_{\text{fus}})$ than 1,3-cyclopropane diacid. Instead, we use as independent variable the effective torsional bond number τ (Dannenfesler and Yalkowsky, 1996). This variable plays a similar role as the CH_n groups in common group-contribution methods, as $\text{\#CH}_2 + \text{\#CH} + \text{\#C}$ is the mostly dominant contribution of the noncyclic carbon atoms to τ . As interactions between functional groups are important both in the liquid and the solid phase, also the number of nonacid (carbonyl and hydroxy) and acid functional groups is taken into account. Finally, the identification of the molecule as a linear even-numbered chain is taken as an independent variable, given its importance for the crystal structure stability (Thalladi et al., 2000). Our estimation method has then the following form

$$\Delta H_{\text{fus}}^{\text{est}}(T_{\text{fus}}) = a_1 + a_2\tau + a_3(n_{\text{OH}} + n_{\text{CO}}) + a_4n_{\text{COOH}} + a_5i_{\text{even}} \quad (20)$$

$$\Delta S_{\text{fus}}^{\text{est}}(T_{\text{fus}}) = a_1 + a_2\tau + a_3(n_{\text{OH}} + n_{\text{CO}}) + a_4n_{\text{COOH}} + a_5i_{\text{even}} \quad (21)$$

with $i_{\text{even}} = 1$ if the molecule is a linear even-numbered chain and 0 otherwise, and n_{OH} , n_{CO} , n_{COOH} the number of hy-

droxy, carbonyl (keto and aldehyde), and acid groups respectively. The fitting equations have the following form:

$$\Delta S_{\text{fus},i}^{\text{exp}} = \frac{\Delta H_{\text{fus},i}^{\text{est}}}{T_{\text{fus},i}^{\text{exp}}} \quad (22)$$

$$\Delta S_{\text{fus},i}^{\text{exp}} = \Delta S_{\text{fus},i}^{\text{est}} \quad (23)$$

$$0 = \frac{\Delta H_{\text{fus},i}^{\text{est}}}{T_{\text{fus},i}^{\text{exp}}} - \Delta S_{\text{fus},i}^{\text{est}} \quad (24)$$

where we have used the superscripts “exp” and “est” to clearly distinguish between experimental and estimated values and i refers to data point i (if only $T_{\text{fus},i}^{\text{exp}}$ is known), or to data couple i (if both $T_{\text{fus},i}^{\text{exp}}$, $\Delta H_{\text{fus},i}^{\text{exp}}$ are known). The last equation is used if only $T_{\text{fus},i}^{\text{exp}}$ is known, the first two if both $T_{\text{fus},i}^{\text{exp}}$, $\Delta H_{\text{fus},i}^{\text{exp}}$ are known.

In Table 1 the optimal parameters, obtained by linear regression, are given, as well as the MD, MAD, R^2 , the predicted MD and MAD, and R_{cv}^2 (cross-validated R^2), of $\Delta H_{\text{fus}}^{\text{est}}$, $\Delta S_{\text{fus}}^{\text{est}}$ and $T_{\text{fus}}^{\text{est}}$. Predicted MD, predicted MAD and R_{cv}^2 are defined identically as the MD, MAD and R^2 , except that for the estimation of data point (or data couple) i , this data point (couple) itself is not used. In this way, the predicted MD, MAD and R_{cv}^2 are a measure of the predictive power of the model, while MD, MAD and R^2 merely show how well the model can fit the observations.

We tried also the following independent variables: cyclicity (1 for a cyclic molecule, zero otherwise), and rotational symmetry number (Dannenfesler and Yalkowsky, 1996; Walters and Yalkowsky, 1996) both in its original form and a modified form. In its original form, the rotational symmetry number is the number of indistinguishable positions that can be obtained by rigidly rotating a rigid molecule about its center of mass; for flexible molecules ($\tau \geq 1$) it is always unity. In the modified form, the flexibility of the molecule was not considered. None of these independent variables improved the predicted MAD significantly, so they were not retained.

6 Comparison with estimation methods from the literature

The methods considered are presented in Table 2. Both the methods of Joback and Reid (1987) (JR) and Marrero and Gani (2001) (MG) are group contribution methods providing both T_{fus} (JR(T), MG(T)) and ΔH_{fus} (JR(H), MG(H)). While the former is relatively simple, the second is a detailed method involving first, second and third order groups. The method of Myrdal and Yalkowsky (1997) (MY) and the more recent variant of Jain et al. (2004a) (JYY) estimate ΔS_{fus} from the number of torsional bonds and rotational symmetry of the molecule. The T_{fus} estimation method of Zhao and Yalkowsky (1999) (ZY) is a composite method: ΔS_{fus}

Table 1. Parameters and statistical diagnostics of the new estimation method.

	a_1	a_2	a_3	a_4	a_5	MD	MAD	R^2	pred. MD	pred. MAD	R_{cv}^2
$\frac{\Delta H_{fus}^{est}}{kJmol^{-1}}$	-12.895	1.807	11.552	15.327	12.358	-0.3	5.2	0.66	-0.2	6.0	0.55
$\frac{\Delta S_{fus}^{est}}{JK^{-1}mol^{-1}}$	-8.508	6.520	23.890	25.379	18.153	-1.0	12.7	0.62	-0.7	14.7	0.51
T_{fus}/K , from $\Delta H_{fus}^{est}, \Delta S_{fus}^{est}$						-4.7	24.8	0.61	-4.9	26.4	0.68
ω_{ls} , from $\Delta H_{fus}^{est}, \Delta S_{fus}^{est}$						0.0	0.32	0.66	0.0	0.35	0.58
ω_{ls} , from $\Delta H_{fus}^{est}, T_{fus}^{exp}$						0.0	0.23	0.81	0.0	0.27	0.74
ω_{ls} , from $\Delta S_{fus}^{est}, T_{fus}^{exp}$						0.0	0.22	0.84	0.0	0.26	0.78

Table 2. Fusion property estimation methods considered in this work.

Notation	Source	Form ^a
JR(T)	Joback and Reid (1987)	$T_{fus}^{JR} = \sum_i n_i g_i$
JR(H)	Joback and Reid (1987)	$\Delta H_{fus}^{JR} = \sum_i n_i g_i$
MG(T)	Marrero and Gani (2001)	$e^{T_{fus}^{MG}} = \sum_i n_i g_i$
MG(H)	Marrero and Gani (2001)	$\Delta H_{fus}^{MG} = \sum_i n_i g_i$
MY(S)	Myrdal and Yalkowsky (1997)	$\Delta S_{fus}^{MY} = g_1$ $+ g_2 \ln \sigma + g_3 \tau^b$
JYY(S)	Jain et al. (2004a)	ΔS_{fus}^J : as ΔS_{fus}^{MY}
ZY(T)	Zhao and Yalkowsky (1999)	$T_{fus}^{ZY} = \frac{\sum_i n_i g_i}{\Delta S_{fus}^{MY}}$
JYY(T)	Jain et al. (2004b)	$T_{fus}^J = \frac{\sum_i n_i g_i}{\Delta S_{fus}^J}$

^a g_i represent parameter values, n_i the frequency of group i .

^b σ is the rotational symmetry number (Dannenfelsner and Yalkowsky, 1996) and τ the effective torsional bond number (Myrdal et al., 1996).

is fixed by the MY method (ΔS_{fus}^{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 $(\sum_i n_i g_i) / \Delta S_{fus}^{MY}$ to experimental T_{fus} . The more recent variant of Jain et al. (2004b) (JYY) is derived along the same lines, but with ΔS_{fus} fixed by the JYY method.

6.1 Fusion temperature

Figure 4 gives estimated vs. experimental T_{fus} for the methods from the literature and the current method. The JR(T)

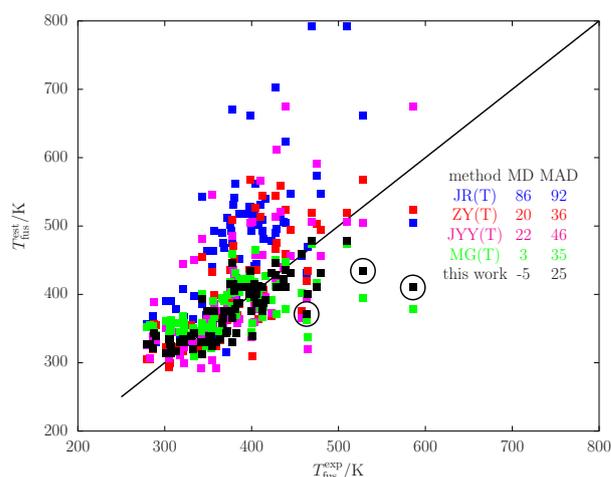


Fig. 4. Estimated vs. experimental T_{fus} for various literature methods, and the method developed in this work. The MD and MAD of the methods are also given. The 1:1 diagonal is indicated (black line). The three most important outliers of the new method are indicated by a circle (from small to high experimental T_{fus} : 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoic acid, galactaric acid, *trans*-1,4-cyclohexane dicarboxylic acid).

method gives a very large error on the fusion temperature. This can be ascribed to the fact that this method considers T_{fus} as a sum of group contributions – while it is actually not a group property (Chickos and Nichols, 2001)–, resulting in large overestimations for larger molecules (e.g. 275 K for citric acid). Clearly, the JR(T) method is not suitable to estimate fusion point of functionalised acids. We note that a similar failure occurs for the estimation of boiling points by the JR method (Stein and Brown, 1994). Of the literature methods, the ZY(T) and MG(T) methods perform best for fusion temperature in terms of MAD, but MG(T) has

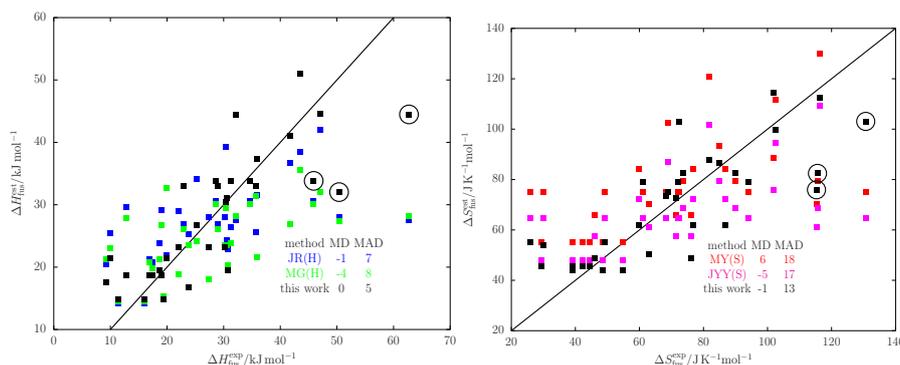


Fig. 5. Estimated vs. experimental ΔH_{fus} (left) and ΔS_{fus} (right) for various literature methods, and for the method developed in this work. The MD and MAD of the methods are also given. The 1:1 diagonal is indicated (black line). The three most important outliers of the new method are indicated by a circle (from small to high experimental ΔH_{fus} : 3-oxoglutaric acid, oxosuccinic acid, tartaric acid).

in addition a low bias. The more recent version of ZY(T), JYY(T), actually performs worse. The method developed in this work has a significantly lower error than the literature methods. For all methods, the error increases with T_{fus} . The most important outliers for the new method - as well as for the best performing of the literature methods, MG(T)- are *trans*-1,4-cyclohexane dicarboxylic diacid, galactaric acid, and 3-hydroxy-2-(hydroxymethyl)-2-methyl propanoic acid. For all three of them the melting point is underestimated. *Trans*-1,4-cyclohexane dicarboxylic diacid has a much higher melting point than the other cyclic dicarboxylic acids in the dataset. Probably the two acid functionalities at opposite and *trans* positions in the ring, allow for a crystal structure that is considerably more stable. The melting point of galactaric acid is much higher than that of its stereo-isomer glucaric acid. So also here, a particularly stable crystal structure is the likely explanation of the poorly estimated T_{fus} .

6.2 Fusion enthalpy and entropy

Our data set for ΔH_{fus} (and hence also for ΔS_{fus}) is considerably smaller than for T_{fus} . For example, the three most important outliers with respect to T_{fus} (see the Sect. 6.1) are not included.

Notwithstanding its high detail, the MG(H) method performs worse than the JR(H) method in estimating fusion enthalpy, and has a relatively high bias (Fig. 5). For fusion entropy estimation, the MY(S) and JYY(S) method have a similar precision and bias. The newly developed method shows again the best performance. Most important outliers for the new method, both for ΔH_{fus} and ΔS_{fus} are oxosuccinic acid, 3-oxoglutaric acid and tartaric acid (the value of Booth et al., 2010), which are in all three cases underestimated. The ΔH_{fus} value of tartaric acid of Booth et al. (2010) is almost twice larger than that of *d*-tartaric acid as present in Acree and Chickos (2010) and NIST. Probably Booth et al. (2010)

investigated a different stereo-isomer that forms a more stable crystal structure. 3-oxoglutaric acid has a substantially higher ΔH_{fus} value than its isomer 2-oxoglutaric acid, which is again an indication of a particularly stable crystal structure.

6.3 Estimation of ω_{l_s}

For the estimation of ω_{l_s} (under assumption of $\Delta C_{p,l_s} = 0$), the estimation of two fusion properties is necessary if no experimental fusion data are available. Combinations with JR(T) give a large positive bias for ω_{l_s} due to the large overestimation of T_{fus} (Fig. 6). Note that the error increases as ω_{l_s} increases. Oxosuccinic acid and tartaric acid are again outliers. Estimations of ω_{l_s} are much better if the fusion temperature is already known. Of the literature methods, MY(S) and JYY(S) in combination with the experimental fusion temperature provide the best results. Table S2 of the Supplement contains the experimental ω_{l_s} and ω_{l_s} estimated using (i) the experimental T_{fus} and (ii) ΔH_{fus} as calculated by the new method.

Again, the current method performs better than the literature methods. 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 Sect. 6.

7 Conclusions

To derive subcooled liquid vapour pressure from solid vapour pressure, knowledge of the fusion properties is necessary. A simple method is developed to estimate the fusion properties of C_2 - C_{10} saturated acids, with one or more other functional groups: hydroxyl, carbonyl, and/or acid. Several fusion property estimation methods from the literature are also tested for these compounds. The newly proposed method has a much narrower scope than the considered literature methods, but has also a significantly smaller error for the target compounds. From the literature methods, best solid-to-

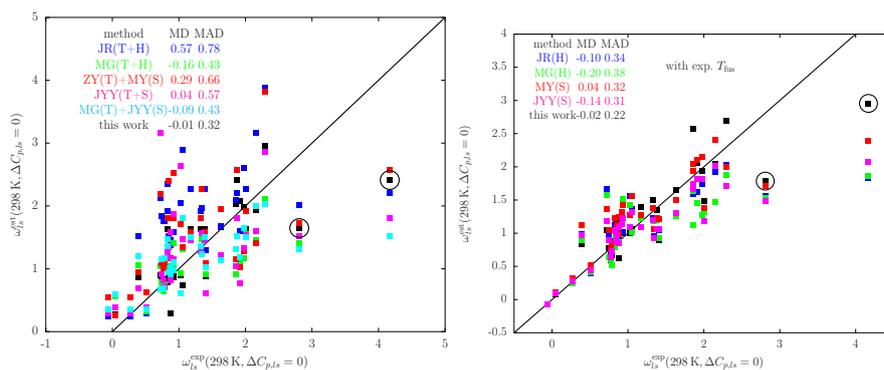


Fig. 6. Estimated vs. experimental ω_{ls} at 298 K, assuming $\Delta C_{p,ls} = 0$. Left: fully estimated. Right: using the experimental T_{fus} , with ΔH_{fus} or ΔS_{fus} estimated. The MD and MAD of the methods are also given. The 1:1 diagonal is indicated (black line). The two most important outliers of the new method are indicated by a circle (from small to high experimental ω_{ls} : oxosuccinic acid, tartaric acid).

subcooled liquid conversion factors are obtained by combining the ΔS_{fus} estimation method of Myrdal and Yalkowsky (1997) or Jain et al. (2004a) with the experimental fusion temperature or with the estimated fusion temperature using the method of Marrero and Gani (2001) if no experimental fusion temperature is available. The T_{fus} estimation method of Joback and Reid (1987) should be avoided as it gives gross overestimations for large T_{fus} .

To the best of our knowledge, no data on $\Delta C_{p,ls}$ is available for functionalised acids, although it is potentially important for a correct solid-subcooled liquid conversion factor, especially for compounds with a high T_{fus} , ΔH_{fus} . Approximating $\Delta C_{p,ls}$ by $C_{p,l}^{Chickos} - C_{p,s}^{Chickos}$ (Chickos, 2003) probably overestimates $\Delta C_{p,ls}$.

The UNIFAC activity coefficient model parameterisations of Peng et al. (2001); Raatikainen and Laaksonen (2005) do not conform with the solubility data of the longer diacids (7–9 carbon atoms) while the original UNIFAC parameterisation, combined with the assumption of $\Delta C_{p,ls} = \Delta S_{fus}$ performs best for the linear diacids (3–9 carbon atoms). Hence experimental knowledge on $\Delta C_{p,ls}$ can also improve our understanding on non-ideality.

Even with the newly developed method, substantial uncertainty remains. This is probably for a large part due to differences in crystal packings; for several species in our dataset, there are large differences in fusion properties although the molecular connectivities are the same (e.g. glucaric vs. galactaric acid). Our model, like the considered literature methods, does not take stereo-information (e.g. *cis* or *trans* isomers) into account. To improve modeling of fusion properties this information should be included. However, this will make the model considerably more complex and moreover, stereo-information is not always available. Another obvious obstacle for the development of better estimation methods is the paucity of experimental fusion data, especially of fusion enthalpies. For example, a fusion enthalpy is available for only five out of 33 compounds in our dataset with one acid

functionality. Therefore, more fusion data measurements are certainly desirable.

Supplementary material related to this article is available online at:

<http://www.atmos-chem-phys.net/11/8385/2011/acp-11-8385-2011-supplement.pdf>.

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