

A protocol for correcting experimental fusion enthalpies to 298.15 K and its application in indirect measurements of sublimation enthalpy at 298.15 K

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Abstract

A protocol for adjusting fusion enthalpies as a function of temperature is described. The protocol combines two simple relationships previously proposed to adjust sublimation and vaporization enthalpies with temperature. This new protocol provides improved accuracy and precision relative to the other theoretical and empirical methods tested. Experimental fusion and vaporization enthalpies measured at different temperatures are adjusted to 298.15 K. Their sum when compared to experimental sublimation enthalpy values at 298.15 K deviates from the experimental values by approximately ± 4 kJ for the 117 compounds used in the database. This protocol appears to function successfully for enthalpies measured from 200 to 500 K. © 1998 Elsevier Science B.V.

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1. Introduction

Sublimation enthalpies are an important property of the solid state in so far as this quantity is a macroscopic measure of the magnitude of intermolecular interactions. The measurement of this quantity serves a variety of useful purposes that include uses in thermochemistry as a correction to condensed phase enthalpies of formation [1], as a means of quantifying mass transport by establishing the relationship between vapor pressure and temperature by means of the Clausius–Clayperon equation [2], and as an experimental measure of the cumulative effect of the

intermolecular potentials that lead to the specific packing observed in the solid state of crystalline materials [3].

A variety of experimental techniques have been developed to directly measure the sublimation enthalpies of solids [4]. These include measurements of mass transport by means of gas-saturation techniques, Knudsen and torsion effusion, head space analysis, and calorimetry. Indirect methods of obtaining sublimation enthalpies have also been employed. Indirect measurements of sublimation enthalpy have been obtained by using Eq. (1). This equation is used infrequently because vaporization enthalpy data on solids at 298.15 K are not usually available and extrapolations of vaporization enthalpies from measurements performed at elevated temperatures to 298.15 K can be problematic. In addition, Eq. (1) as written is

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only an

$$\Delta_{\text{sub}}H_{\text{m}}(298.15 \text{ K}) \approx \Delta_{\text{vap}}H_{\text{m}}(298.15 \text{ K}) + \Delta_{\text{fus}}H_{\text{m}}(T_{\text{fus}}) \quad (1)$$

$$\Delta_{\text{sub}}H_{\text{m}}(298.15 \text{ K}) = \Delta_{\text{vap}}H_{\text{m}}(298.15 \text{ K}) + \Delta_{\text{fus}}H_{\text{m}}(298.15 \text{ K}) \quad (2)$$

approximation of the sublimation enthalpy. This relationship becomes a thermodynamic equality only when the three enthalpies are referenced to the same temperature as given by Eq. (2) for measurements at 298.15 K and enthalpies of any phase transitions occurring between T_{fus} and 289.15 K are included in the $\Delta_{\text{fus}}H_{\text{m}}(298.15 \text{ K})$ term.

Recently, we reported the use of Eq. (3) to correct vaporization enthalpies from the mean temperature of measurement, \bar{T} , to 298.15 K [5]. The term in brackets in Eq. (3) was derived by correlating differences between experimental heat capacities of the liquid and gas phases for a series of compounds with the heat capacity of each respective liquid phase at 298.15 K. The heat capacity of the liquid phase, $C_{\text{pl}}^{\text{estd}}(298.15)$, was estimated using a group method [6].

$$\Delta_{\text{vap}}H_{\text{m}}(298.15 \text{ K}) = \Delta_{\text{vap}}H_{\text{m}}(\bar{T}) + [10.58 + 0.26C_{\text{pl}}^{\text{estd}}(298.15 \text{ K})]\{\bar{T} - 298.15\} \quad (3)$$

The reliability of Eq. (3) was tested against experimental data. Predictions using this equation were compared to differences observed in experimental vaporization enthalpies measured calorimetrically at temperature T , and a reference temperature, usually 298.15 K for each specific compound [7]. Vaporization enthalpies of a total of 135 different compounds were examined. Vaporization enthalpies of these materials were reported over the 260–370 K range. Excluding compounds that form hydrogen bonds, the standard error associated with using Eq. (3) to adjust vaporization enthalpies for effects of temperature was $\pm 490 \text{ J mol}^{-1}$. When compounds capable of hydrogen bonding were also included in the comparisons, the error increased to 770 J mol^{-1} . Eq. (3) has been recently used to adjust the vaporization enthalpies of linear alkanes measured at elevated temperatures to 298.15 K [8].

In addition to Eq. (3), an additional relationship, Eq. (4), was suggested as a means of correcting sublimation enthalpies to 298.15 K [5]. The bracketed

term in Eq. (4) was derived by correlating

$$\Delta_{\text{sub}}H_{\text{m}}(298.15 \text{ K}) = \Delta_{\text{sub}}H_{\text{m}}(\bar{T}) + [0.75 + 0.15C_{\text{pc}}^{\text{estd}}(298.15 \text{ K})]\{\bar{T} - 298.15\} \quad (4)$$

differences between experimental heat capacities of the solid and gas phase for a series of compounds with the heat capacity of each respective solid phase at 298.15 K [5]. The heat capacity of the solid phase, $C_{\text{pc}}^{\text{estd}}(298.15)$, was also estimated by a group additivity method [6,13].

Eq. (4) has not been tested extensively, primarily due to the lack of sufficient experimental data available for comparisons. One of the objectives of this present work was to test the reliability and accuracy of Eq. (4) in correcting sublimation enthalpies to 298.15 K. In this article, we describe a protocol for adjusting fusion enthalpies to 298.15 and obtaining sublimation enthalpies using Eq. (2) by combining temperature adjusted fusion and vaporization enthalpy data. Sublimation enthalpies obtained using this protocol appear accurate to approximately $\pm 4 \text{ kJ mol}^{-1}$ for most compounds.

2. Discussion

Sublimation enthalpies can be estimated using the approximation given by Eq. (1). As noted above, the relationship between sublimation enthalpy and vaporization and fusion enthalpies becomes an equality, Eq. (2) or Eq. (5), if all the enthalpies are referenced to the same temperature.

$$\Delta_{\text{sub}}H_{\text{m}}(T_{\text{fus}}) = \Delta_{\text{vap}}H_{\text{m}}(T_{\text{fus}}) + \Delta_{\text{fus}}H_{\text{m}}(T_{\text{fus}}) + \Delta_{\text{fus}}H_{\text{m}}(T_{\text{fus}}) \quad (5)$$

The melting point, T_{fus} , is the reference temperature most accessible experimentally since fusion enthalpies are usually measured at this temperature. Since this reference point will vary from compound to compound, Eq. (5) is not very useful for comparative purposes. By using a combination of Eqs. (3)–(5), it is possible to achieve the equality associated with Eqs. (2) and (5) and still correct for the effects of temperature on both sublimation and vaporization enthalpies. The protocol suggested involves the use of Eq. (6) to adjust the vaporization enthalpies measured at \bar{T} or 298.15 K to the melting temperature of

the compound, T_{fus} . Following addition of the experimental fusion enthalpy according to Eq. (5), the resulting sublimation enthalpy at T_{fus} is then adjusted back to 298.15 K from T_{fus} , by using Eq. (7). The use of Eqs. (6) and (7) have the combined effect of adjusting the fusion enthalpy from T_{fus} to 298.15 K.

$$\begin{aligned} \Delta_{\text{vap}}H_{\text{m}}(T_{\text{fus}}) &= \Delta_{\text{vap}}H_{\text{m}}(\bar{T}) \\ &+ [10.58 + 0.26C_{\text{plstd}}(298.15 \text{ K})][\bar{T} - T_{\text{fus}}] \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta_{\text{sub}}H_{\text{m}}(298.15 \text{ K}) &= \Delta_{\text{sub}}H_{\text{m}}(T_{\text{fus}}) \\ &+ [0.75 + 0.15C_{\text{pcstd}}(298.15 \text{ K})][T_{\text{fus}} - 298.15] \end{aligned} \quad (7)$$

The effectiveness of using Eqs. (1), (5), (6) and (7) are compared below. In addition, we have compared adjustments of fusion enthalpy from T_{fus} to 298.15 K using Eqs. (8) and (9). Eq. (8) was derived from the thermodynamic relationships used to generate Kirchhoff's equations (see Appendix A). The relationships and approximations used in deriving this equation are described in Appendix A [11]. Similarly, Eq. (9), proposed by Sidgwick, was directly used to adjust fusion enthalpies from T_{fus} to 298.15 K [12]. The use of Eqs. (8) and (9) in conjunction with Eq. (2) both require vaporization and sublimation enthalpies at 298.15 K.

$$\begin{aligned} \Delta_{\text{fus}}H_{\text{m}}(298.15 \text{ K}) &= [298.15][\Delta_{\text{c}}^{\text{f}}C_{\text{p}}(298.15 \text{ K})\ln[298.15/T_{\text{fus}}] \\ &+ \Delta_{\text{fus}}H_{\text{m}}(T_{\text{fus}})/[T_{\text{fus}}]] \end{aligned} \quad (8)$$

$$\begin{aligned} \Delta_{\text{fus}}H_{\text{m}}(298.15 \text{ K}) &= \Delta_{\text{fus}}H_{\text{m}}(T_{\text{fus}}) \\ &+ 54.4[298.15 - T_{\text{fus}}] \end{aligned} \quad (9)$$

Eqs. (4) and (10) (described below) were used to provide $\Delta_{\text{sub}}H_{\text{m}}(298.15 \text{ K})$ values for those measurements not provided by the literature.

3. Results

Sublimation, vaporization and fusion enthalpies could be located for a total of 120 individual compounds, 32 hydrocarbons and 88 other organic compounds including 46 which can form hydrogen bonds. Sublimation enthalpies [4], vaporization enthalpies [7,9] and fusion enthalpies [10] were located in var-

ious compendia. Some recent data from the literature were also used. Vaporization enthalpies at 298.15 K for some compounds are readily available [7]. Vaporization enthalpies for many other compounds were obtained from the Antoine constants by plotting the natural logarithm of vapor pressure vs. $1/T$ over a 30 K range using a Clausius–Clapeyron treatment of the data [9]. The mean temperature over a 30 K range was used as \bar{T} . The vaporization enthalpy was then corrected from \bar{T} , to 298.15 K or T_{fus} using Eq. (3).

Experimental sublimation enthalpies at 298.15 K were used for comparative purposes if available. Otherwise they were adjusted from the mean experimental temperature, \bar{T} , to 298.15 K using Eq. (4) as noted above and also using Eq. (10). Eq. (10) and various modification have been used previously to adjust sublimation enthalpies to 298.15 K [4,5]. R in Eq. (10) refers to the gas constant. For some compounds, several experimental sublimation, vaporization and fusion enthalpies are available. If the values were in good agreement with each other (generally $\pm 4 \text{ kJ mol}^{-1}$), the mean experimental value was chosen. In a few instances where good agreement between experimental values was not observed, the most probable experimental value was chosen on the basis of how well the experimental data were modeled by Eq. (1). Compounds with known phase transitions

$$\begin{aligned} \Delta_{\text{sub}}H_{\text{m}}(298.15 \text{ K}) &= \Delta_{\text{sub}}H_{\text{m}}(\bar{T}) \\ &+ 2R[\bar{T} - 298.15] \end{aligned} \quad (10)$$

occurring between T_{fus} and 298.15 K were examined to determine whether the sublimation enthalpy was measured above or below the transition temperature. Both fusion and sublimation enthalpies were treated consistently with regard to these transitions.

The comparison of the experimental and estimated sublimation enthalpies of 120 compounds using the estimates of Eqs. (1), (5–7), (2) and (8), and (2) and (9) are all summarized in Table 1(A) and (B). Table 1(A) summarizes the distribution of errors obtained by the various protocols using Eq. (10) to adjust sublimation enthalpies to 298.15 K while Table 1(B) contains a similar summary using Eq. (4) for this adjustment. If comparisons with errors exceeding three standard deviations are removed from consideration, the results given in the last three rows of Table 1(A) and (B) are obtained.

Table 1

A comparison of different indirect protocols for obtaining sublimation enthalpies at 298 K

	Eq. (1)	Eqs. (5)–(7)	Eqs. (2) and (8)	Eqs. (2) and (9)
(A) Sublimation enthalpies corrected to 298.15 K using Eq. (10)				
All data				
standard error (J mol ⁻¹)	±6598	±5441	±5824	±6318
sum of the errors (\sum [expt – calc])	-425953	-101278	361412	232412
count	120	120	120	120
Data within 3 standard deviations				
standard error (J mol ⁻¹)	±5804	±4461	±5710	±5643
Sum of the errors (\sum [expt – calc])	-355901	-39574	373611	241707
count	117	117	119	118
(B) Sublimation enthalpies corrected to 298.15 K using Eq. (4)				
All data				
standard error (J mol ⁻¹)	±6170	±5161	±5804	±6011
sum of the errors (\sum [expt – calc])	-386831	-62156	400534	271534
count	120	120	120	120
Data within 3 standard deviations				
standard error (J mol ⁻¹)	±5405	±4210	±5678	±5357
sum of the errors (\sum [expt – calc])	-320512	-4185	407955	277235
count	117	117	119	118

From a comparison of the results in columns 2–5 in Table 1(A) with the corresponding columns of Table 1(B), Eq. (4) appears to provide a better temperature adjustment to 298.15 than does Eq. (10), regardless of the protocol used in adjusting fusion enthalpies to 298.15 K. The results of Table 1(B) are further illustrated in the histograms of Figs. 1–4. Fig. 1 summarizes the error distribution obtained using Eq. (1) to estimate the enthalpy of sublimation at 298.15 K; similarly, Figs. 2–4 summarize results using either Eqs. (5)–(7), (2) and (8), and (2) and (9), respectively.

On the basis of known differences in heat capacity between the solid and liquid phase of most substances, sublimation enthalpies calculated using Eq. (1) should be slightly over-estimated for compounds melting above 298.15 K and underestimated for those melting below this temperature. Fusion enthalpies for compounds melting above room temperature will be smaller at 298.15 K as a result of temperature adjustments. Only a minority of the compounds in the database (22/120) is melted below 298.15 K. Over-estimations using Eq. (1) are revealed in Fig. 1 by the distribution of errors which is skewed to the left of center. This is also reflected in the sum of the residual errors, $\Delta_{\text{sub}}H_{\text{m}}$

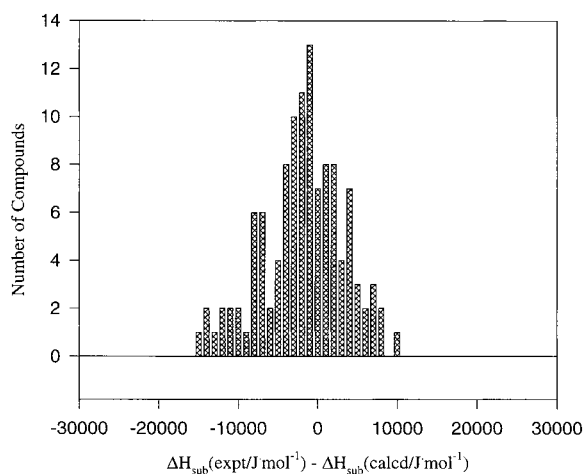


Fig. 1. A histogram illustrating the error distribution between experimental sublimation enthalpies and those calculated with the aid of Eq. (1).

(298.15 K) [expt – calc] in Table 1(B) which adds up to a total of -386831 J. The standard deviation associated with this distribution is ± 6170 J mol⁻¹. Three estimations exceeded 3 standard deviations and are not included either in the figure or statistics associated

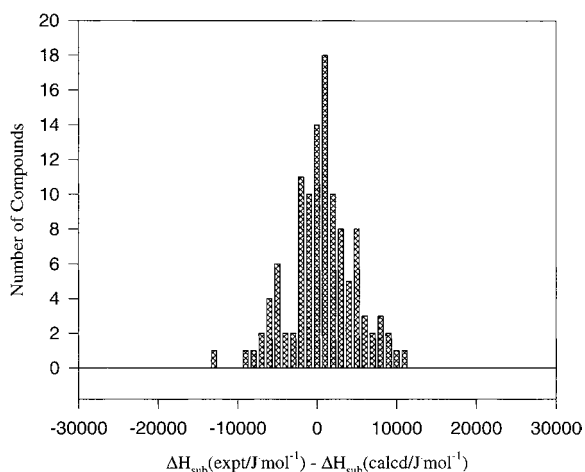


Fig. 2. A histogram illustrating the error distribution between experimental sublimation enthalpies and those calculated with the aid of Eqs. (5)–(7).

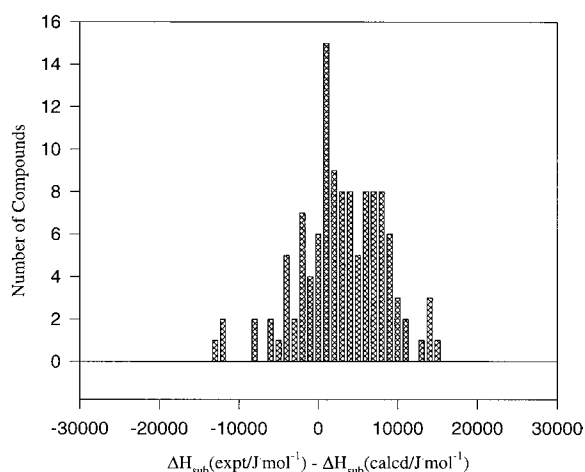


Fig. 4. A histogram illustrating the error distribution between experimental sublimation enthalpies and those calculated with the aid of Eqs. (2) and (9).

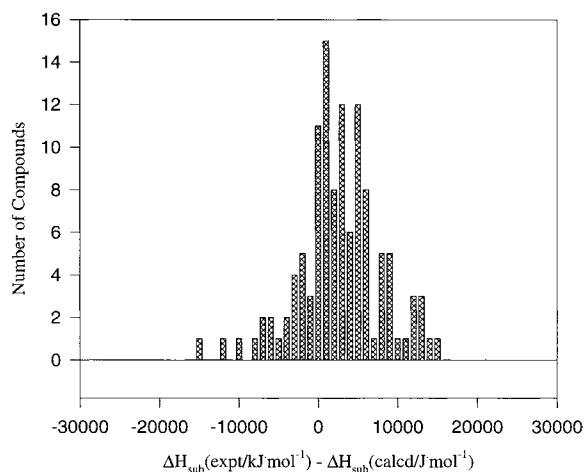


Fig. 3. A histogram illustrating the error distribution between experimental sublimation enthalpies and those calculated with the aid of Eqs. (2) and (8).

with this correlation. Removal of these data resulted in a standard deviation of $\pm 5405 \text{ J mol}^{-1}$ and a residual sum of -320512 .

The results associated in using Eqs. (5)–(7) to adjust sublimation enthalpies are documented in the third column of Table 1(B) and in Fig. 2. Three estimations exceeded 3 standard deviations and removal of these data resulted in a standard deviation

of ± 4210 and an error distribution which appears fairly symmetrical about zero; this is confirmed by the sum of the residual errors in the third column of Table 2 (-4185). The standard deviation associated with this distribution is the smallest of all the methods compared.

The combined use of Eqs. (2) and (8) in obtaining sublimation enthalpies is shown in Fig. 3 and summarized in column 4 of Table 1(B). The use of these two equations produces an unsymmetrical distribution as illustrated by the sum of the residual errors (407955). Eq. (8) appears to overestimate the temperature adjustments to fusion enthalpy. Combination of this equation with Eq. (2) results in an underestimation of the sublimation enthalpy. The standard deviation associated with this distribution is $\pm 5678 \text{ J mol}^{-1}$. Similar results are obtained using Eqs. (2) and (9). This is illustrated in Fig. 4 and in the last column in Table 1(B).

Comparison of the results in these four figures and those of Table 1 suggests that Eqs. (5)–(7) provide the smallest error and the most symmetrical error distribution. The standard error of $\pm 4210 \text{ J mol}^{-1}$ associated with this method of estimating sublimation enthalpies is typical of the uncertainty associated with direct measurements of this quantity.

The temperature adjustment to 298.15 K of compounds with melting points below 298.15 K can sig-

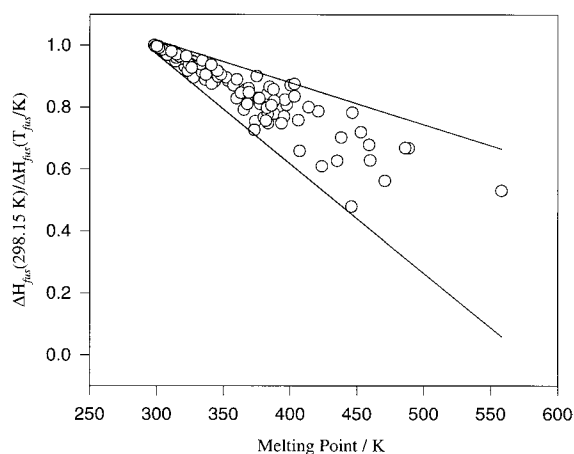


Fig. 5. The fraction of the fusion enthalpy at 298.15 K relative to the value at T_{fus} as a function of the melting point of the substance.

nificantly increase the magnitude of the fusion enthalpy. For examples, the temperature adjustment for ethylene and ethane increased $\Delta_{\text{fus}}H_{\text{m}}$ by 154 and 227%, respectively. For some solids, particularly those characterized with very high melting points or with low fusion enthalpies at T_{fus} (resulting from other phase transitions occurring at temperatures below T_{fus}), temperature adjustments associated with using Eqs. (6) and (7) may approach and exceed the magnitude of the fusion enthalpy. Obviously a negative fusion enthalpy has no physical significance. Temperature adjustments that exceed the magnitude of the fusion enthalpy are likely the result of uncertainties associated in using Eqs. (5)–(7) over large temperature extrapolations or perhaps the result of errors in experimental enthalpies. The total temperature adjustment to $\Delta_{\text{fus}}H_{\text{m}}$ for the 117 compounds examined in this study using Eqs. (5)–(7) varied and depended on the magnitude of T_{fus} . This is illustrated in Fig. 5 where the fraction: $\Delta_{\text{fus}}H_{\text{m}}(298.15 \text{ K})/\Delta_{\text{fus}}H_{\text{m}}(T_{\text{fus}})$, is plotted against the melting point of those compounds with melting points above 298.15 K. As illustrated in the figure, the distribution of values for this fraction increases with increasing melting point. Most of the data appear confined within the region defined by the two intersecting lines. Of particular interest to this discussion is the equation of the lower line given as Eq. (11). This equation describes how the minimum value of this fraction varies with melting point. It

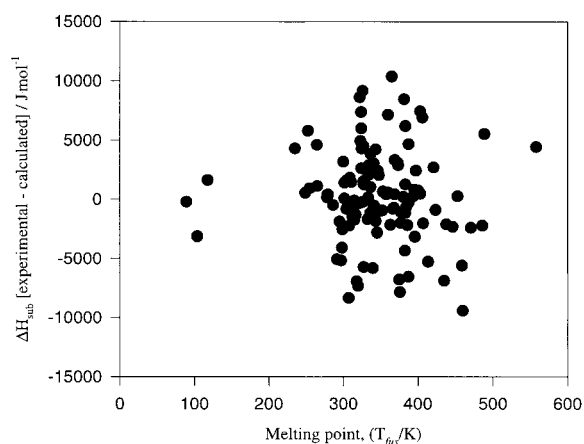


Fig. 6. The distribution of errors in sublimation enthalpy as a function of the melting point of the solid using Eqs. (5)–(7).

clearly suggests that temperature adjustments for some compounds melting above 500 K are likely to be unrealistic.

$$\begin{aligned} & (\Delta_{\text{fus}}H_{\text{m}}(298.15 \text{ K})/\Delta_{\text{fus}}H_{\text{m}}(T_{\text{fus}}))_{\text{min}} \\ & = 2.03 - 0.00353[T(\text{K})] \end{aligned} \quad (11)$$

To determine whether the error associated with the use of Eqs. (5)–(7) is related to the magnitude of the melting point, $\Delta_{\text{sub}}H_{\text{m}}(298.15 \text{ K})[\text{expt} - \text{calc}]$ was plotted against melting point. The magnitude of the errors associated with the 117 compounds in the database is shown in Fig. 6. The errors appear scattered and any relationship between error and melting point over the 200–500 K range is not obvious. These results suggest the absence of a large systematic error associated with using Eqs. (5)–(7) over this temperature range.

4. Conclusion

In conclusion, we find that Eqs. (5)–(7) are capable of correcting the dependence of phase change enthalpies with temperature over the ≈ 200 –500 K range. These relationship appear to give the best error distribution and smallest uncertainty of all the relationships tested and should be applicable to a wide range of organic compounds.

5. Supplementary material

A list of the compounds used in the correlations of Figs. 1–4, their enthalpies of fusion, vaporization and sublimation, literature references and the enthalpies calculated with the aid of Eqs. (1), (2) and (8), (5–7), (2) and (9) is available on request.

Acknowledgements

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Appendix A

The enthalpy change along a phase transition is given by Eq. (12):

$$\frac{d\Delta H}{dT} = \left[\frac{\partial \Delta H}{\partial T} \right]_p + \left[\frac{\partial \Delta H}{\partial p} \right]_T \left[\frac{\partial p}{\partial T} \right]_{\text{trans}} \quad (12)$$

where $[\partial \Delta H / \partial T]_p = \Delta C_p$, the difference in heat capacity associated with the phase change; $[\partial \Delta H / \partial p]_T = -T(\partial V / \partial T)_p + \Delta V$, from $d\Delta H = Td\Delta S + Vdp$; and $[\partial p / \partial T]_{\text{trans}} = (\Delta H / T\Delta V)$, the Clapeyron equation. ΔV refers to the volume change, and ΔH to the enthalpy change associated with the phase transition. These substitutions result in

$$\frac{d\Delta H}{dT} = \Delta C_p + \left[\Delta V - T \left(\frac{\partial V}{\partial T} \right)_p \right] \left(\frac{\Delta H}{T\Delta V} \right). \quad (13)$$

Noting that for vaporization and sublimation, $\Delta V \approx V_m$, the molar volume of the gas, and using the ideal gas law to evaluate $(\partial V / \partial T)_p$ results in Kirchhoff's equations for sublimation and vaporization; $d\Delta H / dT = \Delta C_p$. For phase changes involving melting, if the change in molar volumes with temperature, $(\partial V / \partial T)_p$ is assumed to be small [11] and ΔC_p is assumed to be independent of temperature, Eq. (13) is simplified resulting in Eq. (14).

$$\frac{d\Delta H}{dT} = \Delta C_p + \left(\frac{\Delta H}{T} \right) \quad (14)$$

Eq. (14) is a first-order linear differential equation and can be expressed in the form:

$$dy/dx + Py = Q.$$

This equation can be integrated by multiplying it by the integration factor ρ , where:

$$\rho = e^{\int -dx/x}$$

The solution is given by:

$$\rho y = \int \rho Q dx + C.$$

Using T_{fus} and 298.15 K as the limits of integration, the 298.15 K value of $\Delta_c^1 C_p$ for ΔC_p and treating this term as independent of temperature results in Eq. (8) or equivalently, Eq. (15).

$$\begin{aligned} \Delta_{\text{fus}} S_m(298.15 \text{ K}) - \Delta_{\text{fus}} S_m(T_{\text{fus}}) \\ = \Delta_c^1 C_p(298.15 \text{ K}) \ln[298.15 / T_{\text{fus}}] \end{aligned} \quad (15)$$

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