

Vapor Pressures and Vaporization Enthalpies of a Series of Dialkyl Phthalates by Correlation Gas Chromatography

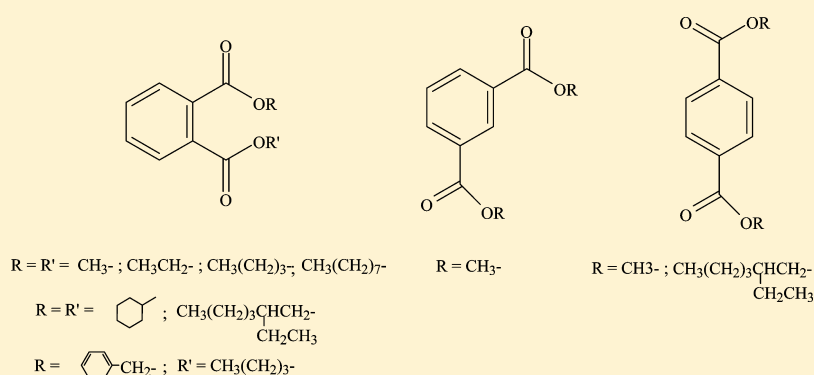
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S Supporting Information



ABSTRACT: Experimental vapor pressures, vaporization, fusion and sublimation enthalpies of a number of dialkyl benzenedicarboxylates have been examined by correlation gas chromatography (CGC) experiments in order to identify a series of experimental measurements that appear to be internally self-consistent. The compounds studied in this regard include dimethyl phthalate dimethyl terephthalate, dimethyl isophthalate, diethyl phthalate, dibutyl phthalate, and *bis*(2-ethylhexyl) phthalate. New vaporization enthalpies and liquid vapor pressure equations ($T/K = 298.15$ to 550) of several other compounds are reported also evaluated by CGC experiments. The compounds, the vaporization, fusion, and sublimation enthalpies and liquid and solid vapor pressures evaluated are summarized in Table 22 of the text.

1. INTRODUCTION

Dialkyl phthalates and related isomers are important industrial products, and many have been produced in large quantities for a considerable period of time. Their importance ranges from their use in polymers as plasticizers to applications in cosmetics.¹ Because of the nature of their properties and longevity of use they are ubiquitous in the environment. The vapor pressures and vaporization enthalpies of some of these materials have been studied repeatedly over the years. Dibutyl phthalate and *bis*(2-ethylhexyl) phthalate have been selected as reference compounds for vapor pressure measurements by the US EPA.²

This work examines the vapor pressures and vaporization enthalpies of several liquid dialkyl benzenedicarboxylates and the fusion, sublimation, and vaporization enthalpies of three corresponding solids. Combining recent experimental measurements from the literature with some results from transpiration and correlation gas chromatography measurements, this work attempts to establish a set of self-consistent experimental values in an area that has been characterized by numerous discordant values.^{3,4} One possible contributor to this discord is the

common usage of the term octyl to refer to both 2-ethylhexyl as well as to the *n*-octyl group in the literature and by suppliers. The compounds examined include dimethyl phthalate dimethyl terephthalate, dimethyl isophthalate, diethyl phthalate, dibutyl phthalate, benzyl butyl phthalate, dicyclohexyl phthalate, *bis*(2-ethylhexyl) phthalate, *bis*(2-ethylhexyl) terephthalate and di-*n*-octyl phthalate. The structures of the dialkyl benzenedicarboxylates studied are provided in Figure 1.

2. EXPERIMENTAL SECTION

2.1. Materials: St. Louis. The origin and analysis of the materials used in this study are provided in Table 1. Analytical standards (0.99+ mass fraction) of dimethyl phthalate, diethyl phthalate, dibutyl phthalate, *bis*(2-ethylhexyl) phthalate and benzyl butyl phthalate were purchased as a mixture, 200 µg/mL in methanol (EPA 606-M Phthalate Ester Mix) from Supelco (48741). *bis*(2-Ethylhexyl) phthalate and *bis*(2-ethylhexyl)

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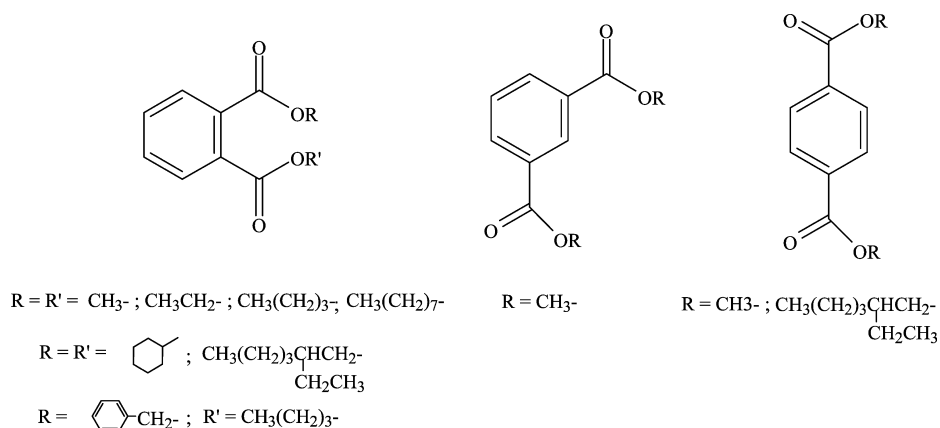


Figure 1. The structures of the dialkyl benzenedicarboxylates studied.

Table 1. Origin and Analysis (Mass Fraction) of the Dialkyl Phthalates

compound	CASRNs	supplier	mass fraction	
			St. Louis	Rostock
dimethyl phthalate	131-11-3	Supelco/ Aldrich	anal. std, ^a /0.99+	
dimethyl isophthalate	1459-93-4	Aldrich	>0.98	
dimethyl terephthalate	120-61-6	Aldrich	>0.99	
diethyl phthalate	84-66-2	Supelco/ Aldrich	anal. std, ^a /0.99	0.999
di-n-butyl phthalate	84-74-2	Supelco/ Fischer	anal. std, ^a /0.99	
benzyl butyl phthalate	85-68-7	Supelco/ Aldrich	anal. std, ^a /0.99	
dicyclohexyl phthalate	84-61-7	Aldrich	0.99	
bis(2-ethylhexyl) phthalate	117-81-7	Supelco/ Aldrich	anal. std, ^a /0.99	
bis(2-ethylhexyl) terephthalate	6422-86-2	Aldrich	0.96+	
di-n-octyl phthalate	117-84-0	Supelco/ Aldrich	anal. std, ^a /0.99	

^aEPA 606-M phthalate ester mix.

terephthalate were purchased as a mixture of two diastereomers, a *meso* and *dl* pair. Individual samples of several of these materials were also purchased. These materials were used as purchased. Both the corresponding dioctyl phthalate and dioctyl terephthalate available from Sigma Aldrich correspond structurally to the *bis*(2-ethylhexyl) material. The structures were confirmed by ¹H NMR spectroscopy on a Bruker Avance 300 NMR spectrometer.

Rostock. The liquid sample of di-*n*-butyl phthalate of 0.99 mass-fraction purity was purchased from Aldrich and further purified by repetitive distillation in vacuum. The degree of purity was determined by GC. No impurities (greater than mass fraction $3 \cdot 10^{-4}$) could be detected in the sample used for transpiration. Analysis was performed on a Hewlett-Packard gas chromatograph 5890 Series II with a flame ionization detector. The dimensions of the capillary column HP-5 (stationary phase cross-linked 5 % phenylmethyl silicone) were the following: the column length, inside diameter, and film thickness were 25 m, 0.32 mm, and 0.25 μm , respectively.

2.2. Methods. Transpiration Measurements (Rostock). Vapor pressures of dibutyl phthalate were measured by

transpiration. Details of this method are provided in the Supporting Information. Additional details of these experiments are available elsewhere.^{5,6} Table 2 reports results of the vapor

Table 2. Vapor Pressure of Dibutyl Phthalate by Transpiration

T/K^a	m/mg^b	$V(\text{N}_2)/\text{dm}^3^c$	Gas-flow, dm^3/h	p/Pa^d	$u(p)/\%^e$
$\Delta_f^\circ H(356 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (86.8 \pm 0.4)^e$					
333.2	0.85	33.68	4.21	0.224	2.73
338.4	0.85	20.65	4.13	0.365	1.87
343.4	0.81	12.24	4.08	0.586	1.35
348.0	0.78	8.23	4.08	0.838	1.10
353.6	0.54	3.40	4.08	1.40	0.86
358.7	0.74	3.06	4.08	2.15	0.73
363.7	0.73	2.04	4.08	3.16	0.66
368.7	0.74	1.43	4.08	4.59	0.61
373.6	0.78	1.02	4.08	6.75	0.57
378.5	0.73	0.68	4.08	9.48	0.55

^aSaturation temperature ($u(T) = 0.1 \text{ K}$). ^bMass of transferred sample condensed at $T = 243 \text{ K}$. ^cVolume of nitrogen ($u(V) = 0.005 \text{ dm}^3$) used to transfer m ($u(m) = 0.0001 \text{ g}$) of the sample. ^dVapor pressure at temperature T , calculated from the m and the residual vapor pressure at $T = 243 \text{ K}$. ^eThe uncertainty in the pressure measurements estimated by the expression $u(p) = 0.005(p/\text{Pa}) + 0.05$ recommended in ref 35.

pressure measurements. The data were fit to eq 1 where the intercept ($A' = (18.34 \pm 0.13)$ and slope ($B' = (10444.6 \pm 46.3)$) were obtained by plotting $\ln(p/p_o)$ versus $1/T$ where $p_o/p_a = 101325$ and R is the gas constant, $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The equation was characterized by a correlation coefficient of $r^2 = 0.9998$. The results are summarized in Table 9 discussed below. Additional details are included in the Supporting Information.

$$\ln(p/p_o) = A' - B'/RT \quad (1)$$

Correlation Gas Chromatography (St. Louis). Retention times were measured on a 5890 gas chromatograph running Chemstation using a Supelco 15 m \times 0.32 mm SPB-5 capillary column (1.0 μm film thickness), helium as the carrier gas, and a split ratio of approximately 100/1. A Vernier stainless steel temperature probe using a Go!Link USB interface running Logger Lite software was used to monitor the temperature that was maintained at $\pm 0.1 \text{ K}$ by the gas chromatography. At the temperature of the experiments, the solvent, either methanol or methylene chloride, was not retained by the column. The

residence time of each analyte on the column, t_a , was calculated from its retention time and the retention time of the solvent by difference. Experimental retention times are provided in the Supporting Information. Plots of $\ln(t_o/t_a)$ versus $1/T$ of each analyte resulted in straight lines with correlation coefficients, $r^2 > 0.99$. The term t_o refers to the reference time, 60 s. The enthalpy of transfer of each analyte from the column to the gas phase, $\Delta H_{tm}(T_m)$, was calculated as the product of the slope of the line and the gas constant, $-\text{slope} \cdot R$. The temperature T_m refers to the mean temperature of measurement. Results of a second plot of vaporization enthalpy, $\Delta_f^s H(298.15 \text{ K})$ against $\Delta H_{tm}(T_m)$ are discussed below.

The slope of the line from plots of $\ln(t_o/t_a)$ versus $1/T$ measures the enthalpy of transfer from the condensed phase of the column to the gas phase, $\Delta H_{tm}(T_m)$ and is numerically equal to the sum of the vaporization enthalpy, $\Delta_f^s H(T_m)$, and the enthalpy of interaction (or solution) of the analyte with the stationary phase, $\Delta H_{sln}(T_m)$ at T_m .^{7,8} The latter term has been found to be small in comparison to $\Delta_f^s H(T_m)$, a function of temperature, and at times endothermic.⁸ Provided the standards are appropriately chosen and of comparable size, the vaporization enthalpy of the standards at any given temperature, T , has been found to correlate linearly with the enthalpy of transfer, $\Delta H_{tm}(T_m)$.^{7–10} Proper selection of the standards corrects for heat capacity differences between T_m and T and for the enthalpy of interaction with the column. While the hydrocarbon portion of the molecule may be varied, the type and number of functional groups are important criteria to be considered in selection of appropriate standards as are their retention times.

Correlation of $\ln(p/p_o)$ of the benzenedicarboxylates used as standards with their $\ln(t_o/t_a)$ values as a function of temperature, has also resulted in linear relationships characterized with correlation coefficients, $r^2 > 0.99$. These correlations were performed at $T/K = 10$ intervals over the temperature range $T/K = (298.15 \text{ to } 550)$. The vapor pressure–temperature dependence that was obtained was then fit to a third order polynomial also discussed below. The term p_o in this work refers to 101325 Pa.

2.3. Fusion Enthalpy Measurements. Dicyclohexyl phthalate is the only solid material examined whose fusion enthalpy has not been measured previously. Measurements were conducted on a Perkin-Elmer DSC 7 instrument controlled by the Pyris Software. The instrument was standardized using indium metal with a mass fraction of 0.9999 supplied by the manufacturer, calorimetric grade benzoic acid supplied by Fisher, and Gold Label scintillation grade naphthalene supplied by Aldrich ($w > 0.99$). The samples were hermetically sealed in 50 μL pans supplied by Perkin-Elmer. A nitrogen flow rate of 0.3 $\text{mL} \cdot \text{s}^{-1}$ was passed over the cells. The samples were heated at a rate of 0.053 $\text{K} \cdot \text{s}^{-1}$. The resulting fusion enthalpy measured for dicyclohexyl phthalate is reported in Table 11 below. Additional details are available in the Supporting Information.

2.4. Temperature Adjustments. Temperature adjustments of enthalpy from the mean temperature of measurement to a common temperature was achieved using eqs 2 to 4.¹¹ These equations have been shown to provide reasonable temperature adjustments resulting from differences in the heat capacities of the two respective phases. The heat capacities of both condensed phases were estimated by group additivity.¹² Experimental heat capacities of the liquid phase for dimethyl phthalate, diethyl phthalate, dibutyl phthalate, and bis(2-

ethylhexyl) phthalate and for the crystalline phase for dimethyl isophthalate and dimethyl terephthalate have been measured.^{13–15} These values are compared to estimated values in the Supporting Information. Estimated values were used in the adjustment since eqs 2 to 4 were derived in this manner. The largest discrepancy between the experimental and estimated value was 6 %.

$$\begin{aligned} \Delta_f^s H_m(298.15 \text{ K})/(\text{kJ} \cdot \text{mol}^{-1}) &= \Delta_f^s H_m(T_m)/(\text{kJ} \cdot \text{mol}^{-1}) \\ &+ [(10.58 + 0.26C_p(l))/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})] \\ &[(T_m/K - 298.15)]/1000 \end{aligned} \quad (2)$$

$$\begin{aligned} \Delta_{cr}^1 H(298.15 \text{ K})/(\text{kJ} \cdot \text{mol}^{-1}) &= \Delta_{cr}^1 H(T_{fus})/\text{kJ} \cdot \text{mol}^{-1} \\ &+ [(0.15C_p(cr) - 0.26 \cdot C_p(l))/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) - 9.83] \\ &[T_{fus}/K - 298.15]/1000 \end{aligned} \quad (3)$$

$$\begin{aligned} \Delta_{cr}^s H_m(298.15 \text{ K})/(\text{kJ} \cdot \text{mol}^{-1}) &= \Delta_{cr}^s H_m(T_m)/(\text{kJ} \cdot \text{mol}^{-1}) \\ &+ [(0.75 + 0.15C_p(l))/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})](T_m/K - 298.15) \\ &/1000 \end{aligned} \quad (4)$$

2.5. Uncertainties. Uncertainties in temperature adjustments have been calculated using a standard deviation of $\pm 16 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for $C_p(l)$. This uncertainty was derived for substances with heat capacities averaging about (200 to 250) $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. Many of the substances in this study have much larger heat capacities and since a number of them have been measured experimentally, the following protocol was followed. Uncertainties were calculated using the difference between estimated and the experimental number if the difference exceeded $\pm 16 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and ± 16 if otherwise. The experimental uncertainty used is provided in the Supporting Information. Uncertainties in the temperature adjustment of fusion and sublimation enthalpies, eqs 3 and 4, are estimates and amount to 30 % of the total adjustment.¹¹ Uncertainties resulting from correlations and transpiration measurements are reported as standard deviations (u). Uncertainties associated with combined results were evaluated as $(u_1^2 + u_2^2 + \dots)^{0.5}$. Uncertainties in derived results were evaluated similarly unless noted otherwise.

2.6. Vaporization Enthalpy Estimations. Estimation of the vaporization enthalpies of the dialkyl phthalates reported below were calculated using eq 5.¹⁶ The various terms in the equation are defined as follows: the n_C term refers to the number of carbon atoms; n_Q refers to the number of quaternary sp^3 hybridized carbon atoms; b_i refers to the group contribution of the functional groups, in this case an ester (10.5 $\text{kJ} \cdot \text{mol}^{-1}$); n_i refers to the number of such groups (2); F_i refers to the substitution pattern of the carbons to which the function group is attached, calculated as an average if the two positions of attachment differ as is the case here (primary sp^3 carbon: $F = 1.62$, secondary sp^3 carbon, $F = 1.08$, quaternary sp^2 carbon, $F = 0.85$, tertiary $\text{sp}^3 = 0.6$); the C term includes an ortho substitution correction, and an alkyl branching correction if the branching occurs on an sp^3 carbon ($-2.0 \text{ kJ} \cdot \text{mol}^{-1}$ for each correction). Average deviations in the use of the equation used in the estimations is typically 5 % of the value for hydrocarbons and substances containing a single functional group and somewhat larger, 8 % in this case, for compounds with more than one.¹⁶

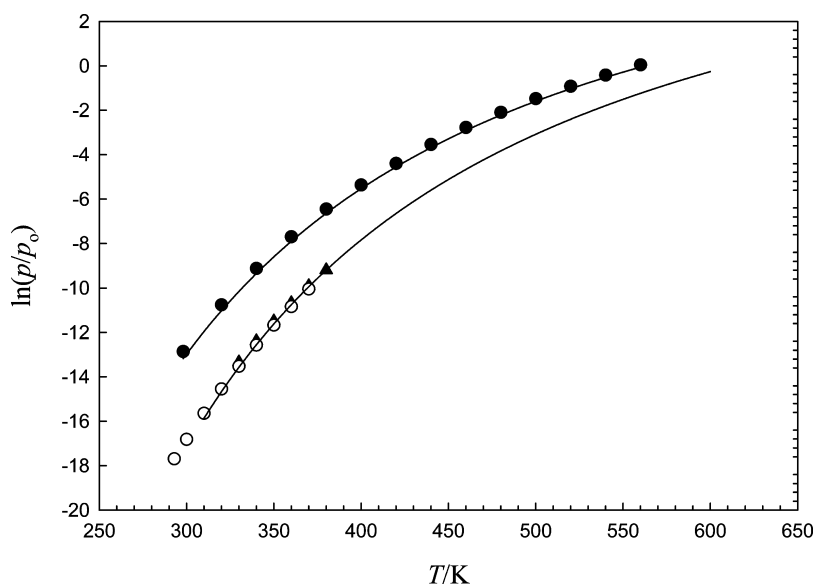


Figure 2. Bottom curve: A plot of $\ln(p/p_o)$ versus T/K for vapor pressures reported for dibutyl phthalate by Small et al. (line),¹⁷ Hales et al. (O),¹⁸ and this work (▲). Top curve: A plot of $\ln(p/p_o)$ versus T/K for vapor pressures calculated by correlation for dimethyl isophthalate (line) and vapor pressures calculated using the Wagner eq (●).¹⁵

Table 3. Parameters of the Cox Equation (6)

	A_o	$-10^3 \cdot A_1/K$	$10^6 \cdot A_2/K^2$	$p_o/T_o/K$	T_{range}/K
dimethyl phthalate ^a	3.076854	1.650657	1.171631	101.325 kPa/555.799	324 to 522
diethyl phthalate ^b	3.844479	0.9201487	0.5406641	0.0029 Pa/269.922	270 to 520

^aReference 3. ^bReference 4.

Table 4. Parameters of the Wagner Equation (7)

	A	B	C	D	T_c/K	p_c/kPa	T_{range}/K
dimethyl isophthalate ^a	-10.17884	4.62669	-6.96976	-2.77645	766	2650	350 to 607

^aReference 15.

Table 5. Parameters of Equation 8

	a	b	c	T_{range}/K
di- <i>n</i> -butyl phthalate ^a	15.992	-8739.43	-330691	293 to 373
di- <i>n</i> -butyl phthalate ^b	9.6344	-3836.11	-1261126	310 to 600

^aReference 18. ^bReference 17.

$$\Delta_f^g H(298 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = 4.69(n_C - n_Q) + 1.3n_Q + n_i \sum F_i b_i + 3.0 + C \quad (5)$$

3. STANDARDS

3.1. Vapor Pressure Standards. Experimental vapor pressures for a number of dialkyl phthalates have been reported using several different equations and formats. Recent values for dimethyl and diethyl phthalate have been reported in the form of the Cox equation, eq 6.^{3,4} Liquid vapor pressures for dimethyl isophthalate have been reported in the form of the Wagner equation,¹⁵ eq 7, and corresponding vapor pressures for di-*n*-butyl phthalate are available in the form of eqs 1 and 8. Both the Cox and Wagner equations are known to extrapolate well with temperature. How well eq 8 extrapolates is not clear. The work of Small et al.¹⁷ on dibutyl phthalate covers the most extensive range of vapor pressures as a function of temperature for this compound. However since this study is a compilation of

older data, concern arose regarding the accuracy of the vapor pressures generated from this equation. As a means of validating the reliability of this equation, the vapor pressures calculated were compared to those measured in this work by transpiration and those reported by Hales et al.,¹⁸ which were also fit to eq 8. Comparison of all three results plotted as $\ln(p/p_o)$ as a function of temperature where $p_o/\text{Pa} = 101325$ are illustrated in the lower curve of Figure 2 over the temperature range reported. The fit of all the data is quite good; all three sets of vapor pressure were averaged and fit to the third order polynomial, eq 9 over the temperature range, $T/K = (293 \text{ to } 600)$. Equation 9 has also been found to extrapolate well with temperature.^{9,10} The constants of eqs 1, and 6 to 9 are provided in Tables (3 to 7).

$$\ln(p/p_o) = (1 - T_o/T) \exp[A_o + A_1(T/K) + A_2(T/K)^2] \quad (6)$$

$$\ln(p/p_c) = 1/(T/T_c)[A(1 - T/T_c) + B(1 - T/T_c)^{1.5} + C(1 - T/T_c)^{2.5} + D(1 - T/T_c)^5] \quad (7)$$

$$\ln(p/p_o) = a + b(T/K)^{-1} + c(T/K)^{-2} \quad (8)$$

$$\ln(p/p_o) = A''(T/K)^{-3} + B''(T/K)^{-2} + C''(T/K)^{-1} + D'' \quad (9)$$

Table 6. Parameters of the Clausius Clapeyron eq 1

	A'	B'	T _{range} /K
di- <i>n</i> -butyl phthalate ^a	18.34 ± 0.13	10444.6 ± 46.3	333–379
benzyl butyl phthalate ^b	9.54	10701	416–516
dicyclohexyl phthalate ^b	18.55	11671.8	391–475
di- <i>n</i> -octyl phthalate ^b	18.17	11967.5	423–523

^aThis work. ^bReference 24.

The recommended vapor pressures from the EPA Product Properties Test Guidelines² reported in Table 8 were not used in these evaluations since references to the original literature were not available but the resulting vapor pressures calculated for dibutyl phthalate by eq 9 are well within the uncertainties proposed by the guidelines as described below. The pressures for dibutyl phthalate in all vapor pressure correlations were the values calculated using eq 9 and the constants provided in Table 7. Also included in Table 8 are the vapor pressures recommended by the EPA for *bis*(2-ethylhexyl) phthalate and the vaporization enthalpies calculated from this data. These values will be discussed below.

3.2. Vaporization Enthalpy Standards. Table 9 summarizes a portion of the most recent vaporization enthalpy values available in the literature. For those measurements measured at mean temperatures other than $T/K = 298.15$, temperature adjustments including those for dibutyl phthalate measured by transpiration are included in this table. Also included in this table are values estimated by eq 5. The compounds used as standards initially in this work included dimethyl phthalate, diethyl phthalate, and dibutyl phthalate. The vaporization enthalpies of two other compounds also involved in the evaluation of the vaporization enthalpies of *bis*(2-ethylhexyl) phthalate and di-*n*-octyl phthalate are values for dimethyl isophthalate and dimethyl terephthalate. The selection of values for these latter two compounds is discussed below. The values chosen as standards for dimethyl phthalate and diethyl phthalate are those reported by Rohac et al.^{3,4} The vaporization enthalpies reported by these workers were also accompanied by experimental vapor pressure measurements over a broad temperature range. The vaporization enthalpy chosen as the standard value for dibutyl phthalate is an average value of work reported by Hales et al.¹⁸ (94.1 ± 1.0), Verevkin et al.¹⁹ (96.0 ± 0.8), and the transpiration results from this work (95.0 ± 1.7), an average of (95.0 ± 1.1) kJ·mol⁻¹. The vaporization enthalpy resulting from the use of vapor pressures calculated using eq 9 at a mean temperature of $T/K = 350$, the temperature common

to measurements by Small et al.,¹⁷ Hales et al.,¹⁸ and this work resulted in a vaporization enthalpy at $T/K = 298.15$ of (96.5 ± 1.1) kJ·mol⁻¹, a value within experimental error of the standard value used. This value, (96.5 ± 1.1) kJ·mol⁻¹, and the vaporization enthalpy calculated from the vapor pressures reported in the EPA guidelines, (89.8 ± 0.3) kJ·mol⁻¹, were not included in calculating the standard value. The uncertainty in the EPA value reported in Table 8 only includes the standard deviation associated with the slope of the line using the vapor pressure values reported and the uncertainty associated with the temperature adjustment. It does not include any uncertainty associated with the range of vapor pressures reported in the table.

3.3. Dimethyl Isophthalate and Dimethyl Terephthalate. An examination of some of the recent thermochemical measurements for dimethyl isophthalate and dimethyl terephthalate reveals some inconsistencies in the values reported. Sublimation and fusion enthalpies for these two materials are available. Sublimation enthalpies at $T/K = 298.15$ are provided in Table 10. Two sublimation enthalpy values are available for both compounds,^{14,20} and both sets of values compare within their experimental uncertainties. Fusion enthalpies reported in the literature and their temperature adjustment to $T/K = 298.15$ are provided in Table 11.^{21–23} Two of the three values available for dimethyl terephthalate are in good agreement and were averaged. Two sets of vaporization enthalpies were calculated for both compounds from sublimation and fusion enthalpies by difference once the fusion enthalpies were adjusted to $T/K = 298.15$. Vaporization enthalpies of (76.5 ± 2.2 and 79.0 ± 2.3) and (73.9 ± 1.0 and 78.8 ± 1.2) kJ·mol⁻¹, were calculated for dimethyl terephthalate and dimethyl isophthalate, respectively. Although the value of (78.8 ± 1.2) kJ·mol⁻¹ for dimethyl isophthalate is in good agreement with the value measured directly from vapor pressure measurements, (77.2 ± 0.8),¹⁵ this value at $T/K = 298.15$ is the result of vapor pressures extrapolated from measurements at $T/K = (350–607)$. In view of the ambiguities in the fusion enthalpies of both compounds and the temperature extrapolation for dimethyl isophthalate, correlation gas chromatography experiments were conducted to identify the most probable vaporization enthalpy for each of the two compounds.

4. RESULTS AND DISCUSSION

4.1. Vaporization Enthalpies at $T/K = 298.15$.

4.1.1. Dimethyl Terephthalate and Isophthalate. A series of gas chromatography experiments were performed as a means of selecting the most probable vaporization enthalpies for dimethyl terephthalate and isophthalate. Vapor pressures for dimethyl isophthalate were treated as unknown despite the availability of reliable values as an independent means of evaluating the reliability of these correlations.¹⁵ Dimethyl, diethyl, and dibutyl phthalate were used as reference standards. Since dimethyl terephthalate and isophthalate coeluted at some temperatures, separate runs were conducted for each. Values of $\ln(t_o/t_a)$ for duplicate runs were first measured as a function of temperature over a $T/K = 30$ range at $T/K = 5$ intervals at a

Table 7. Parameters of Equation 9 Derived from the Work of Small et al.,^a Hales et al.,^b and Transpiration^c

	A''·10 ⁻⁶ /T ³	B''·10 ⁻⁴ /T ²	C''·10 ⁻² /T ¹	D''	T _{range} /K
di- <i>n</i> -butyl phthalate	346.91	−362.407	14.3696	5.780	293 to 600

^aReference 17. ^bReference 24. ^cThis work.

Table 8. EPA Product Properties Test Guidelines (OPPTS 830.7950) for Vapor Pressure^a

	T	$10^4 p/\text{Pa}$	$\Delta_i^s H_m(303 \text{ K})$	$\Delta_i^s H_m(298.15 \text{ K})$
	T/K	$10^4 p/\text{Pa}$ EPA	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
di- <i>n</i> -butyl phthalate	283.2	6.5 ± 2.1	89.1 ± 0.3	89.8 ± 0.3
	293.2	23 ± 7		
	303.2	78 ± 17		
	313.2	240 ± 90		
	323.2	700 ± 80		
calculated ^b	298.15	43	115.6 ± 0.4	116.7 ± 0.5
	T/K	$10^6 p/\text{Pa}$		
bis(2-ethylhexyl) phthalate	283.2	1.1		
	293.2	6		
	303.2	28		
	313.2	120		
	323.2	490		
calculated ^b	298.15	13		

^aReference 2. ^bCalculated using eq 1.

Table 9. Literature Vaporization Enthalpies of Various Dialkyl Phthalates

	$\Delta_i^s H_m(T_m)$	T_m	$C_p(l)$	$\Delta C_p(l) \cdot \Delta T$	$\Delta_i^s H_m(298.15 \text{ K})$	
	$\text{kJ}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	lit.	est (eq 5)
dimethyl phthalate ^a					77.0 ± 1.2	73.8 ± 5.9
diethyl phthalate ^b					82.1 ± 0.5	77.5 ± 6.2
di- <i>n</i> -butyl phthalate ^c					96.0 ± 0.8	96.3 ± 7.7
di- <i>n</i> -butyl phthalate ^d	86.8 ± 0.4	356	505.4	8.2 ± 1.7	95.0 ± 1.7	
di- <i>n</i> -butyl phthalate ^e	89.2 ± 0.1	333	505.4	4.9 ± 1.0	94.1 ± 1.0	
di- <i>n</i> -butyl phthalate ^f	83.6 ± 0.2	452	505.4	21.8 ± 4.5	105.4 ± 4.5	
di- <i>n</i> -butyl phthalate ^g	89.1 ± 0.3	303	505.4	0.7 ± 0.1	89.8 ± 0.3	
benzyl butyl phthalate ^c	89.0	466	531	24.9 ± 2.7	113.9 ± 2.7	108.4 ± 8.7
benzyl butyl phthalate ^h	90.8	323	531	3.7 ± 0.8	94.5 ± 0.8	108.4 ± 8.7
dicyclohexyl phthalate ^{c,i}	97.0	406	544.4	16.4 ± 1.7	113.4 ± 1.7	110 ± 8.8
bis(2-ethylhexyl) phthalate ^g	115.6 ± 0.4	303	747.6	1.0 ± 0.2	116.7 ± 0.5	129.8 ± 13.0
bis(2-ethylhexyl) phthalate ^j	113.2	333	747.6	7.1 ± 1.4	120.3 ± 1.4	
di- <i>n</i> -octyl phthalate ^k	107.5	408	760.6	22.9 ± 4.5	130.4 ± 4.5	133.8 ± 13.0
di- <i>n</i> -octyl phthalate ^c	99.5	473	760.6	36.4 ± 7.2	135.9 ± 7.2	

^aReference 3. ^bReference 4. ^cReference 24. ^dThis work. ^eReference 18. ^fReference 32. ^gReference 2. ^hReference 25. ⁱReference 26. ^jReference 33. ^kReference 36.Table 10. Sublimation Enthalpies Adjusted to $T/\text{K} = 298.15$ for Dimethyl Isophthalate and Terephthalate

	$\Delta_{cr}^s H_m(T_m)$	T_m	$C_p(\text{cr})$	$\Delta C_p(\text{cr}) \cdot \Delta T$	$\Delta_{cr}^s H_m(298.15 \text{ K})$	method ^{ref}
	$\text{kJ}\cdot\text{mol}^{-1}$	K	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	
dimethyl terephthalate	101.2 ± 0.5	363.7	240.8	3.6 ± 1.8	104.8 ± 1.9	calorimetric ^a
	103.8 ± 0.3	320.6		1.1 ± 0.3	104.9 ± 0.4	mass effusion ^b
dimethyl isophthalate	100.7 ± 0.4	334.3	240.8	1.8 ± 0.5	102.5 ± 0.6	calorimetric ^a
	100.7 ± 0.2	302		0.2 ± 0.1	100.9 ± 0.2^b	mass effusion ^b

^aReference 20. ^bReference 14.

mean temperature of $T/\text{K} = 500$ for dimethyl terephthalate and $T/\text{K} = 435$ for dimethyl isophthalate and plotted against $1/T$ for both the standards and the targets. The resulting slopes and intercepts from runs 1/2 and 3/4, were used to evaluate an average value of (t_o/t_a) , $(t_o/t_a)_{\text{avg}}$ as a function of temperature; this term was then correlated against the corresponding $\ln(p/p_o)$ of the standards. An example of the results of the correlation between $(t_o/t_a)_{\text{avg}}$ and $\ln(p/p_o)$ is provided in Table 13 for the temperature, $T/\text{K} = 298.15$. Values of $\ln(p/p_o)$ of the standards were calculated using eqs 6, 7, and 9 using the appropriate constants from Tables 3 and 7. Equations 10 and

11, listed below Table 13 describe the linearity of the correlation for dimethyl terephthalate (runs 1 and 2) and dimethyl isophthalate (runs 3 and 4) at this temperature. The last column of Table 13 compares the vapor pressures calculated from experimental values to those obtained by correlation at $T/\text{K} = 298.15$. The vapor pressures of the standards are reproduced within 10 % or less of their literature values. The vapor pressure for dimethyl isophthalate calculated by correlation, $p/\text{Pa} = 0.192$, is somewhat smaller than the value, $p/\text{Pa} = 0.263$ extrapolated to $T/\text{K} = 298.15$ using the Wagner equation.¹⁵

Table 11. Fusion Enthalpies of Dimethyl Isophthalate, Dimethyl Terephthalate and Dicyclohexyl Phthalate Adjusted to $T/K = 298.15$

	$\Delta_{cr}^l H_m(T_m)$ kJ·mol ⁻¹	T_{fus} K	$C_p(l)/C_p(cr)$ J·mol ⁻¹ ·K ⁻¹	$\Delta C_p \cdot \Delta T$ kJ·mol ⁻¹	$\Delta_{cr}^l H_m(298.15\text{ K})$ kJ·mol ⁻¹
dimethyl terephthalate	34.87 ^a	414.3	314/240.8	-6.4 ± 1.9	28.4 ± 1.9
	32.9 ± 1.0 ^{b,c}	413.8		-6.4 ± 1.9	26.5 ± 2.1
	31.63 ^d	413.7		-6.4 ± 1.9	25.2 ± 1.9
dimethyl isophthalate	30.2 ± 0.4 ^e	341.5	314/240.8	-2.4 ± 0.8	27.8 ± 0.9
	25.3 ± 0.8 ^b	341.2		-2.4 ± 0.8	22.9 ± 1.1
dicyclohexyl phthalate ^f	32.3 ± 1.4	336.5 ± 0.3	544.4/437	-3.29 ± 1.0	29.0 ± 1.7

^aReference 21. ^bReference 22. ^cWeight loss was observed. ^dReference 23. ^eReference 15. ^fThis work, see Supporting Information for details.

Table 12. Vaporization Enthalpies at $T/K = 298.15$ from Sublimation and Fusion Enthalpies for Dimethyl Isophthalate and Terephthalate

	$\Delta_{cr}^g H_m(298.15\text{ K})^a$ kJ·mol ⁻¹	$\Delta_{cr}^l H_m(298.15\text{ K})$ kJ·mol ⁻¹	$\Delta_v^g H_m(298.15\text{ K})^b$ kJ·mol ⁻¹
dimethyl terephthalate	104.9 ± 1.2	28.4 ± 1.9	76.5 ± 2.2
		25.9 ± 2.0 ^c	79.0 ± 2.3
dimethyl isophthalate	101.7 ± 0.4	27.8 ± 0.9	73.9 ± 1.0
		22.9 ± 1.1	78.8 ± 1.2

^aAverage values from Table 10. ^bCalculated from the following equation: $\Delta_v^g H_m(298.15\text{ K}) = \Delta_{cr}^g H_m(298.15\text{ K}) - \Delta_{cr}^l H_m(298.15\text{ K})$. ^cAn average of (26.5 ± 2.1) and (25.2 ± 1.9) kJ·mol⁻¹.

Table 13. Correlations between $\ln(t_o/t_a)_{avg}$ and Liquid $\ln(p/p_o)_{exp}$ at $T/K = 298.15$ for Runs 1/2 and 3/4^a

	-slope/K	intercept	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$	$p \cdot 10^3/\text{Pa calc/lit}$
run 1/run 2						
dimethyl phthalate	5262.39	11.549				
	5295.37	11.628	-6.117	-12.716	-12.667	319/304
dimethyl terephthalate	5434.18	11.7439				
	5463.56	11.808	-6.506		-13.068	214/na ^b
diethyl phthalate	5839.50	12.272				
	5862.46	12.331	-7.323	-13.840	-13.908	92.3/98.8
dibutyl phthalate	7248.39	13.936				
	7273.57	13.998	-10.386	-17.080	-17.061	3.9/4.3 ^c
run 3/run 4						
dimethyl phthalate	5925.84	12.973				
	5884.79	12.883	-6.88	-12.7	-12.7	323/304
dimethyl isophthalate	6165.75	13.267				
	6160.71	13.258	-7.41		-13.2	192/263 ^d
diethyl phthalate	6558.37	13.812				
	6550.36	13.797	-8.18	-13.8	-13.9	90.8/98.8
dibutyl phthalate	8087.86	15.727				
	8070.92	15.692	-11.4	-17.1	-17.1	4.0/4.3 ^c
run 1/2: $\ln(p/p_o) = (1.029 \pm 0.028) \ln(p/p_o) - (6.373 \pm 0.224)$				$r^2 = 0.9993$		(10)
run 3/4: $\ln(p/p_o) = (1.029 \pm 0.032) \ln(p/p_o) - (5.95 \pm 0.29)$				$r^2 = 0.9989$		(11)

^aRuns 1 and 2: slope and intercept measured at a mean temperature of $T_m/K = 500$; runs 3 and 4; $T_m/K = 435$. ^bNot available. ^cEPA guidelines.

^dExtrapolation of the Wagner eq, ref 15.

Correlations, similar to those in Table 13 were repeated over the temperature range, $T/K = (298.15 \text{ to } 550)$, at $T/K = 10$ intervals and the resulting vapor pressures as a function of temperature fit to eq 9. Table 14 summarizes the constants of eq 9 obtained for both the targets and standards. Column 6 of the table illustrates how well the experimental boiling temperatures were reproduced using these constants. The boiling temperatures of the standards are reproduced within $T/K = \pm 2$ as is the value for dimethyl terephthalate. The boiling temperature of dimethyl isophthalate of $T_b/K = 562$ is reproduced within $\Delta T/K = 7$ of the literature value ($T_b/K = 555$). For comparison, the Wagner eq predicts a boiling

temperature of $T_b/K = 558$.¹⁵ A comparison of the results calculated by correlation using eq 9 for dimethyl isophthalate and those obtained using the Wagner eq over the temperature range $T/K = (298.15 \text{ to } 560)$ is provided by the upper curve in Figure 2.

The vapor pressures calculated for dimethyl terephthalate using the appropriate constants for eq 9 over a $T/K = 30$ temperature range at $T_m/K = 313.15$ according to eq 1, results in a vaporization enthalpy of $(77.1 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$. The temperature $T_m/K = 313.15$ was chosen to lie within the temperature range of the correlations. An adjustment to $T/K = 298.15$ using eq 2 results in vaporization enthalpy of $(78.5 \pm$

Table 14. Constants for Equation 9, Boiling Temperatures, and Vaporization Enthalpies for Dimethyl Terephthalate, Dimethyl Isophthalate, and the Standards from Runs 1/2 and 3/4

run 1/2	$A''' \cdot 10^{-6}$	$B'' \cdot 10^{-4}$	$C'' \cdot 10^{-2}$	D''	T_b/K	$\Delta_i^s H_m(298.15\text{ K})^a$
					calc/lit ³⁴	kJ·mol ⁻¹
dimethyl phthalate	74.2963	-136.828	-26.2627	8.729	555/557	78.5 ± 0.3
dimethyl terephthalate	100.8643	-158.906	-22.0239	8.388	560/561	
diethyl phthalate	145.8162	-196.376	-15.9193	8.019	571/568	
dibutyl phthalate	100.8643	-357.347	13.4093	5.837	613/613	
run 3/4						
dimethyl phthalate	76.08322	-138.330	-25.7508	8.671	555/557	78.9 ± 0.3
dimethyl isophthalate	106.3007	-163.485	-21.3244	8.358	562/555	
diethyl phthalate	143.9568	-194.787	-16.5069	8.091	571/568	
dibutyl phthalate	339.4365	-357.435	13.4852	5.824	613/613	

^aCalculated using the constants for eq 9 for runs 1 and 2 or 5 and 6 and eq 1 at $T/K = 313$ and adjusted to $T/K = 298.15$.

Table 15. Evaluation of $\Delta_i^s H_m(298\text{ K})$ for Benzyl Butyl Phthalate and bis(2-Ethylhexyl) Phthalate

run 5	-slope T/K	intercept	$\Delta H_{tm}(500\text{ K})$	$\Delta_i^s H_m(298.15\text{ K})$	$\Delta_i^s H_m(298.15\text{ K})$
			kJ·mol ⁻¹	kJ·mol ⁻¹ (lit)	kJ·mol ⁻¹ (calc)
dimethyl phthalate	5206.7	10.782	43.29	77.0 ± 1.2	76.6 ± 2.8
dimethyl isophthalate	5506.9	11.201	45.78	78.8 ± 1.2 ^a	79.4 ± 2.8
diethyl phthalate	5776.1	11.491	48.02	82.1 ± 0.5	81.9 ± 2.9
di- <i>n</i> -butyl phthalate	7173.5	13.136	59.64	95.0 ± 1.1 ^b	95.0 ± 3.2
benzyl butyl phthalate	8346.5	14.276	69.39		105.9 ± 3.6
bis(2-ethylhexyl) phthalate	9404.5	15.817	78.19		115.8 ± 3.9
run 5					
$\Delta_i^s H_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.12 \pm 0.04)\Delta H_{tm}(500\text{ K}) - (28.0 \pm 2.1)$				$r^2 = 0.9971$	(12)
run 6					
$\Delta_i^s H_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.12 \pm 0.04)\Delta H_{tm}(500\text{ K}) - (28.0 \pm 2.1)$				$r^2 = 0.9972$	(13)

Table 16. Evaluation of $\Delta_i^s H_m(298\text{ K})$ for Benzyl Butyl Phthalate and Di-*n*-octyl Phthalate

run 7	slope T/K	intercept	$\Delta H_{tm}(521\text{ K})$	$\Delta_i^s H_m(298.15\text{ K})$	$\Delta_i^s H_m(298.15\text{ K})$
			kJ·mol ⁻¹	kJ·mol ⁻¹ (lit)	kJ·mol ⁻¹ (calc)
dimethyl phthalate	-4995.2	10.356	41.53	77.0 ± 1.2	76.8 ± 1.0
diethyl phthalate	-5543.3	11.023	46.08	82.1 ± 0.5	82.1 ± 1.0
di- <i>n</i> -butyl phthalate	-6898.5	12.585	57.35	95.0 ± 1.1 ^b	95.4 ± 1.1
benzyl butyl phthalate	-8051.0	13.685	66.93		106.7 ± 1.2
bis(2-ethylhexyl) phthalate	-9051.6	15.114	75.25	116.7 ± 0.5	116.5 ± 1.3
di- <i>n</i> -octyl phthalate	-9668.7	15.794	80.38		122.6 ± 1.4
run 7					
$\Delta_i^s H_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.18 \pm 0.014)\Delta H_{tm}(521\text{ K}) - (27.8 \pm 0.8)$				$r^2 = 0.9997$	(14)
run 8					
$\Delta_i^s H_m(298.15\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.19 \pm 0.014)\Delta H_{tm}(521\text{ K}) - (25.3 \pm 0.84)$				$r^2 = 0.9997$	(15)

0.3) kJ·mol⁻¹. This value compares very favorably with the value of (79.0 ± 2.3) kJ·mol⁻¹ calculated from the average sublimation enthalpy of (104.9 ± 1.2) and an average fusion enthalpy of (25.9 ± 2.0) kJ·mol⁻¹ both at $T/K = 298.15$ from Table 12. The literature value of (79.0 ± 2.0) kJ·mol⁻¹ was chosen as the standard value used for dimethyl terephthalate in subsequent correlations.

A similar treatment of the vapor pressure results for dimethyl isophthalate using the appropriate constants for eq 9 at $T/K = 313.15$ resulted in a vaporization enthalpy of (77.6 ± 0.2) kJ·mol⁻¹. An adjustment to $T/K = 298.15$ results in a value of (78.9 ± 0.3) kJ·mol⁻¹ in good agreement with the value of (78.8 ± 1.2) kJ·mol⁻¹ calculated by difference between the sublimation and fusion enthalpies of (100.7 ± 0.2) and (22.9 ± 1.1) kJ·mol⁻¹, Table 12. The literature value of (78.8 ± 1.2) kJ·mol⁻¹ was chosen as the standard value for dimethyl isophthalate to be used subsequently.

4.12. Vaporization Enthalpies of Dicyclohexyl Phthalate, Benzyl Butyl Phthalate, bis(2-Ethylhexyl) Phthalate, bis(2-Ethylhexyl) Terephthalate, and Di-*n*-octyl Phthalate. Using the vaporization enthalpies of dimethyl, diethyl, and di-*n*-butyl phthalate and now the most probable value for dimethyl isophthalate as standards, the vaporization enthalpies of benzyl butyl phthalate and bis(2-ethylhexyl) phthalate were evaluated. Results are reported as runs 5 and 6 in Table 15 and are characterized by eqs 12 and 13 also listed below the table. The vaporization enthalpy for bis(2-ethylhexyl) phthalate evaluated by correlation in runs 5 and 6 of (115.8 ± 3.9) kJ·mol⁻¹ (see Table 18) is within experimental error of the EPA value of (116.7 ± 0.5) kJ·mol⁻¹ calculated from the vapor pressures reported in Table 8. The EPA value of (116.7 ± 0.5) kJ·mol⁻¹ was used as the standard value for this material in subsequent evaluations. Results for benzyl butyl phthalate are discussed below.

Table 17. Evaluation of $\Delta_f^s H_m(298 \text{ K})$ for Dicyclohexyl Phthalate, and *bis*(2-Ethylhexyl) Terephthalate

run 1	-slope T/K	intercept	$\Delta H_{\text{tm}}(520 \text{ K})$	$\Delta_f^s H_m(298.15 \text{ K})$	$\Delta_f^s H_m(298.15 \text{ K})$
			$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit)	$\text{kJ}\cdot\text{mol}^{-1}$ (calc)
dimethyl phthalate	5262.4	11.549	43.75	77.0 ± 1.2	76.9 ± 1.1
dimethyl terephthalate	5438.2	11.744	45.21	79.0 ± 2.0^a	78.6 ± 1.1
diethyl phthalate	5839.5	12.272	48.55	82.1 ± 0.5	82.2 ± 1.1
di- <i>n</i> -butyl phthalate	7248.4	13.936	60.26	95.0 ± 1.1^b	95.5 ± 1.2
dicyclohexyl phthalate	8788.8	15.307	73.07		109.9 ± 1.4
<i>bis</i> (2-ethylhexyl) phthalate	9487.3	16.624	78.87	116.7 ± 0.5	116.4 ± 1.4
<i>bis</i> (2-ethylhexyl) terephthalate	10212.0	17.478	84.9		123.2 ± 1.5
run 1					
$\Delta_f^s H_m(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.12 \pm 0.015)\Delta H_{\text{tm}}(500 \text{ K}) - (27.7 \pm 0.84)$			$r^2 = 0.9995$		(16)
run 2					
$\Delta_f^s H_m(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.12 \pm 0.014)\Delta H_{\text{tm}}(500 \text{ K}) - (27.5 \pm 0.8)$			$r^2 = 0.9995$		(17)

^aFrom Table 12. ^bAn average of (96.0 ± 0.8) , (95.0 ± 1.1) , and (94.1 ± 1.0) $\text{kJ}\cdot\text{mol}^{-1}$.

Table 18. A Summary of the Vaporization Enthalpies ($\text{kJ}\cdot\text{mol}^{-1}$) from Runs 1 and 2 and 5 to 8

	run 1/2	run 5/6	run 7/8	average	lit
dimethyl phthalate	$76.7 \pm 0.8/76.8 \pm 0.7$	$76.6 \pm 2.8/76.6 \pm 2.7$	$76.8 \pm 1.0/76.7 \pm 1.9$	76.7 ± 1.7	77.0 ± 1.2
dimethyl terephthalate	$78.6 \pm 1.0/78.6 \pm 1.1$			78.6 ± 1.1	79.0 ± 2.0
dimethyl isophthalate		$79.4 \pm 2.8/79.4 \pm 2.8$		79.4 ± 2.8	78.8 ± 1.2
diethyl phthalate	$82.2 \pm 0.8/82.1 \pm 0.7$	$81.9 \pm 2.9/81.9 \pm 2.9$	$82.1 \pm 1.0/82.1 \pm 1.1$	82.1 ± 1.6	82.1 ± 0.5
di- <i>n</i> -butyl phthalate	$95.4 \pm 0.9/95.4 \pm 0.8$	$95.0 \pm 3.2/95.0 \pm 3.2$	$95.4 \pm 1.1/95.2 \pm 1.2$	95.2 ± 1.7	95.0 ± 1.0
dicyclohexyl phthalate	$109.9 \pm 1.0/109.9 \pm 0.9$			109.9 ± 1.0	
benzyl butyl phthalate		$105.9 \pm 3.6/105.9 \pm 3.6$	$106.7 \pm 1.2/106.1 \pm 1.3$	106.2 ± 2.4	
<i>bis</i> (2-ethylhexyl) phthalate	$116.5 \pm 1.0/116.5 \pm 0.9$	$115.8 \pm 3.9/115.8 \pm 3.6$	$116.5 \pm 1.3/116.5 \pm 1.4$	115.9 ± 3.8^a	116.7 ± 0.5
<i>bis</i> (2-ethylhexyl) terephthalate	$123.3 \pm 1.1/123.3 \pm 1.0$			123.3 ± 1.1	
di- <i>n</i> -octyl phthalate			$122.6 \pm 1.4/122.6 \pm 1.4$	122.6 ± 1.4	

^aEvaluated as an unknown only in runs 5 and 6.

Runs 7 and 8 were also used to evaluate benzyl butyl phthalate and also included di-*n*-octyl phthalate as an unknown. The EPA vaporization enthalpy for *bis*(2-ethylhexyl) phthalate was used as a standard. Table 16 summarizes the results of run 7. Equations 14 and 15 listed below the table summarize the linearity of both correlations.

Dicyclohexyl phthalate, *bis*(2-ethylhexyl) phthalate and *bis*(2-ethylhexyl) terephthalate were also included in the mixture that was used in runs 1 and 2 to evaluate the vapor pressure of dimethyl terephthalate described above. Using both *bis*(2-ethylhexyl) phthalate and the most probable value for dimethyl isophthalate as vaporization enthalpy standards that also included dimethyl, diethyl, and dibutyl phthalate, vaporization enthalpies for dicyclohexyl phthalate and *bis*(2-ethylhexyl) terephthalate were evaluated. The results are described in Table 17. Equations 16 and 17 characterize the quality of these correlations. Similar details for all duplicate runs are available in the Supporting Information. The results of all runs used to evaluate vaporization enthalpies are summarized in Table 18 which also includes run averages and literature values of the standards.

The average value evaluated in runs 5 through 8 for benzyl butyl phthalate is (106.2 ± 2.4) $\text{kJ}\cdot\text{mol}^{-1}$. Literature values range from $(94.5 \text{ to } 113.9 \pm 2.7)^{24,25}$ $\text{kJ}\cdot\text{mol}^{-1}$. As indicated in Table 9, the latter value required a large temperature adjustment, and this could be a source of some of the discrepancy. The estimated value of (108.4 ± 8.7) $\text{kJ}\cdot\text{mol}^{-1}$ compares favorably to the value measured. A value of (109.9 ± 1.0) $\text{kJ}\cdot\text{mol}^{-1}$ was evaluated by correlation for dicyclohexyl phthalate. This compares with a literature value of $(113.4 \pm 1.7)^{26}$ $\text{kJ}\cdot\text{mol}^{-1}$ and an estimated value of (110 ± 8.8) $\text{kJ}\cdot\text{mol}^{-1}$.

The value of (122.6 ± 1.4) $\text{kJ}\cdot\text{mol}^{-1}$ obtained in this work for di-*n*-octyl phthalate is also considerably smaller than the two literature values, $(130.4 \pm 4.5)^{22}$ and $(135.9 \pm 7.2)^{24}$ $\text{kJ}\cdot\text{mol}^{-1}$. Using the literature values, a difference of roughly $(14\text{--}19)$ $\text{kJ}\cdot\text{mol}^{-1}$ is calculated between the vaporization enthalpies of di-*n*-octyl phthalate and *bis*(2-ethylhexyl) phthalate, two structurally similar isomers. This work measures a difference of (5.9 ± 1.5) $\text{kJ}\cdot\text{mol}^{-1}$ between the two, a value more in line with the effects of branching observed in other systems $(2 \text{ kJ}\cdot\text{mol}^{-1} \cdot \text{branch}^{-1})^{16}$. Uncertainty in the large temperature adjustment of over 20 % of the value may be partially responsible for the larger difference observed with the literature values.^{24,26}

A difference of (6.6 ± 1.2) $\text{kJ}\cdot\text{mol}^{-1}$ is calculated in this work between *bis*(2-ethylhexyl) terephthalate $(123.3 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1})$ and the standard value for *bis*(2-ethylhexyl) phthalate $(116.7 \pm 0.5 \text{ kJ}\cdot\text{mol}^{-1})$. As noted previously, samples of *bis*(2-ethylhexyl) phthalate and *bis*(2-ethylhexyl) terephthalate both consist of a mixture of two diastereomers that were not separated by the chromatography. The vaporization enthalpies evaluated are for the mixture and also include the contributions of the enthalpy of mixing, both for the diastereomers and the enantiomers. Since in this case the structures are very similar, mixing effects are likely to be small.

4.2. Liquid Vapor Pressures. Vapor pressures were calculated using, eqs 6 to 9, and the constants are cited in Table 3 for dimethyl, diethyl, and dibutyl phthalate. The same protocol was followed for all vapor pressure correlations as described above for dimethyl terephthalate. The temperature range included $T/\text{K} = (298.15 \text{ to } 550)$, and vapor pressures were evaluated at 10 K intervals. The correlation coefficients, r^2 , exceeded 0.99 at all temperatures. The vapor pressures as a

Table 19. Evaluation of the Constants of Equation 9, Normal Boiling Temperatures and Liquid Vapor pressures (Pa) at $T/K = 298.15$

	$A'' \cdot 10^{-6}$	$B'' \cdot 10^{-4}$	$C'' \cdot 10^{-2}$	D''	T_b/K calc/lit	$p \cdot 10^6/\text{Pa}$ 298.15 K calc/lit
			runs 1 and 2			
dicyclohexyl phthalate	635.470	−602.922	64.3113	1.319	490/497 ^{a,b}	80/116 ^b
bis(2-ethylhexyl) phthalate	638.697	−606.365	58.1740	2.577	677/657 ^b	28/13 ^d
bis(2-ethylhexyl) terephthalate	738.488	−689.358	73.3120	1.448	699/673 ^c	5.4/175 ^{c,e}
			runs 5 and 6			
benzyl butyl phthalate	542.368	−527.001	47.268	2.921	667/643 ^{b,c}	200/666 ^g
bis(2-ethylhexyl) phthalate	628.672	−600.317	56.198	2.765	677/657 ^b	23/13 ^d
runs 7 and 8						
di- <i>n</i> -octyl phthalate	724.729	−680.153	71.484	1.548	700/663 ^{c,f}	5.5/13.3 ^b

^aAt $p/\text{kPa} = 0.533$ $T_b/K = 497$. ^bReference 27. ^cReference 28. ^dReference 2. ^eEstimate. ^fAlso $T_b/K = 498$ at $p/\text{Pa} = 333$, lit ($T_b/K = 501$) ref 28. ^gReference 34.

function of temperature were then fit to eq 9. Table 19 only includes the constants of eq 9 for compounds treated as unknown. The vapor pressures of dimethyl, diethyl, and dibutyl phthalate were used as standards in all correlations. Tables similar to Table 13 and 21 that include all the compounds in the mixture for runs 1, 2, and 5 to 8 are available in the Supporting Information as are the Antoine constants discussed below.

4.21. Runs 1 and 2: Dicyclohexyl Phthalate, and bis(2-Ethylhexyl) Terephthalate. The vapor pressures of dimethyl terephthalate, dicyclohexyl phthalate, bis(2-ethylhexyl) phthalate, and bis(2-ethylhexyl) terephthalate were treated as unknown in runs 1 and 2. Results for dimethyl terephthalate discussed above are summarized in Table 14. Since this material is a solid at $T/K = 298.15$, subcooled liquid vapor pressures are not available at this temperature for comparison to the value calculated, $p/\text{Pa} = 214 \cdot 10^{-3}$. Since bis(2-ethylhexyl) phthalate was also treated as an unknown in runs 5 and 6, results for this material are discussed below.

The normal boiling temperatures of dicyclohexyl phthalate is not available for comparison. A boiling temperature at reduced pressure ($T_b/K = 497$ at $p/\text{kPa} = 0.53$)²⁷ is available and can be compared to $T_b/K = 490$, calculated using eq 9 at this pressure, Table 19. The vapor pressure calculated for this material at $T/K = 298.15$, $p/\text{Pa} = 80 \cdot 10^{-6}$, compares to the literature value of $p/\text{Pa} = 116 \cdot 10^{-6}$.²⁷ Additionally, vapor pressures of $p/\text{Pa} = (1.3$ and $247)$ at $T/K = (391$ and $475)$, respectively, calculated from the constants reported in Table 6²⁴ compare to values of $p/\text{Pa} = (1.63$ and $268)$ calculated at these two temperatures by eq 9.

For bis(2-ethylhexyl) terephthalate, experimental vapor pressures at $T/K = 298.15$ do not seem to be available. An estimated vapor pressure at $T/K = 298.15$ ²⁸ of $p/\text{Pa} = 175 \cdot 10^{-6}$ can be compared to a value of $p/\text{Pa} = 5.4 \cdot 10^{-6}$ calculated by eq 9. An experimental boiling temperature of $T_b/K = 673$ ²⁸ compares to a predicted value of $T_b/K = 699$ using eq 9.

4.22. Runs 5 and 6: bis(2-Ethylhexyl) and Benzyl Butyl Phthalate. Correlations involving runs 5 and 6 also included vapor pressures calculated using the Wagner eq for dimethyl isophthalate¹⁵ as a standard and treated the vapor pressures of benzyl butyl phthalate and bis(2-ethylhexyl) phthalate as unknown. The normal boiling temperatures of bis(2-ethylhexyl) phthalate calculated in runs 1/2 and 5/6 by correlation both differ from the literature value by $\Delta T/K = 20$, suggesting that the vapor pressures at elevated temperatures may not be very reliable. At a reduced pressure of $p/\text{kPa} = 0.67$, a boiling temperature of $T_b/K = 502$ has been reported,²⁸ and this value can be compared to a calculated temperature of $T_b/K = (498$

(run 1 and 2)/499 (runs 5 and 6)). A vapor pressure of $p/\text{Pa} = 799$ is calculated from the Antoine constants at $T/K = 500$ and compares to values of $p/\text{Pa} = (729$ (runs 1 and 2)/697 (runs 5 and 6), Table 19) calculated from the appropriate constants of eq 9 at this temperature.²⁴ The vapor pressure calculated at $T/K = 298.15$ of $p/\text{Pa} = (28 \cdot 10^{-6}$ (runs 1 and 2)/23 $\cdot 10^{-6}$ (runs 5 and 6)) compares with the EPA recommendation of $p/\text{Pa} = 13 \cdot 10^{-6}$. An earlier review of this compound's vapor pressure recommended a value of $p/\text{Pa} = 32 \cdot 10^{-6}$ at this temperature.²⁹

A normal boiling temperature for benzyl butyl phthalate of $T_b/K = 643$ has been reported^{27,28} that compares with a value of $T_b/K = 666$ evaluated in this work, a difference of $\Delta T/K = 24$. At $T/K = (416$ and $515)$, literature vapor pressures of $p/\text{Pa} = (9.4$ and $1380)$ are calculated using eq 1 and the constants in Table 6. These can be compared to values from this work of $p/\text{Pa} = (18.0$ and $2350)$, respectively. At $T/K = 298.15$, a literature vapor pressure^{27,30} of $p/\text{Pa} = 11 \cdot 10^{-4}$ compares to a value of $p/\text{Pa} = 2 \cdot 10^{-4}$ evaluated in this work using eq 9 and the appropriate constants in Table 19.

4.23. Runs 7 and 8: Di-*n*-octyl Phthalate. The standards used in this correlation included the vapor pressures calculated using eq 9 and the constants for benzyl butyl phthalate and bis(2-ethylhexyl) phthalate evaluated in runs 5 and 6 (Table 19). The experimental boiling temperature of di-*n*-octyl phthalate differs from the value calculated using eq 9 by $\Delta T/K = 37$ suggesting that this vapor pressure may not be very reliable at temperatures nearing boiling. Predicted boiling temperatures at lower pressures appear more reliable. At $p/\text{Pa} = 333$, a value of $T_b/K = 501$ has been reported.²⁸ Equation 9 from runs 7 and 8 predict a boiling temperature $T_b/K = 496.7$. At $p/\text{Pa} = 266$, a value of $T_b/K = 487.2$ has been reported,²⁸ whereas eq 9 predicts a boiling temperature of $T_b/K = 491.9$. The vapor pressures for di-*n*-octyl phthalate reported in the compendium by Stephenson and Malanowski²⁴ using eq 1 and the constants reported in Table 6 are in good agreement over the temperature range indicated in the table. At the two experimental temperature limits, $T/K = (423$ and $523)$, Table 6), vapor pressures calculated are $p/\text{Pa} = (4.1$ and $911)$, respectively. Vapor pressures calculated using eq 9 and the constants from Table 19, runs 7 and 8 at these two temperatures are $p/\text{Pa} = 4.6$ and $p/\text{Pa} = 1035$, respectively.

4.3. Solid Vapor Pressures. Dimethyl terephthalate and isophthalate and dicyclohexyl phthalate are crystalline solids at room temperature. Since the vapor pressures of their liquid phase are available as a function of temperature from runs 1 and 2, vaporization enthalpies were calculated at the fusion temperature using eq 9 for all three compounds and using

Table 20. Sublimation Enthalpies and Solid Vapor Pressures (p_{cr}/Pa) of Dimethyl Terephthalate and Isophthalate and Dicyclohexyl Phthalate at $T/\text{K} = 298.15$

	$\Delta_f^s H_m(T_{fus})^a$	$\Delta_{cr}^l H_m(T_{fus})$	$\Delta_{cr}^s H_m(T_{fus})$	$\Delta_{cr}^s H_m(298.15 \text{ K})$	p_{cr}/Pa 298.15 K
	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ calc/lit	calc/lit
dimethyl terephthalate	67.5	32.9	100.4	104.1/104.9	0.009/0.01 ^c
dimethyl isophthalate	74.6	25.3	99.8	101.5/100.7	0.057/0.099 ^d
	73.2 ^b	25.3	98.5	100.0/100.7	0.077/0.099
dicyclohexyl phthalate	104.4	32.3 \pm 1.4	136.7 \pm 1.7	139.2/na ^e	1.2 \cdot 10 ⁻⁶ /na ^e

^aCalculated using eq 9 unless indicated otherwise. ^bCalculated from vapor pressures using the Wagner eq. ^cDimethyl terephthalate: p_{cr}/Pa from $\log(p/\text{Pa}) = (16.2 \pm 0.1) - (5423 \pm 17)/T$; $p_{cr}/\text{Pa} = (0.01 \pm 0.0012)$; ref 14. ^dDimethyl isophthalate: p_{cr}/Pa from $\log(p/\text{Pa}) = (16.6 \pm 0.1) - (5249 \pm 12)/T$; $p_{cr}/\text{Pa} = (0.099 \pm 0.009)$; ref 14. ^eNot available

Table 21. A Summary of Literature Vaporization, Fusion, and Sublimation Enthalpies Consistent with the Results of this Study

	$\Delta_f^s H_m(298.15)$	$\Delta_{cr}^l H_m(T_{fus})$	$\Delta_{cr}^s H_m(298.15)$	$p \cdot 10^4/\text{Pa}$
	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	298.15 K
dimethyl phthalate	77.0 \pm 1.2			p_l : 3040
dimethyl terephthalate	79.0 \pm 2.0	32.3 \pm 1.0	104.9 \pm 1.2	p_{cr} : 85
dimethyl isophthalate	78.8 \pm 1.2	25.3 \pm 0.8	101.7 \pm 0.4	p_l : 2631; p_{cr} : 568
diethyl phthalate	82.1 \pm 0.5			p_l : 988
di- <i>n</i> -butyl phthalate				p_l : 43
bis(2-ethylhexyl) phthalate	116.7 \pm 0.5			p_l : 0.13

Table 22. A Summary of New Values from This Work

	$\Delta_f^s H_m(298.15)$	$\Delta_{cr}^l H_m(T_{fus})$	$\Delta_{cr}^s H_m(298.15)$	$(p) \cdot 10^4/\text{Pa}$
	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	298.15 K
dimethyl terephthalate				p_l : 2140
di- <i>n</i> -butyl phthalate	95.0 \pm 1.1 ^a			
benzyl butyl phthalate	106.2 \pm 2.4			p_l : 2.0
dicyclohexyl phthalate	109.9 \pm 1.0	32.3 \pm 1.4	138.3 \pm 1.7	p_l : 0.80; p_{cr} : 0.012
bis(2-ethylhexyl) terephthalate	123.3 \pm 1.1			p_l : 0.054
di- <i>n</i> -octyl phthalate	122.6 \pm 1.4			p_l : 0.055

^aAn average of literature values and this work.

the Wagner eq for dimethyl isophthalate. Table 20 summarizes the calculated vaporization and sublimation enthalpy at T_{fus} using the most probable fusion enthalpies for dimethyl terephthalate and isophthalate. Assuming the vapor pressures at T_{fus} as common to both the solid and liquid phases, the vapor pressures of all three solids, p_{cr}/Pa , were calculated at a mean temperature of $T/\text{K} = 298.15$ using the integrated form of the Clausius–Clapeyron equation modified by inclusion of a heat capacity term for the temperature adjustment, eq 18.³¹ The vapor pressures of the solids were then used to calculate the sublimation enthalpy at the mean temperature of $T/\text{K} = 298.15$. Both the resulting sublimation enthalpies and vapor pressures at this temperature are compared to the literature values in the last two columns of Table 20. Agreement with vapor pressures measured directly for both compounds is within a factor of 2 of the literature values. The sublimation enthalpies are in excellent agreement with the literature values.

$$\ln(p_{cr}/\text{Pa}) = [\Delta_{cr}^s H(T_{fus}) + \Delta_{cr}^s C_p \Delta T] \\ [1/T_{fus}/\text{K} - 1/298.15]/R + \ln(p_{T_{fus}}/\text{Pa}) \quad (18)$$

where: $\Delta_{cr}^s C_p \cdot \Delta T = [0.75 + 0.15C_p(\text{cr})][(T_{fus}/\text{K} - 298.15)/2]$.

5. SUMMARY

The literature values of vapor pressure and vaporization enthalpies for dimethyl phthalate were combined with values for diethyl phthalate and dibutyl phthalate with some additional experimental vapor pressure measurements by transpiration for dibutyl phthalate from this work and the results from correlation gas chromatography experiments to obtain a set of reasonably self-consistent values for vapor pressure, fusion, and vaporization enthalpy for dimethyl isophthalate and terephthalate. The recommended vapor pressure for dibutyl phthalate has been independently reproduced, and a vaporization enthalpy for this material was recommended. Additionally, the recommended vaporization enthalpy and vapor pressure for bis(2-ethylhexyl) phthalate have been independently confirmed, and vaporization enthalpies and vapor pressure equations for benzyl butyl, dicyclohexyl, and di-*n*-octyl phthalate have been evaluated. Fusion and sublimation enthalpies for dicyclohexyl phthalate have also been determined as have vapor pressures for the solid and liquid phases at $T/\text{K} = 298.15$. Vapor pressures for the liquid phase have been evaluated over a broad range of temperatures. The literature values most consistent with the results of this study and the values evaluated in this work are summarized in Tables 21 and 22.

■ ASSOCIATED CONTENT

● Supporting Information

Tables of the experimental retention times described in the text, details regarding the fusion enthalpy of dicyclohexyl phthalate, the transpiration experiments, experimental and estimated heat capacities and constants for eq 9 for all runs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ NOTATION

C = correction term ($-2.0 \text{ kJ}\cdot\text{mol}^{-1}$) for carbon branching and ortho substitution

CGC = correlation gas chromatography

$C_p(\text{cr})$ = molar heat capacity of the solid

$C_p(\text{l})$ = molar heat capacity of the liquid

$\Delta_{\text{cr}}^{\text{g}}H(T)$ = the sublimation enthalpy at temperature T/K

$\Delta_{\text{cr}}^{\text{l}}H(T_{\text{fus}})$ = molar fusion enthalpy at the fusion temperature

$\Delta_{\text{cr}}^{\text{l}}H(T)$ = molar fusion enthalpy adjusted to temperature T/K

$\Delta_{\text{f}}^{\text{g}}H(T)$ = the molar enthalpy of vaporization at temperature T

$\Delta H_{\text{sln}}(T_{\text{m}})$ = the molar enthalpy of interaction (solution) of the analyte with the stationary phase of the column

$\Delta H_{\text{tm}}(T_{\text{m}})$ = the molar enthalpy of transfer (vaporization) from the stationary phase of the column to the gas phase

F = substitution pattern of the carbon attached to a functional group

p_{cr} = vapor pressure of the crystalline material

p_{l} = vapor pressure of the liquid

$p_{\text{o}} = 101325 \text{ Pa}$

t_{a} = difference between the retention time of the analyte and nonretained reference

T_{fus} = the melting temperature

T_{m} = the mean temperature of measurement

$t_{\text{o}} = 60 \text{ s}$

u = uncertainty, one standard deviation unless noted otherwise

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