

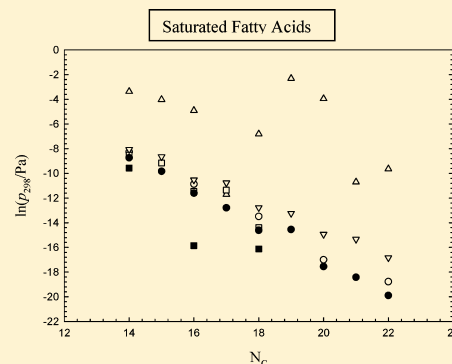
# Vapor Pressures and Vaporization, Sublimation, and Fusion Enthalpies of Some Fatty Acids

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## Supporting Information

**ABSTRACT:** Sublimation enthalpies are calculated at  $T/K = 298.15$  by combining both literature and measured vaporization enthalpies with available fusion enthalpies of a series of saturated and unsaturated fatty acids. The results are used to predict vapor pressures of both the subcooled liquid and solid state for those materials that are solids at  $T/K = 298.15$ . Equations for the prediction of vapor pressure from  $T/K = 298.15$  to the boiling temperature are provided for all liquid materials studied. The results are compared to vapor pressures in the literature measured by other methods. Vaporization enthalpies were measured for the following compounds by correlation gas chromatography ( $\Delta H_{\text{vap}}(298.15 \text{ K})$ ,  $\text{kJ}\cdot\text{mol}^{-1}$ ):  $\alpha$ -linolenic acid, ( $136.9 \pm 10.4$ );  $\gamma$ -linolenic acid, ( $135.9 \pm 6.8$ ); linoleic acid, ( $134.1 \pm 10.3$ ); elaidic acid, ( $133.0 \pm 10.3$ ); heneicosanoic acid, ( $149.2 \pm 7.1$ ); erucic acid, ( $149.2 \pm 7.1$ ); and docosanoic acid ( $154.7 \pm 7.3$ ). A solid–solid transition enthalpy and fusion enthalpy, respectively, for docosanoic acid by differential scanning calorimetry (DSC) was also measured ( $\text{kJ}\cdot\text{mol}^{-1}$ , K): ( $3.57 \pm 0.3$ ,  $340.9 \pm 0.2$ ); ( $66.3 \pm 0.2$ ,  $352.3 \pm 0.1$ ). The saturated acids that were studied include tetradecanoic acid through to docosanoic acid.



## INTRODUCTION

The linear fatty acids are of immense industrial and biological importance. Large-scale production of these materials from both anthropogenic and biogenic sources also pose environmental concerns.<sup>1,2</sup> A number of the carboxylic acids that are studied in this research have been associated with secondary ambient aerosols.<sup>3</sup> Despite the fact that these compounds have been studied for well over a century, most of the thermochemical data that has been accumulated has been on the saturated fatty acids, many of which are solids at room temperature. Much less information is available on the corresponding unsaturated acids, many of which tend to be liquids at room temperature. This article reports the vaporization enthalpies and vapor pressures of several unsaturated fatty acids and the vaporization and sublimation enthalpy of two  $C_{21}$  and  $C_{22}$  saturated fatty acids. The vaporization enthalpies were evaluated by correlation-gas chromatography by taking advantage of the critically reviewed vapor pressure and vaporization enthalpy data that has been reported by De Kruif et al.<sup>4</sup> on the saturated  $C_{14}$ – $C_{20}$  fatty acids. The vaporization enthalpy data that are available have been adjusted to  $T/K = 298.15$  and used as such. Vapor pressures also obtained through correlations were assessed by comparison to experimental boiling temperatures whenever possible. The fusion enthalpy of docosanoic acid is also reported, and recent fusion enthalpies reported for the  $C_{14}$ – $C_{20}$  carboxylic acids are briefly summarized and discussed. The compounds investigated include  $\alpha$ -linolenic acid ( $C_{18}H_{30}O_2$ , *cis,cis,cis*-9,12,15-octadecatrienoic acid),  $\gamma$ -linolenic acid ( $C_{18}H_{30}O_2$ , *cis,cis,cis*-6,9,12-octadecatrienoic acid), linoleic acid ( $C_{18}H_{32}O_2$ , *cis,cis*-9,12-octadecadienoic acid), elaidic acid ( $C_{18}H_{34}O_2$ , *trans*-9-octadecenoic

acid), heneicosanoic acid ( $C_{21}H_{42}O_2$ ), erucic acid ( $C_{22}H_{42}O_2$ , *cis*-13-docosenoic acid), and docosanoic acid. The structures of the unsaturated acids are shown in Figure 1. Vapor pressures of both the subcooled liquid and of the solid state at  $T/K = 298.15$  are also calculated for the saturated  $C_{14}$ – $C_{22}$  fatty acids and compared to available data.

## EXPERIMENTAL SECTION

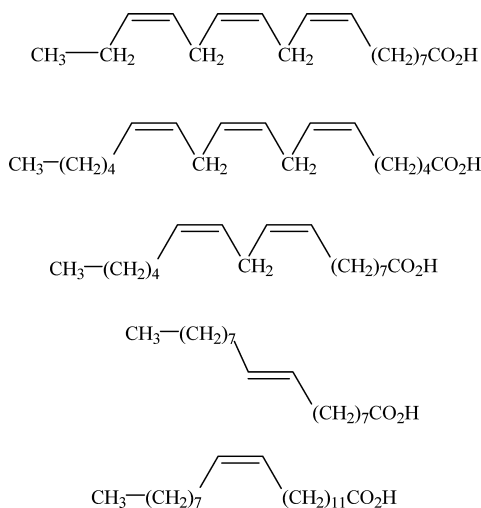
**Materials and Methods.** The fatty acids were obtained in kit form from Supelco. The compounds are identified and characterized in Table 1. The liquid samples were provided in sealed ampules by the supplier. The purity of the sample is generally not an issue since the experiments are conducted as dilute mixtures and the chromatography separates any other components present. All of the samples were analyzed by gas chromatography before use. Their analysis is reported in Table 1. Experiments were conducted on a Hewlett-Packard 5890 Series II gas chromatography equipped with an FID detector on a 30 m, 0.32 mm ID J&W FFAP column using helium as the carrier gas. Both injector and detector were maintained at 300 °C using methylene chloride as the solvent and also as the nonretained reference material. Chromatographs were recorded on an HP Chemstation.

Chromatographs were recorded over a  $T/K = 30$  range at 5 K intervals. Column temperatures were controlled by the instrument to  $\pm 0.1$  K and monitored independently using a Fluke

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**Figure 1.** Structures of the unsaturated fatty acids studied. From top to bottom:  $\alpha$ -linolenic acid,  $\gamma$ -linolenic acid, linoleic acid, elaidic acid, and erucic acid.

**Table 1. Description of the Chemical Samples<sup>a</sup>**

CAS no.	chemical name	supplier	mass fraction
544-63-8	tetradecanoic acid (myristic acid, (c))	Supelco	0.996
1002-84-2	pentadecanoic acid (c)	Supelco	0.991
57-10-3	hexadecanoic acid (palmitic acid, (c))	Supelco	0.984
506-12-7	heptadecanoic acid (margaric acid, (c))	Supelco	0.986
506-26-3	<i>cis,cis,cis</i> -6,9,12-octadecatrienoic acid ( $\gamma$ -linolenic acid, (l))	Supelco	0.992
463-40-1	<i>cis,cis,cis</i> -9,12,15-octadecatrienoic acid ( $\alpha$ -linolenic acid, (l))	Supelco	0.997
60-33-3	<i>cis,cis</i> -9,12-octadecadienoic acid (linoleic acid, (l))	Supelco	0.997
112-79-8	<i>trans</i> -9-octadecenoic acid (elaidic acid, (c))	Supelco	0.97
57-11-4	octadecanoic acid (stearic acid, (c))	Supelco	0.951
646-30-0	nonadecanoic acid, (c)	Supelco	0.963
506-30-9	eicosanoic acid (arachidic acid, (c))	Supelco	0.985
2363-71-5	heneicosanoic acid, (c)	Supelco	0.954
112-86-7	<i>cis</i> -13-docosanoic acid (erucic acid, (c))	Supelco	0.997
112-85-6	docosanoic acid (behenic acid, (c))	Supelco	0.991

<sup>a</sup>The chemicals that were used were all commercial samples, and all were analyzed by gas chromatography; chemical purities from the supplier were not available; (c): crystalline; (l): liquid at  $T/K = 298$ .

50S K/J digital thermometer. Enthalpies of transfer were calculated from the product of the slope of line obtained from  $\ln(t_o/t_a)$  vs  $1/T$  plots and the gas constant. The term  $t_o$  refers to the reference time, 1 min, and  $t_a$  refers to the adjusted retention time obtained by difference between the retention time of the analyte and that of a nonretained reference, in this case the

solvent. At the temperatures of these experiments, CH<sub>2</sub>Cl<sub>2</sub> is not retained. All plots were characterized by correlation coefficients,  $r^2$ , of  $>0.99$ . Retention times and additional details are available in the Supporting Information provided. The enthalpy of transfer,  $\Delta H_{tm}(T_m)$ , is thermodynamically related to the corresponding vaporization enthalpy,  $\Delta H_{vap}(T_m)$ , by eq 1 where the term  $\Delta H_{intr}(T_m)$  refers to the enthalpy of interaction of the analyte with the column.<sup>5</sup> Somewhat surprisingly, this has often been found to be an endothermic term since the enthalpy of transfer has generally been found to be numerically smaller than the vaporization enthalpy when both are evaluated at the average temperature of the gas chromatographic experiments.<sup>6</sup> Exceptions have been observed with chiral analytes on chiral columns.<sup>6</sup> Provided suitable standards are used, the enthalpies of transfer are found to correlate linearly with the vaporization enthalpies of the standards when adjusted to a common temperature.<sup>6-12</sup> The correlation equation derived from the standards is then used to evaluate the vaporization enthalpies of the target substances using their measured enthalpies of transfer.

$$\Delta H_{tm}(T_m) = \Delta H_{vap}(T_m) + \Delta H_{intr}(T_m) \quad (1)$$

**Uncertainties.** All combined uncertainties in the tables were calculated as  $(u_1^2 + u_2^2 + \dots)^{0.5}$ . Uncertainties for values derived from linear correlations were calculated from both the uncertainties in the slope and intercept of the correlation equations derived between the vaporization enthalpies of the standards and the enthalpies of transfer.

**Fusion Enthalpies.** The fusion enthalpy of docosanoic acid was measured on a Perkin-Elmer DSC-7 using the Pyris Series Thermal Analysis software under a flow of nitrogen gas at a rate of 5 K·min<sup>-1</sup> in hermetically sealed aluminum pans. The pans were weighed before and after each experiment. No mass loss was detected. The instrument is a power compensated model. The instrument was calibrated using an indium standard,  $w = 0.99999$ , (J·g<sup>-1</sup>,  $T/K$ : 28.5, 429.8) provided by the manufacturer and the heat calibration checked using Gold Label scintillation grade naphthalene,  $w = > 0.99$  (Aldrich) by comparing with recommended values [kJ·mol<sup>-1</sup>,  $T/K$ : (19.1 ± 0.1) kJ, (353.3 ± 0.1); lit.<sup>13</sup> (19.06 ± 0.08), (353.4 ± 0.04)]. These results were within the experimental uncertainties. Naphthalene was chosen because of the proximity of its melting temperature to that of docosanoic acid. Measurements for the solid acid are reported in Table 2, and Figure 2 provides a representative differential scanning calorimetry (DSC) scan. In addition to fusion, docosanoic acid exhibited an additional phase transition that appeared as two overlapping transitions, a broad one and a larger, sharper transition exhibiting a peak at  $T/K = (338 \pm 0.2)$ . Due to peak overlap and broadness of the peaks, the uncertainty in the peak position and enthalpy of the phase transitions is probably of the order of  $T/K = \pm 0.5$  and  $\pm 0.5$  kJ·mol<sup>-1</sup>. The enthalpy reported is for the sum of both transitions obtained by integration of the peaks by the software. An onset temperature

**Table 2. A Summary of the Fusion Enthalpy Measurements**

	sample/mg	$T_i/K$	$\Delta H_f(T_i)$	$T_{fus}^a/K$	$\Delta H_{fus}(T_{fus})$
			kJ·mol <sup>-1</sup>		kJ·mol <sup>-1</sup>
docosanoic acid	13.9	340.8	3.84	352.3	66.3
	11.55	340.7	3.53	352.3	66.2
	11.06	341.2	3.34	352.4	66.5
	avg	340.9 ± 0.2	3.57 ± 0.3	352.3 ± 0.1	66.3 ± 0.2

<sup>a</sup>Reported as onset temperatures (lit.<sup>35</sup> mp 353.1 K); all uncertainties are standard deviations.

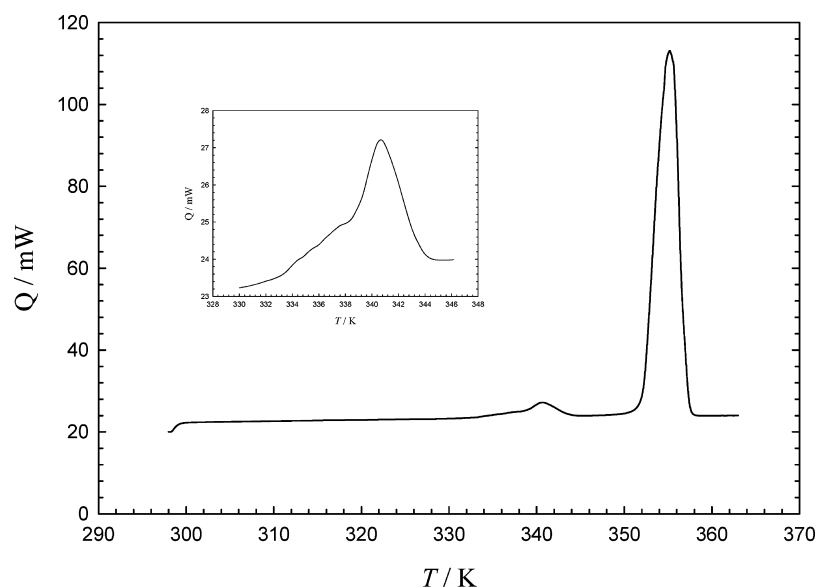


Figure 2. DSC plot of endothermic heat flow,  $Q$ , as a function of temperature for docosanoic acid.

Table 3. Recent Literature Enthalpies of Solid–Solid and Solid Liquid Phase Transitions of Some Fatty Acids

	$T_i/K$	$\Delta H_i(T_i)^a$		$\Delta H_{fus}(T_{fus})$		$\Delta H_{tpce}$	ref
		$\text{kJ}\cdot\text{mol}^{-1}$	$T_{fus}/K$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$		
tetradecanoic acid			327.3	$45.1 \pm 0.1$			16
			327.4	$44.7 \pm 1.8$			18
pentadecanoic acid	315	$1.8 \pm 0.4$	326.6	$45.0 \pm 1.3$	$46.8 \pm 1.4$		14
	325.3	$6.4 \pm 0.7$	326.6	$45.0 \pm 1.3$	$51.4 \pm 1.5$		14
	318.7	$8.1 \pm 0.1$	325.7	$41.5 \pm 0.1$	$49.6 \pm 0.1^b$		17
	321.9	$8.2 \pm 0.6$	325.5	$40.4 \pm 0.6$	$48.6 \pm 0.8^b$		15
	295.5	$0.3 \pm 0.1$	325.5	$40.4 \pm 0.6$	$40.7 \pm 0.6^b$		15
hexadecanoic acid	319.3	$7.3 \pm 0.3$	325.9	$42.7 \pm 1.7$	$50.0 \pm 1.7^b$		18
			335.7	$53.7 \pm 0.1$			16
heptadecanoic acid			335.8	$53.4 \pm 2.1$			18
	324.7	$2.6 \pm 0.7$	334.7	$53.0 \pm 1.0$	$55.6 \pm 1.2$		14
	331	$7.6 \pm 0.5$	334.7	$53.0 \pm 1.0$	$60.6 \pm 1.1$		14
	316.7	$3.1 \pm 0.2$	334.7	$53.0 \pm 1.0$	$56.1 \pm 1.0$		14
	317.5	$4.9 \pm 0.4$	334.7	$53.0 \pm 1.0$	$57.9 \pm 1.1$		14
trans-9-octadecenoic acid	329.2	$7.4 \pm 0.1$	334.3	$51.3 \pm 0.1$	$58.7 \pm 0.1^b$		17
	329.6	$7.3 \pm 0.3$	334.4	$51.5 \pm 2.1$	$58.8 \pm 2.1^b$		18
	331.2	$7.5 \pm 0.9$	333.5	$46.5 \pm 0.9$	$54.0 \pm 1.3^b$		15
octadecanoic acid			317	58.6			19
			342.5	$61.2 \pm 0.2$			16
			342.6	$63.0 \pm 2.5$	$63.0 \pm 2.5$		18
			344	61.5	61.5		19
	331.6	$2.8 \pm 0.3$	342.4	$63.2 \pm 1.4$	$66.0 \pm 1.7$		14
	327.4	$4.3 \pm 0.3$	342.4	$63.2 \pm 1.4$	$67.5 \pm 1.4$		14
	324.4	$5.4 \pm 0.3$	342.4	$63.2 \pm 1.4$	$68.6 \pm 1.4$		14
	325.9	$5.7 \pm 0.3$	342.4	$63.2 \pm 1.4$	$68.9 \pm 1.4$		14
	338	$9.2 \pm 0.2$	341.2	$57.6 \pm 0.3$	$66.8 \pm 0.3^b$		17
	339	$7.4 \pm 0.6$	340.4	$57.0 \pm 0.1$	$64.4 \pm 0.6^b$		15
nonadecanoic acid	337.6	$9.9 \pm 0.4$	341.3	$57.8 \pm 2.3$	$67.7 \pm 2.3^b$		19
			348.2	$69.2 \pm 0.4$			16
			348.4	$72.0 \pm 2.9$	$72.0 \pm 2.9$		18
	333.3	$6.1 \pm 0.2$	347.6	$71.6 \pm 1.6$	$77.7 \pm 1.6$		14
	332.8	$4.1 \pm 0.3$	347.6	$71.6 \pm 1.6$	$75.7 \pm 1.6$		14
heneicosanoic acid	332.6	$5.9 \pm 0.2$	347.6	$71.6 \pm 1.6$	$75.5 \pm 1.6$		14
	344.6	$5.0 \pm 1.0$	346.7	$63.0 \pm 3.0$	$68.0 \pm 3.2^b$		15
	340.9	$3.6 \pm 0.2$	352.3	$66.3 \pm 0.2$	$69.9 \pm 0.4^b$		tw <sup>c</sup>

<sup>a</sup>Enthalpy of transition at the transition temperature  $T_i$ ; values from the same reference refer to different polymorphic forms. <sup>b</sup>Total phase transitions from  $T/K = (298 \text{ to } T_{fus})$ ; in cases with multiple phase transitions all uncertainties are combined values. <sup>c</sup>This work.

Table 4. Temperature Adjustments of Fusion or Total Phase Change Enthalpy<sup>16,17</sup>

	$T_{\text{tp}}/\text{K}$	$\Delta H_{\text{tpce}}(T_{\text{tp}})^{\text{a}}$	$C_{\text{p}}(\text{l})/C_{\text{p}}(\text{cr})$	$\Delta C_{\text{p}}\Delta T$	$\Delta H_{\text{tpce}}(298\text{ K})^{\text{a}}$
		$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
tetradecanoic acid	327.3 <sup>b</sup>	45.1 ± 0.1	505.1/412.5	-2.3 ± 0.7	42.8 ± 0.7 <sup>b</sup>
pentadecanoic acid	325.7	49.6 ± 0.1	537/439.4	-2.3 ± 0.7	47.3 ± 0.7
hexadecanoic acid	335.7 <sup>b</sup>	53.7 ± 0.1	568.9/466.3	-3.3 ± 1.0	50.4 ± 1.0 <sup>b</sup>
heptadecanoic acid	334.3	58.7 ± 0.1	600.8/493.2	-3.3 ± 1.0	55.4 ± 1.0
elaidic acid	317 <sup>c</sup>	58.6	624.5/509.1	-1.8 ± 0.5	56.8 ± 0.5
octadecanoic acid	342.5 <sup>b</sup>	61.2 ± 0.1	632.7/520.1	-4.3 ± 1.3	56.9 ± 1.3 <sup>b</sup>
nonadecanoic acid	341.2	66.8 ± 0.3	664.6/547	-4.3 ± 1.3	62.5 ± 1.3
eicosanoic acid	348.2 <sup>b</sup>	69.2 ± 0.4	696.5/573.9	-5.2 ± 1.6	64.0 ± 1.6 <sup>b</sup>
heneicosanoic acid	346.7	68.0 ± 3.2	728.4/600.8	-5.3 ± 1.6	62.7 ± 3.6
docosanoic acid	352.3 <sup>d</sup>	69.9 ± 0.4 <sup>e</sup>	760.3/627.7	-6.1 ± 1.8	63.8 ± 1.8

<sup>a</sup>Total phase change enthalpy, solid–solid and solid–liquid;  $T_{\text{tp}}$ : triple point temperature; all uncertainties are combined values. <sup>b</sup>Fusion enthalpy.

<sup>c</sup>Melting temperature. <sup>d</sup>Onset temperature. <sup>e</sup>Includes the enthalpy of a shoulder observed at approximately  $T/\text{K} = 338$ , this work.

Table 5. Vaporization Enthalpy Adjustments to  $T/\text{K} = 298.15$ 

	$\Delta H_{\text{vap}}(T)$		$C_{\text{p}}(\text{l})$	$\Delta C_{\text{p}}\Delta T$	$\Delta H_{\text{vap}}(298\text{ K})$
	$\text{kJ}\cdot\text{mol}^{-1}$ (lit)	$T/\text{K}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
tetradecanoic acid	104.1 ± 2.0	348.6	505.1	7.2 ± 0.8	111.3 ± 2.2
pentadecanoic acid	108.4 ± 2.0	357.1	537	8.8 ± 0.9	117.2 ± 2.2
hexadecanoic acid	110.2 ± 2.0	364.1	568.9	10.5 ± 1.1	120.7 ± 2.3
heptadecanoic acid	112.7 ± 2.0	372	600.8	12.3 ± 1.2	125.0 ± 2.3
octadecanoic acid	118.9 ± 2.0	379	632.7	14.2 ± 1.3	133.1 ± 2.4
nonadecanoic acid	121.8 ± 2.0	386.1	664.6	16.1 ± 1.4	137.9 ± 2.4
eicosanoic acid	125.5 ± 2.0	392.5	696.5	18.1 ± 1.5	143.6 ± 2.5

of  $T/\text{K} = (352.3 \pm 0.1)$  for fusion compares very favorably with the literature value<sup>35</sup>  $T/\text{K} = (353.1 \pm 0.1)$ . To eliminate the possibility that the broad peak was due to the loss of water, not detected by the FID detector, the fusion of a sample was measured in a open capsule and heated by the DSC to  $T/\text{K} = 373$ . No mass loss was detected upon cooling.

## LITERATURE REVIEW

**Literature Fusion Enthalpies.** The fusion enthalpies associated with the solid to liquid phase transition of the fatty acids is complicated by the occurrence of polymorphism. The various transitions associated with these acids have been studied by X-ray and powder pattern studies as well as by thermal analysis.<sup>14,15</sup> Table 3 summarizes some of the recent measurements reported on the fatty acids related to this study. For the even carboxylic acids of this study, the actual solid to liquid transition appears to occur from the same structural form, referred to as the orthorhombic (C) structure.<sup>14,16</sup> This does not appear to be the case for the odd fatty acids.<sup>15</sup>

Fusion enthalpies at  $T/\text{K} = 298.15$  are required to evaluate sublimation enthalpies according to the thermochemical cycle described by eq 2. In view of the complexity and confusion in the literature<sup>14</sup> associated with the number of different polymorphic forms and their accompanying transition and fusion enthalpies, only a single entry for each fatty acid has been adjusted to  $T/\text{K} = 298.15$ . The fusion enthalpies of Schaake et al.<sup>16,17</sup> for most of the odd and all of the even series carboxylic acids were chosen since the experimental vaporization enthalpies that are available, and used in this work, were also measured by the same research group.<sup>4,16,17</sup> The fusion enthalpy for heneicosanoic acid was taken from the work of Gbabode et al.<sup>15</sup> Solid–solid phase transitions reported by Schaake et al. occurring at  $T/\text{K} > 298.15$  for the odd carbon series have been included in calculating the total phase transition enthalpy,  $\Delta H_{\text{tpce}}$ , since the transitions were

Table 6. Thermodynamic Properties of the Carboxylic Acid Standards Used in eq 5<sup>a</sup>

	$\theta/\text{K}$	$-\Delta G^{\circ}(\theta)$	$\Delta H^{\circ}(\theta)$	$-\Delta C_{\text{p}}(\theta)$	$p(\theta)/\text{Pa}$
		$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	
tetradecanoic acid	417.43	15970	91360	151	100
pentadecanoic acid	426.59	16410	94570	170	102
hexadecanoic acid	426.59	14430	97710	159	59
heptadecanoic acid	435.04	14760	100720	173	59
octadecanoic acid	443.15	15080	102810	181	60

<sup>a</sup>From ref 4.

measured on the same materials. For the even carbon series (excluding dodecanoic acid), only the fusion enthalpies were adjusted for temperature for comparison with experimental sublimation enthalpies that were previously measured on the orthorhombic or C form. The temperature adjustments of fusion enthalpies have been achieved using eq 3.<sup>20</sup> The heat capacities of both the solid and the liquid phase at  $T/\text{K} = 298$  were estimated.<sup>20</sup> Experimental heat capacities of the solid phase at this temperature are available for many of the acids.<sup>16,17</sup> A table illustrating the comparison between estimated and experimental values is provided in the Supporting Information. The estimated  $C_{\text{p}}(\text{cr})$  values deviated from the experimental by an absolute average deviation of 3.2 %. A 30 % uncertainty has been associated with the use of eq 3.<sup>20</sup> Estimated  $C_{\text{p}}(\text{cr})$  values were used in place of experimental ones since eq 3 and eqs 4 and 14 described below were derived in this manner. Experimental heat capacities of the liquid phase ( $C_{\text{p}}(\text{l})$ ) are not available. The results of the temperature adjustments using eq 3 are provided in Table 4.

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

$$\begin{aligned} \Delta H_{\text{tpcc}}(298.15 \text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) &= \Delta H_{\text{fus}}(T_{\text{fus}}) + \Delta H_{\text{t}}(T_{\text{t}}) \\ &+ [(0.15C_p(\text{cr}) - 0.26C_p(\text{l}))]/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) - 9.83] \\ &\times [T_{\text{fus}}/\text{K} - 298.15]/1000 \quad T_{\text{t}}/\text{K} > 298 \quad (3) \end{aligned}$$

**Literature Vaporization Enthalpies.** The vaporization enthalpies reported by De Kruif et al. for the saturated fatty acids are available at different temperatures. Temperature adjustments to  $T/\text{K} = 298.15$  were achieved by using eq 4 which has generally proven to be satisfactory.<sup>20</sup> The  $C_p(\text{l})$  term in eq 4 refers to the heat capacity at  $T/\text{K} = 298.15$  and was estimated by group additivity.<sup>21</sup> An uncertainty of  $16 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  has been associated with the temperature independent term of this equation. The temperature adjustments from temperature  $T$  to  $T/\text{K} = 298.15$  are reported in Table 5. Since all of these acids are solids at this temperature, the vaporization enthalpies calculated are for the subcooled liquid.

$$\begin{aligned} \Delta H_{\text{vap}}(298.15 \text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) \\ = \Delta H_{\text{vap}}(T_{\text{m}}) + [(10.58 + 0.26\cdot C_p(\text{l}))]/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \\ \times (T_{\text{m}}/\text{K} - 298.15 \text{ K})/1000 \quad (4) \end{aligned}$$

**Literature Vapor Pressures.** Vapor pressures of the saturated fatty acids in Table 6 are available in the form of the equation of Clark and Glew, eq 5.<sup>22</sup> This equation has been shown to extrapolate well with temperature. Values for the appropriate terms identified in eq 5 are provided in Table 6. The reference pressure  $p_o$  in eq 5 is 1 Pa.

$$\begin{aligned} R\cdot\ln(p/p_o) &= -\Delta G^\circ(\theta)/\theta + \Delta H^\circ(\theta)(1/\theta - 1/T) \\ &+ \Delta C_p(\theta)\{\theta/T - 1 + \ln(T/\theta)\} \quad (5) \end{aligned}$$

**Table 7. Correlation of Vaporization Enthalpies with Enthalpies of Transfer of Some Fatty Acids**

	slope		$\Delta H_{\text{tm}}(T_{\text{m}})$ kJ·mol <sup>-1</sup>	$\Delta H_{\text{vap}}(298 \text{ K})$ kJ·mol <sup>-1</sup> (lit.) <sup>a</sup>	$\Delta H_{\text{vap}}(298 \text{ K})$ kJ·mol <sup>-1</sup> (calc)
	$T/\text{K}$	intercept			
Run 1					
tetradecanoic acid	-8716.6	16.577	72.47	111.3 ± 2.2	111.2 ± 8.6
pentadecanoic acid	-9061.6	16.977	75.33	117.2 ± 2.2	116.5 ± 9.0
hexadecanoic acid	-9421.5	17.404	78.33	120.7 ± 2.3	121.9 ± 9.3
heptadecanoic acid	-9776.8	17.824	81.28	125.0 ± 2.3 <sup>b</sup>	127.3 ± 9.7
octadecanoic acid	-10134.2	18.251	84.25	133.1 ± 2.4	132.7 ± 10.1
elaidic acid	-10183.4	18.259	84.66		133.4 ± 10.1
linoleic acid	-10268.2	18.264	85.37		134.7 ± 10.2
α-linolenic acid	-10424.2	18.394	86.66		137.1 ± 10.3
$\Delta_{\text{t}}^{\text{s}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.82 \pm 0.12)\Delta H_{\text{tm}}(490 \text{ K}) - (20.5 \pm 9.3)$ ; $r^2 = 0.9915$ (6)					
Run 2					
tetradecanoic acid	-8631.3	16.401	71.76	111.3 ± 2.2	111.1 ± 9.0
pentadecanoic acid	-8969.6	16.787	74.57	117.2 ± 2.2	116.6 ± 9.3
hexadecanoic acid	-9301.0	17.155	77.33	120.7 ± 2.3	121.9 ± 9.7
heptadecanoic acid	-9635.4	17.532	80.1	125.0 ± 2.3 <sup>b</sup>	127.3 ± 10.0
octadecanoic acid	-9967.0	17.905	82.86	133.1 ± 2.4	132.6 ± 10.4
elaidic acid	-9966.3	17.811	82.86		132.6 ± 10.4
linoleic acid	-10021.6	17.756	83.32		133.5 ± 10.4
α-linolenic acid	-10219.0	17.972	84.96		136.7 ± 10.6
$\Delta_{\text{t}}^{\text{s}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.94 \pm 0.13)\Delta_{\text{tm}}^{\text{s}}H_{\text{m}}(490 \text{ K}) - (27.8 \pm 9.6)$ ; $r^2 = 0.9917$ (7)					
Run 3					
hexadecanoic acid	-9074.2	16.7	75.44	120.7 ± 2.3	121.2 ± 5.6
heptadecanoic acid	-9411.7	17.1	78.25	127.3 ± 9.9	126.7 ± 5.7
octadecanoic acid	-9760.2	17.5	81.14	133.1 ± 2.0	132.5 ± 5.8
elaidic acid	-10085.8	17.9	83.85	133.0 ± 10.3	133.1 ± 5.9
linoleic acid	-9884.4	17.5	82.17	134.1 ± 10.3	134.5 ± 5.9
nonadecanoic acid	-9796.6	17.5	81.44	137.9 ± 2.4	137.9 ± 5.9
γ-linolenic acid	-10054.1	17.7	83.59		135.8 ± 5.9
α-linolenic acid	-10426.8	18.3	86.68	136.9 ± 10.4	137.3 ± 5.9
eicosanoic acid	-9963.9	17.6	82.84	143.6 ± 2.5	143.5 ± 6.1
henicosanoic acid	-10753.1	18.7	89.4		148.9 ± 6.2
docosanoic acid	-11089.5	19	92.19		154.4 ± 6.3
erucic acid	-10219.0	17.972	84.96		154.4 ± 6.3
$\Delta_{\text{t}}^{\text{s}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.99 \pm 0.05)\Delta_{\text{tm}}^{\text{s}}H_{\text{m}}(500 \text{ K}) - (28.8 \pm 4.2)$ ; $r^2 = 0.9961$ (8)					
Run 4					
hexadecanoic acid	-9125.1	16.816	75.86	120.7 ± 2.0	121.2 ± 7.4
heptadecanoic acid	-9464.5	17.208	78.68	127.3 ± 9.9	126.9 ± 7.5
octadecanoic acid	-9801.2	17.591	81.48	133.1 ± 2.0	132.6 ± 7.7

Table 7. continued

	slope		$\Delta H_{\text{tm}}(T_m)$ kJ·mol <sup>-1</sup>	$\Delta H_{\text{vap}}(298 \text{ K})$ kJ·mol <sup>-1</sup> (lit.) <sup>a</sup>	$\Delta H_{\text{vap}}(298 \text{ K})$ kJ·mol <sup>-1</sup> (calc)
	T/K	intercept			
Run 4					
elaidic acid	-9834.8	17.58	81.76	133.0 ± 10.3	133.2 ± 7.7
linoleic acid	-9909.7	17.56	82.39	134.1 ± 10.3	134.5 ± 7.7
nonadecanoic acid	-10121.5	17.944	84.15	137.9 ± 2.4	138.0 ± 7.8
γ-linolenic acid	-9997.6	17.631	83.12		135.9 ± 7.7
α-linolenic acid	-10082.5	17.72	83.82	136.9 ± 10.4	137.4 ± 7.8
eicosanoic acid	-10458.8	18.336	86.95	143.6 ± 2.5	143.8 ± 7.9
hencosanoic acid	-10790.4	18.727	89.71		149.4 ± 8.0
docosanoic acid	-11113.6	19.084	92.39		154.9 ± 8.2
erucic acid	-11098.4	18.975	92.27		154.6 ± 8.2

$$\Delta_f^{\circ}H_m(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (2.04 \pm 0.07)\Delta_{\text{tm}}^{\circ}H_m(500 \text{ K}) - (33.5 \pm 5.4); r^2 = 0.9958 \quad (9)$$

<sup>a</sup>Values used as standards unless otherwise noted. <sup>b</sup>Literature value not used as a standard in the correlation, but as a test sample

Table 8. A Summary of Runs 1–4 and Comparison with Literature and Estimated Values

	Run 1	Run 2	Run 3	Run 4	$\Delta H_{\text{vap}}(298 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$		
					avg <sup>a</sup>	lit.	est. <sup>b</sup>
tetradecanoic acid	111.2 ± 8.6	111.1 ± 9.0			111.2 ± 8.8	111.3 ± 2.2	107.5
pentadecanoic acid	116.5 ± 9.0	116.6 ± 9.3			116.6 ± 9.2	117.2 ± 2.2	112.2
hexadecanoic acid	121.9 ± 9.3	121.9 ± 9.7	121.2 ± 5.6	121.2 ± 7.4	121.6 ± 8.0	120.7 ± 2.3	116.8
heptadecanoic acid	127.3 ± 9.7	127.3 ± 10.0	126.7 ± 5.7	126.9 ± 7.5	127.3 ± 9.9 <sup>c</sup>	125.0 ± 2.3	121.5
octadecanoic acid	132.7 ± 10.1	132.6 ± 10.4	132.5 ± 5.8	132.6 ± 7.7	132.6 ± 8.6	133.1 ± 2.4	126.2
elaidic acid	133.4 ± 10.1	132.6 ± 10.4	133.1 ± 5.9	133.2 ± 7.7	133.0 ± 10.3 <sup>c</sup>		126.2
linoleic acid	134.7 ± 10.2	133.5 ± 10.4	134.5 ± 5.9	134.5 ± 7.7	134.1 ± 10.3 <sup>c</sup>		126.2
nonadecanoic acid			137.9 ± 5.9	138.0 ± 7.8	138.0 ± 6.8	137.9 ± 2.4	130.9
γ-linolenic acid			135.8 ± 5.9	135.9 ± 7.7	135.9 ± 6.8		126.2
α-linolenic acid	137.1 ± 10.3	136.7 ± 10.6	137.3 ± 5.9	137.4 ± 7.8	136.9 ± 10.4 <sup>c</sup>		126.2
eicosanoic acid			143.5 ± 6.1	143.8 ± 7.9	143.7 ± 8.0	143.6 ± 2.5	135.6
hencosanoic acid			148.9 ± 6.2	149.4 ± 8.0	149.2 ± 7.1		140.3
docosanoic acid			154.4 ± 6.3	154.9 ± 8.2	154.7 ± 7.3		145.0
erucic acid			154.4 ± 6.3	154.6 ± 8.2	154.5 ± 7.3		146.0

<sup>a</sup>Uncertainties are average values. <sup>b</sup>Estimated value using eq 10. <sup>c</sup>Average based only on Runs 1 and 2.

## RESULTS

**Vaporization Enthalpies.** Table 7 summarizes the results of four correlations between the enthalpy of transfer measured by gas chromatography and literature vaporization enthalpies. The retention times used to calculate the enthalpies of transfer in these correlations are available in the Supporting Information. Equations 6 through 9 below each correlation define the quality of the linear relationship observed between  $\Delta_{\text{tm}}^{\circ}H_m(T_m)$  and  $\Delta H_{\text{vap}}(298 \text{ K})$  for each run. Since the vaporization enthalpies evaluated are quite large, the uncertainties associated with the intercept are likewise larger in magnitude than normally observed. As a means of evaluating how well the vaporization enthalpies can be reproduced by these correlations, heptadecanoic acid was also used as an unknown in the first two correlations using the saturated C<sub>14</sub>–C<sub>16</sub> and C<sub>18</sub> carboxylic acids as standards. The resulting value agrees with the literature value within 2.5 kJ·mol<sup>-1</sup>. The results suggest that the uncertainties in these measurements are likely more in the range of ± 5 kJ·mol<sup>-1</sup> (2σ). The vaporization enthalpies of elaidic, linoleic, and α-linolenic acids were also evaluated in the first two runs, and their values were then used as additional standards in runs 3 and 4. The vaporization enthalpy value of heptadecanoic acid evaluated in the first two runs was also used as a standard in subsequent correlations.

The results of all the correlations are summarized and averaged in Table 8. The uncertainties reported in column six are also averages. Also included in this table in the last column are vaporization enthalpies estimated using the following simple equation:<sup>23</sup>

$$\begin{aligned} \Delta H_{\text{vap}}(298.15 \text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) \\ = 4.69(n_C - n_Q) + 1.3n_Q + b + 3.0 \end{aligned} \quad (10)$$

where  $n_C$  refers to the total number of carbon atoms,  $n_Q$  to the number of quaternary sp<sup>3</sup> hybridized carbon atoms, and  $b$  is the contribution of the functional group; the carboxylic acid contributes 38.8 kJ·mol<sup>-1</sup>. Agreement between the experimental and the estimated values is quite good. The results in Table 8 also suggest that, as the amount of unsaturation increases, both vaporization enthalpies increase as do the retention times (see Supporting Information).

**Liquid Vapor Pressures and Boiling Temperatures.** One means of validating the vaporization enthalpies summarized in Table 8 is to use them in conjunction with other data to calculate vapor pressures. These in turn can be used to predict boiling temperatures. Experimental boiling temperatures are available for some of the acids studied. As documented previously,<sup>8,24,25</sup> vapor pressures can be calculated from the resulting relationship between the equations relating the temperature dependence of

Table 9. Correlation of  $\ln(t_o/t_a)$  with Experimental  $\ln(p/p_{atm})$  Values at  $T/K = 298.15$ 

	slope/K	intercept	slope/K	intercept	$\ln(t_o/t_a)_{av}$	$\ln(p/p_{atm})^a$ , lit	$\ln(p/p_{atm})$ , calc
Part A: Runs 1 and 2	(1)	(1)	(2)	(2)			
tetradecanoic acid	-8716.6	16.577	-8631.3	16.401	-12.60	-18.61	-18.7 ± 0.8
pentadecanoic acid	-9061.6	16.977	-8969.6	16.787	-13.35	-19.87	-19.7 ± 0.8
hexadecanoic acid	-9421.5	17.404	-9301.0	17.155	-14.12	-20.71	-20.8 ± 0.9
heptadecanoic acid	-9776.8	17.824	-9635.4	17.532	-14.87	-21.92	-21.9 ± 0.9
octadecanoic acid	-10134.2	18.251	-9967.0	17.905	-15.63	-22.96	-23.0 ± 0.9
elaidic acid	-10183.4	18.259	-9966.3	17.811	-15.75		-23.1 ± 0.9
linoleic acid	-10268.2	18.264	-10021.6	17.756	-16.00		-23.5 ± 0.9
$\alpha$ -linolenic acid	-10424.2	18.394	-10219.0	17.972	-16.43		-24.1 ± 0.9
$\ln(p/p_{atm})_{calc} = (1.422 \pm 0.044)\ln(t_o/t_a) - (0.74 \pm 0.617) \quad r^2 = 0.9972 \quad (11)$							
Part B: Runs 3 and 4	(3)	(3)	(4)	(4)			
hexadecanoic acid	-9074.2	16.816	-9125.1	16.816	-13.75	-20.71	-20.8 ± 0.6
heptadecanoic acid	-9411.7	17.208	-9464.5	17.208	-14.5	-21.92	-21.9 ± 0.6
octadecanoic acid	-9760.2	17.591	-9801.2	17.591	-15.25	-22.96	-22.9 ± 0.6
elaidic acid	-10085.8	17.58	-9834.8	17.58	-15.38	-23.13 <sup>b</sup>	-23.1 ± 0.6
linoleic acid	-9796.6	17.944	-10121.5	17.944	-15.66	-23.49 <sup>b</sup>	-23.5 ± 0.6
nonadecanoic acid	-10054.1	17.631	-9997.6	17.631	-15.98		-24.0 ± 0.6
$\gamma$ -linolenic acid	-9963.9	18.336	-10458.8	18.336	-15.88		-23.8 ± 0.6
$\alpha$ -linolenic acid	-10426.8	17.56	-9909.7	17.56	-16.08	-24.09 <sup>b</sup>	-24.1 ± 0.6
eicosanoic acid	-9884.4	17.72	-10082.5	17.72	-16.72		-25.1 ± 0.7
hencosanoic acid	-10753.1	18.727	-10790.4	18.727	-17.44		-26.1 ± 0.7
docosanoic acid	-11089.5	19.084	-11113.6	19.084	-18.17		-27.1 ± 0.7
erucic acid	-10219.0	18.975	-11098.4	18.975	-18.24		-27.2 ± 0.7
$\ln(p/p_{atm})_{calc} = (1.441 \pm 0.029)\ln(t_o/t_a) - (0.948 \pm 0.437) \quad r^2 = 0.9984 \quad (12)$							

<sup>a</sup>Values used as standards. <sup>b</sup>Calculated using the constants of eq 13 from runs 1 and 2.

retention time,  $\ln(t_o/t_a)$ , and the corresponding vapor pressure–temperature dependence of the standards, as  $\ln(p/p_{atm})$ . Table 9A and B illustrates these correlations at  $T/K = 298.15$ . The retention times of the standards at this temperature, the  $C_{14}$ – $C_{18}$  carboxylic acids, were calculated from the slopes and intercepts of runs 1 and 2 and runs 3 and 4 of Table 7 and the two sets averaged separately. The resulting values of  $\ln(t_o/t_a)_{avg}$  were correlated against the corresponding  $\ln(p/p_{atm})$  values of the standards calculated by eq 5. In these correlations, the term  $p_{atm}$  refers to the reference pressure,  $p/Pa = 101\,325$ . The resulting equations obtained from each correlation, eqs 11 and 12 obtained at  $T/K = 298.15$ , were used to calculate the corresponding  $\ln(p/p_{atm})$  values of the remaining acids in the mixture. This process was repeated over 15 K intervals from  $T/K = (298.15 \text{ to } 600)$  for set 1 consisting of runs 1 and 2 and  $T/K = (298.15 \text{ to } 630)$  for set 2 consisting of runs 3 and 4. The values of  $\ln(p/p_{atm})$  as a function of temperature calculated from each correlation were tabulated and fit to the third-order polynomial, eq 13. In Table 9B, values of  $\ln(p/p_{atm})$  for hexadecanoic through octadecanoic acid were calculated using eq 5, and the remaining acids that were evaluated in Table 9A and used as standards in runs 3 and 4 were calculated using eq 13. The constants of eq 13 obtained from both sets of runs are tabulated in Table 10. In all correlations performed as a function of temperature, the correlation coefficient at each temperature,  $r^2$ , exceeded 0.99. The upper temperature limits for combined correlations from runs 1 and 2, and runs 3 and 4 were chosen so as not to exceed the boiling temperature of the most volatile component.

$$\ln(p/p_{atm})_{calc} = AT^{-3} + BT^{-2} + CT^{-1} + D \quad (13)$$

As mentioned above, one means of validating the gas chromatographic results is to use eq 13 to predict boiling temperatures. Normal boiling temperatures are available for the

standards and for nonadecanoic acid. Boiling temperatures for tetradecanoic through octadecanoic acid, compounds used as vapor pressure standards and calculated from the correlations, are also included in Table 10 to illustrate the quality of both the  $\ln(p/p_{atm})$  vs  $\ln(t_o/t_a)$  correlations and that of the estimates generated by extrapolations of eq 13. While unlike the equation of Clark and Glew, eq 5, the constants  $A$  to  $D$  of eq 13 have no physical significance. However, vapor pressures calculated by eq 13 extrapolate well with temperature as indicated by how well the experimental boiling temperatures for heptadecanoic and octadecanoic, calculated by extrapolations of approximately 40 K, are predicted by runs 1 and 2. The boiling temperature for nonadecanoic acid, calculated from runs 3 and 4 by extrapolation of approximately 50 K, is also in good agreement with the experimental value. A comparison of the results of duplicate runs 1 and 2 and 3 and 4 in Table 10 for six of the acids resulted in an average precision of  $\pm 0.4$  K. When appropriate standards are chosen for the correlations, the accuracy in predicting boiling temperature by this method has usually been within  $\pm 5$  K.<sup>24,25,36,37</sup>

Boiling temperatures for a few of the other acids of this study are available at reduced pressures. Boiling temperatures at reduced pressures generally tend to be less reliable. These results are summarized in Table 11. Equation 13 can also be used to predict approximate vapor pressures at  $T/K = 298.15$ .

**Subcooled Liquid Vapor Pressures at  $T/K = 298$ .** Interest in the vapor pressures of the subcooled liquid form arises from the fact that fatty acids are one of many components present in aerosols and as such are not necessarily present in crystalline form. Partitioning between the gas and condensed phase has been modeled by an empirical relationship using the vapor pressure of the subcooled liquid.<sup>30</sup> Column 3 of Table 12 lists subcooled vapor pressures evaluated in this work at  $T/K = 298.15$

Table 10. Coefficients of eq 13 for the Fatty Acids from Runs 1 to 4 and Calculated and Experimental Boiling Temperatures

	runs	A·10 <sup>-8</sup>	B·10 <sup>-6</sup>	C·10 <sup>-3</sup>	D	BT/K	
						calc.	lit. <sup>4</sup>
tetradecanoic acid	1 and 2	4.35 ± 0.14	-4.83 ± 0.11	4.65 ± 0.26	3.70 ± 0.21	598.4	599
pentadecanoic acid	1 and 2	4.53 ± 0.15	-5.03 ± 0.11	4.81 ± 0.27	3.62 ± 0.22	610.3	612.3
hexadecanoic acid	1 and 2	4.71 ± 0.16	-5.23 ± 0.12	4.98 ± 0.28	3.55 ± 0.22	622.1	622.3
	3 and 4	5.00 ± 0.21	-5.40 ± 0.16	5.33 ± 0.37	3.32 ± 0.29	622.2	622.3
heptadecanoic acid	1 and 2	4.88 ± 0.16	-5.42 ± 0.12	5.13 ± 0.29	3.49 ± 0.23	633.3	634.7
	3 and 4	5.08 ± 0.14	-5.55 ± 0.10	5.40 ± 0.24	3.29 ± 0.19	633.8	634.7
octadecanoic acid	1 and 2	5.06 ± 0.17	-5.62 ± 0.12	5.28 ± 0.30	3.44 ± 0.24	644.2	648.1
	3 and 4	5.17 ± 0.07	-5.69 ± 0.05	5.47 ± 0.12	3.27 ± 0.09	645.1	648.1
elaidic acid	1 and 2	5.20 ± 0.18	-5.74 ± 0.14	5.59 ± 0.33	3.09 ± 0.26	650.5	
	3 and 4	5.27 ± 0.06	-5.79 ± 0.04	5.72 ± 0.10	3.00 ± 0.08	650.1	
linoleic acid	1 and 2	5.44 ± 0.20	-5.95 ± 0.15	6.06 ± 0.37	2.55 ± 0.29	661.4	
	3 and 4	5.44 ± 0.04	-6.00 ± 0.03	6.09 ± 0.01	2.53 ± 0.05	661.1	
α-linolenic acid	1 and 2	5.59 ± 0.21	-6.10 ± 0.16	6.29 ± 0.38	2.35 ± 0.30	669.9	
	3 and 4	5.63 ± 0.01	-6.15 ± 0.01	6.46 ± 0.01	2.18 ± 0.01	670.9	
nonadecanoic acid	3 and 4	5.28 ± 0.01	-5.86 ± 0.01	5.61 ± 0.01	3.17 ± 0.01	656.8	659.2 <sup>a</sup>
γ-linolenic acid	3 and 4	5.60 ± 0.02	-6.10 ± 0.02	6.41 ± 0.04	2.22 ± 0.03	667.3	
eicosanoic acid	3 and 4	5.49 ± 0.07	-6.10 ± 0.05	5.93 ± 0.013	2.95 ± 0.01	670.9	
heneicosanoic acid	3 and 4	5.42 ± 0.15	-6.12 ± 0.11	5.70 ± 0.26	3.19 ± 0.20	677.1	
docosanoic acid	3 and 4	5.52 ± 0.22	-6.28 ± 0.16	5.81 ± 0.38	3.12 ± 0.29	688.2	
erucic acid	3 and 4	5.70 ± 0.22	-6.42 ± 0.16	6.22 ± 0.38	2.63 ± 0.29	695.9	

<sup>a</sup>Reference 34.

Table 11. A Summary of Various Literature Boiling Temperatures (BT) at Reduced Pressures

	ln(p/p <sub>0</sub> )	BT/K Runs 3 and 4		lit.
		calc	BT/K lit.	
linoleic acid	-7.33	450.9	450.2	26
nonadecanoic acid	-4.33	510.8	503.2, 511	28, 29
α-linolenic acid	-8.47	437.7	420.2	27

and compares them to either an EPA database or estimates, generated from the EPI Suite.<sup>31</sup> The uncertainties in these values were calculated from the uncertainties reported in the last column of Table 9A and B. This resulted in vapor pressures that vary by a factor of approximately (1.8 to 2.5) of the value reported in Table 12. As indicated in this table, the vapor pressures of the subcooled liquid are quite low. Agreement for tetradecanoic acid through octadecanoic acid is reasonably good considering the vapor pressures reported are in micro-Pascals. Agreement between this work and the estimated values is considerably worse. As the last two columns of Table 12 indicate, the EPI Suite estimates<sup>31</sup> do not show the trend in vapor pressure observed in this work with increasing molecular size.

**Sublimation Enthalpies and Solid–Gas Vapor Pressures.** Sublimation enthalpies can be evaluated from the available fusion and vaporization enthalpies at the melting temperature according to eq 2. The presence of the numerous polymorphic forms reported in Table 3 obviously complicates the calculation of sublimation enthalpy. Table 13 summarizes the sublimation enthalpies calculated using the vaporization and fusion enthalpies or total phase change enthalpies reported in articles by De Kruif et al.<sup>4</sup> and Schaake et al.<sup>16,17</sup> whose measurements were made on the same samples.<sup>4</sup> Fusion enthalpies for heneicosanoic acid are from Gbabode et al.<sup>15</sup> and results for C<sub>22</sub> are from this work. Vaporization enthalpies are included at both T/K = 298.15 and at the triple point (T<sub>tp</sub>) or melting temperature (T<sub>fus</sub>). The first set of vaporization enthalpies listed at T = T<sub>tp</sub>, column 3 of Table 13, are results from De Kruif et al.<sup>4</sup> adjusted to this temperature using

Table 12. Predicted Vapor Pressures at T/K = 298.15 of the Subcooled Liquid

	runs	p·10 <sup>6</sup> /Pa		MW <sup>b</sup>
		tw <sup>a</sup>	lit.	
tetradecanoic acid	1 and 2	800	340, <sup>c</sup> 360 <sup>d</sup>	228.4
pentadecanoic acid	1 and 2	274	108 <sup>e</sup>	242.4
hexadecanoic acid	1 and 2, 3 and 4	93, 98	117, <sup>e</sup> 14 <sup>c</sup>	256.4
heptadecanoic acid	1 and 2, 3 and 4	31, 33	19 <sup>e</sup>	270.5
octadecanoic acid	1 and 2, 3 and 4	11, 11	261, <sup>e</sup> 2.2 <sup>c</sup>	284.5
elaidic acid	1 and 2, 3 and 4	9.2, 9.3	288 <sup>e</sup>	282.5
linoleic acid	1 and 2, 3 and 4	6.4, 6.2	116 <sup>e</sup>	280.5
α-linolenic acid	1 and 2, 3 and 4	3.5, 3.4	72 <sup>e</sup>	278.4
nonadecanoic acid	3 and 4	3.9	26·10 <sup>4d</sup>	298.5
γ-linolenic acid	3 and 4	4.5	na <sup>f</sup>	278.4
eicosanoic acid	3 and 4	1.3	0.76 <sup>d</sup>	312.5
heneicosanoic acid	3 and 4	0.5	430 <sup>d</sup>	326.6
docosanoic acid	3 and 4	0.2	223 <sup>d</sup>	340.6
erucic acid	3 and 4	0.1	182 <sup>d</sup>	338.6

<sup>a</sup>This work. The vapor pressures are believed known to within a factor of 1.8 to 2.5 of the value reported. <sup>b</sup>Molecular weight used as a rough measure of molecular size. <sup>c</sup>Measured by temperature-programmed desorption, ref 1. <sup>d</sup>Estimated using EPI Suite, ref 31. <sup>e</sup>Experimental database, EPI Suite, ref 31. <sup>f</sup>Not available.

eq 4. The second set of vaporization enthalpies were obtained from vapor pressures calculated using eq 13, the constants listed in Table 10, and the Clausius–Clapeyron equation for liquids at a temperature centered at the triple point. Agreement between the two sets of values in column 3 are within the combined uncertainties associated with both the measurements and their temperature adjustments.

The sublimation enthalpies calculated in column 5 of Table 13 using eq 2 are the sum of vaporization and fusion enthalpies evaluated at T/K = 298.15 K for the orthorhombic or C form. They are for the most part in good agreement with the literature values of Davies and Malpass<sup>32</sup> obtained by Knudsen effusion. The measurements conducted on the even carboxylic acids



Table 13. Sublimation Enthalpies of the Fatty Acids

	$\Delta H_{\text{tpce}}(298 \text{ K})$	$\Delta H_{\text{vap}}(T)^a$	$\Delta H_{\text{vap}}(298 \text{ K})^b$	$\Delta H_{\text{sub}}(298 \text{ K})^c$	$\Delta H_{\text{sub}}(298 \text{ K})^d$
	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit.)
tetradecanoic acid	$42.8 \pm 0.7^e$	107.1/105.6	$111.3 \pm 2.2$	$154.1 \pm 2.3^f$	$148.8 \pm 3.9$
pentadecanoic acid	$47.3 \pm 0.7$	113.2/110.3	$117.2 \pm 2.2$	$164.5 \pm 2.3$	
hexadecanoic acid	$50.4 \pm 1.0^e$	114.7/112.9	$120.7 \pm 2.3$	$171.1 \pm 2.5^f$	$166.7 \pm 4.4$
heptadecanoic acid	$55.4 \pm 1.0$	119.0/117.7	$125.0 \pm 2.3$	$180.4 \pm 2.5$	
elaidic acid	$56.8 \pm 0.5$	129.7/125.6	$133.0 \pm 10.3$	$189.8 \pm 10.3$	
octadecanoic acid	$56.9 \pm 1.3^e$	125.3/121.1	$133.1 \pm 2.4$	$190.0 \pm 2.7^f$	$172.2 \pm 4.5$
nonadecanoic acid	$62.5 \pm 1.3$	130.0/125.7	$137.9 \pm 2.4$	$200.4 \pm 2.7$	
eicosanoic acid	$64.0 \pm 1.6^e$	134.0/129.0	$143.6 \pm 2.5$	$207.6 \pm 3.0^f$	$206.5 \pm 7.8$
heneicosanoic acid	$62.7 \pm 3.6$	139.6 <sup>g</sup> /133.7	$149.2 \pm 7.1$	$211.9 \pm 8.0$	
docosanoic acid	$63.8 \pm 1.8$	143.4 <sup>g</sup> /137.0	$154.7 \pm 7.3$	$218.5 \pm 7.5$	$201.8 \pm 8.3$

<sup>a</sup>The first value corresponds to  $\Delta H_{\text{vap}}$  adjusted to  $T_{\text{tp}}$  or  $T_{\text{fus}}$  using eq 4, and the second value was calculated by extrapolating the vapor pressures calculated using eq 13 over a  $T/K = 30$  temperature range centered at either at  $T_{\text{tp}}$  or  $T_{\text{fus}}$ ;  $T_{\text{tp}}$ : triple point. <sup>b</sup>Temperature adjustments from  $T/K = (T_{\text{m}} \text{ to } 298.15)$  using eq 4; Table 5 or this work. <sup>c</sup>The sum of columns 2 and 4; uncertainties are combined values. <sup>d</sup>From Davies and Malpass; <sup>32</sup> temperature adjustments from  $T/K = (T_{\text{m}} \text{ to } 298.15)$  using eq 14. <sup>e</sup>Fusion enthalpy. <sup>f</sup>Sublimation enthalpy for the orthorhombic (C)<sup>16</sup> form of the acid. <sup>g</sup>This work, adjusted to  $T_{\text{fus}}$  from  $T/K = 298.15$  using eq 4.

Table 14. A Comparison of Vapor Pressures (Pa) and Sublimation Enthalpies ( $\text{kJ}\cdot\text{mol}^{-1}$ ) at  $T/K = 298.15$ 

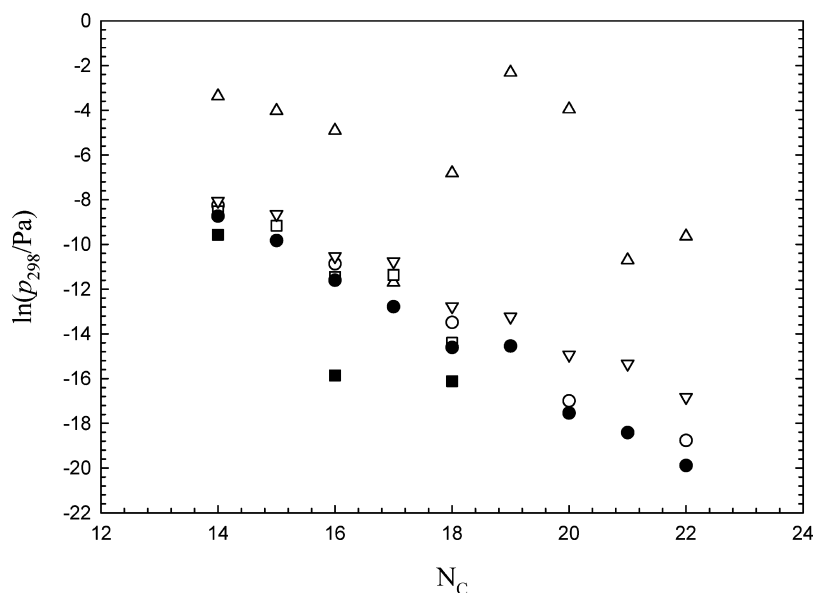
reference	$tw^a$	1	2	3	$32^b$	31
			Tetradecanoic Acid			
$p_s(298 \text{ K})/\text{Pa}$	$(1.6 \pm 0.1) \cdot 10^{-4}$	$3.15 \cdot 10^{-4}$	$0.7 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	$2.58 \cdot 10^{-4}$	$3.46 \cdot 10^{-2}$
$\Delta H_{\text{sub}}(298 \text{ K})$	$154.1 \pm 2.3$	123.1	168.6	163.8	$148.8 \pm 3.9$	
			Pentadecanoic Acid			
$p_s(298 \text{ K})/\text{Pa}$	$(5.4 \pm 0.4) \cdot 10^{-5}$	$17.5 \cdot 10^{-5}$		$10.5 \cdot 10^{-5}$		$1.8 \cdot 10^{-2}$
$\Delta H_{\text{sub}}(298 \text{ K})$	$164.5 \pm 2.3$	142.0		163.7		
			Hexadecanoic Acid			
$p_s(298 \text{ K})/\text{Pa}$	$(9.1 \pm 0.1) \cdot 10^{-6}$	$26.6 \cdot 10^{-6}$	$0.13 \cdot 10^{-6}$	$10.6 \cdot 10^{-6}$	$19.0 \cdot 10^{-6}$	$7.4 \cdot 10^{-3}$
$\Delta H_{\text{sub}}(298 \text{ K})$	$169.3 \pm 2.7$	132.8	$193.8 \pm 11$	177.4	$166.7 \pm 4.4$	
			Heptadecanoic Acid			
$p_s(298 \text{ K})/\text{Pa}$	$(2.8 \pm 0.1) \cdot 10^{-6}$	$21.0 \cdot 10^{-6}$		$11.6 \cdot 10^{-6}$		$8.31 \cdot 10^{-6}$
$\Delta H_{\text{sub}}(298 \text{ K})$	$180.4 \pm 2.5$	150.0		178.0		
			Elaidic Acid			
$p_s(298 \text{ K})/\text{Pa}$	$(2.2 \pm 0.2) \cdot 10^{-6}$					$6.84 \cdot 10^{-3}$
$\Delta H_{\text{sub}}(298 \text{ K})$	$189.7 \pm 10.3$					
			Octadecanoic Acid			
$p_s(298 \text{ K})/\text{Pa}$	$(4.5 \pm 0.7) \cdot 10^{-7}$	$28.3 \cdot 10^{-7}$	$1.0 \cdot 10^{-7}$	$5.6 \cdot 10^{-7}$	$13.8 \cdot 10^{-7}$	$1.1 \cdot 10^{-3}$
$\Delta H_{\text{sub}}(298 \text{ K})$	$190.0 \pm 2.7$	158.8	$204.1 \pm 9$	190.9	$172.2 \pm 4.5$	
			Nonadecanoic Acid			
$p_s(298 \text{ K})/\text{Pa}$	$(4.8 \pm 0.4) \cdot 10^{-7}$	$17.8 \cdot 10^{-7}$				$9.94 \cdot 10^{-2}$
$\Delta H_{\text{sub}}(298 \text{ K})$	$200.4 \pm 2.7$	145.0				
			Eicosanoic Acid			
$p_s(298 \text{ K})/\text{Pa}$	$(2.4 \pm 0.5) \cdot 10^{-8}$	$32.5 \cdot 10^{-8}$			$4.13 \cdot 10^{-8}$	$1.93 \cdot 10^{-2}$
$\Delta H_{\text{sub}}(298 \text{ K})$	$207.6 \pm 3.0$	151.0			$206.5 \pm 7.8$	
			Heneicosanoic Acid			
$p_s(298 \text{ K})/\text{Pa}$	$(1.0 \pm 0.2) \cdot 10^{-8}$	$21.8 \cdot 10^{-8}$				$2.25 \cdot 10^{-5}$
$\Delta H_{\text{sub}}(298 \text{ K})$	$208.1 \pm 7.3$	147.9				
			Docosanoic Acid			
$p_s(298 \text{ K})/\text{Pa}$	$(2.3 \pm 0.6) \cdot 10^{-9}$	$48.9 \cdot 10^{-9}$			$7.04 \cdot 10^{-9}$	$6.52 \cdot 10^{-5}$
$\Delta H_{\text{sub}}(298 \text{ K})$	$218.4 \pm 7.5$	153.0			$205.3 \pm 8.3$	

<sup>a</sup>This work. The vapor pressures are believed known to within a factor of 3 of the value reported.<sup>33</sup> The uncertainty reported provides a simple measure of the vapor pressure differences calculated using the two enthalpy values reported in column 3 of Table 13. <sup>b</sup>The results assume the absence of any phase transitions occurring between the temperature of measurement and  $T/K = 298.15$ .

reported by Davies and Malpass used samples that were melted and resolidified near their melting temperature to ensure that their measurements were performed on acids in their C form.<sup>14</sup> Only the results reported for octadecanoic acid are in strong disagreement.

**Solid–Gas Vapor Pressures.** Direct experimental measurement of subcooled vapor pressures is possible for only a few

compounds. Consequently, current interest on atmospherically relevant compounds found in aerosols has focused on vapor pressure measurements of the solid state. Experimental techniques employed include the use of a tandem differential mobility analyzer,<sup>3</sup> and more recently, thermal desorption mass spectrometry studies have been reported.<sup>1,2</sup> Also available are the



**Figure 3.** A plot of  $\ln(p_{298}/\text{Pa})$  against the number of carbon atoms of the solid saturated fatty acids; ●, this work; ■, Cappa et al.;<sup>2</sup> □, Tao and McMurry;<sup>3</sup> ▽, Chattopadhyay and Ziemann;<sup>1</sup> ○, Davies and Malpass;<sup>32</sup> △, EPI Suite.<sup>31</sup> The results of this work is reasonably well-described by the linear relationship:  $\ln(p_{298}/\text{Pa}) = -(1.4 \pm 0.06)N_C + (10.99 \pm 1.15)$ ;  $r^2 = 0.9860$ .

vapor pressure data of Davies and Malpass from Knudsen effusion studies.<sup>32</sup> The calculation of sublimation vapor pressures is also possible using a combination of gas chromatography and computation.<sup>33</sup> The latter method relies on using available vapor pressure measurements from the literature either evaluated at or extrapolated to the fusion temperature or triple point. Vaporization enthalpies obtained by gas chromatography and adjusted to the triple point temperature (or  $T_{\text{fus}}$ ) when combined with experimental fusion enthalpies provide access to both the sublimation enthalpy and the vapor pressure common to both the solid and liquid at this temperature. If the melting temperature is near room temperature, adjusting the sublimation enthalpy to the mean temperature,  $(T_{\text{fus}} + 298.15)/2$ , by inclusion of a heat capacity adjustment term, eq 14, and using the Clausius–Clapeyron equation for solids, eq 15, provides a value for the vapor pressure at  $T/K = 298.15$ . Equation 14 has previously been shown to provide reasonable enthalpic temperature adjustments for solids.<sup>20</sup> For those substances with additional solid–solid phase transitions, the calculation need be performed in steps. Equation 15 is used to calculate the vapor pressure at the transition temperature. Addition of the phase transition enthalpy to the sublimation enthalpy along with a second heat capacity adjustment followed by a second calculation performed from the transition temperature to  $T/K = 298.15$  provides a vapor pressure at  $T/K = 298.15$ . The vapor pressure evaluated at the transition temperature,  $T_v$ , from the first calculation is then used in eq 15. A similar protocol can be used for compounds whose melting temperature is further removed from  $T/K = 298.15$ . This protocol has been shown previously to reproduce experimental sublimation vapor pressures measured by experimental methods to within a factor of 3.<sup>33</sup>

$$\Delta C_p(\text{cr})\Delta T = (0.75 + 0.15C_p(\text{cr})) \times ((T_{\text{fus}/\text{tp}}/K - 298.15 \text{ K})/2) \quad (14)$$

$$\ln(p_{298}) = [\Delta H_{\text{sub}}(T_{\text{fus}/\text{tp}}) + \Delta C_p(\text{cr})\Delta T] \times [1/T_{\text{fus}/\text{tp}}/K - 1/298.15]/R + \ln(p_{(T_{\text{fus}/\text{tp}})}) \quad (15)$$

Table 14 summarizes the vapor pressures calculated using this protocol (eq 15) and the sublimation enthalpies of Table 13 and compares the results to available vapor pressures and sublimation enthalpies from the recent literature. The second column in Table 14 includes the results of this work taking into account the solid–solid phase transitions as measured by Schaake et al.<sup>17</sup> for the carboxylic acids with an odd number of carbon atoms. The vapor pressures reported in column 2 of Table 14 is an average calculated using the two vaporization enthalpies cited in column 3 of Table 13 to calculate the sublimation enthalpy. The uncertainty in the vapor pressure cited reflects the numerical differences in vapor pressure obtained using the two different vaporization enthalpies in Table 13 as discussed above. For example, the two vapor pressures calculated for tetradecanoic acid were  $(1.5 \text{ and } 1.7) \cdot 10^{-4}$  Pa. As noted previously, this method of obtaining vapor pressures of the solid phase is only capable of reproducing experimental vapor pressures within a factor of 3.<sup>33</sup> A third calculation (not included) that totally ignored the enthalpies associated with the phase transitions of the fatty acids studied did not have a very large impact on the vapor pressures calculated. Column 3 lists the sublimation enthalpies reported by Chattopadhyay and Ziemann<sup>1</sup> on organic aerosol particles as measured by thermal desorption methods. All were measured at temperatures below any of the solid–solid phase transitions listed in Table 3. Sublimation enthalpies reported by these workers were adjusted to  $T/K = 298.15$  using eq 14 to account for the heat capacity differences between the solid and gas phase. As noted in the table, these sublimation enthalpies are considerably smaller than those listed in column 2 and the vapor pressures greater than the results reported by the others. The sublimation enthalpies and vapor pressures reported by Cappa et al.<sup>2</sup> in column 4 also on organic aerosol particles by thermal desorption methods were provided at  $T/K = 298.15$  by the authors. Measurements were

conducted over a range of temperatures up to the melting temperature of the acids. Details on how the properties reported at  $T/K = 298$  were obtained are not available.<sup>2</sup> The sublimation enthalpy values reported by these workers are considerably larger than calculated using eq 2, while the reported vapor pressures are smaller in magnitude. The vapor pressures and vaporization enthalpies reported by Tao and McMurry<sup>3</sup> using a tandem differential mobility analyzer are provided in column 5. Both vapor pressure and sublimation enthalpies were calculated using the equations cited in their text. Since additional details are not reported, it is difficult to evaluate the data. Their results however are generally in good agreement with this work. The experimental results reported by Davies and Malpass<sup>32</sup> obtained by Knudsen effusion are reported in column 6. As noted above, their measurements on the even acids were performed on samples in their C form.<sup>14</sup> The sublimation enthalpies reported are generally consistent with the results of this work as are the vapor pressures calculated by extrapolating their equations describing the temperature dependence of sublimation pressure. It is surprising that despite the large difference in sublimation enthalpy reported for octadecanoic acid between their work and ours, the vapor pressures calculated by the two methods are within the experimental uncertainty noted above. The last column lists the values available from the EPI Suite.<sup>31</sup> The trend in vapor pressure as a function of the number of carbon atoms observed in this work is obviously not reproduced.

A qualitative evaluation of these results is summarized by Figure 3 where the vapor pressures of the saturated fatty acids is reported in logarithmic terms and compared as a function of the number of carbon atoms. With the exception of nonadecanoic acid, the results from this work (solid circles) appear remarkably linear with carbon number. The relationship between  $\ln(p_{298})$  and carbon number is provided in the caption under the figure.

Finally, comparing the vapor pressures of the subcooled liquid (Table 12) to the solid at  $T/K = 298.15$  (Table 14) reveals a difference of roughly a factor of 4 for tetradecanoic acid based on this work. This increases to a factor of roughly 100 for docosanoic acid.

## CONCLUSION

Literature and measured vaporization, sublimation, and fusion enthalpies are combined and are used to predict vapor pressures of both the solid and subcooled liquid state of a series of saturated and unsaturated fatty acids. The results are compared to similar properties reported in studies aimed at the development of estimations useful for predicting vapor pressures of compounds with low volatility typically found in atmospheric aerosols. While significant differences are observed in sublimation enthalpies as reported by different workers and techniques, the vapor pressures, given their magnitude, appear to be generally in qualitative agreement.

## ASSOCIATED CONTENT

### Supporting Information

Tables of the experimental retention times and a table with estimated and experimental  $C_p(\text{cr})$  values described in the text. 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.

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