

# Hypothetical Thermodynamic Properties: Vapor Pressures and Vaporization Enthalpies of the Even $n$ -Alkanes from $C_{40}$ to $C_{76}$ at $T = 298.15$ K by Correlation—Gas Chromatography. Are the Vaporization Enthalpies a Linear Function of Carbon Number?

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The temperature dependence of gas chromatographic retention times of tetracontane to hexaheptacontane is reported. These data are used in combination with earlier work to evaluate the vaporization enthalpies and vapor pressures of these  $n$ -alkanes from  $T = (298.15$  to  $540)$  K. The vapor pressure and vaporization enthalpy results obtained are compared with data calculated by the program PERT2 and Antoine constants estimated by Kudchadker and Zwolinski. The results are also compared with a model previously developed from empirical data which predicts that vaporization enthalpies measured at the boiling temperatures should approach a maximum value and then asymptotically approach zero as the chain length approaches infinity. Some curvature is indeed observed as the number of carbon atoms exceeds sixty.

## Introduction

The  $n$ -alkanes serve as excellent standards for the measurement of vaporization enthalpies of hydrocarbons at  $T = 298.15$  K, regardless of the physical state of the hydrocarbon.<sup>1–4</sup> Recently we have reported the vaporization enthalpies of the hydrocarbons, heneicosane to octatriacontane ( $C_{21}$  to  $C_{38}$ ), and described a protocol that can be used to evaluate the subcooled liquid–vapor pressure values of these materials.<sup>1,2</sup> Equations were reported that were capable of reproducing the vapor pressures of the liquid state of these materials from  $T = (298.15$  to  $575)$  K. The vapor pressures generated by these equations were tested against literature values available at elevated temperatures; agreement between the two was excellent. Interest in subcooled liquid–vapor pressures of the larger  $n$ -alkanes is related to the fact that these compounds can serve as excellent standards in the evaluation of vaporization enthalpies and liquid–vapor pressures of other hydrocarbons.<sup>3,4</sup> The vapor pressures are also of interest to the petroleum industry. A number of the larger  $n$ -alkanes are commercially available, relatively inert, and nontoxic, and vapor pressures are presently available up to  $C_{38}$  over a considerable temperature and pressure range. This work expands data available for these particular compounds up to hexaheptacontane.

The vapor pressures and vaporization enthalpies of the larger  $n$ -alkanes ( $>C_{21}$ ) have been evaluated using the technique of correlation-gas chromatography. This technique relies entirely on the use of standards in assessment. Standards exhibiting vaporization enthalpies and vapor pressures similar in magnitude to those of the  $n$ -alkanes of this study at  $T = 298.15$  K are generally unavailable. Therefore it has been necessary to use the properties of the  $n$ -alkanes evaluated previously as standards for these studies. This method has been referred to previously as a stepladder approach and is based on extrapolation.<sup>1,2</sup> The use of such an extrapolation can be risky since any errors present

in early correlations can be amplified in subsequent ones. However, there are no experimental vapor pressure data available for comparisons with these compounds. What is available are a few rough estimates obtained from molecular distillation studies.<sup>5</sup> Consequently, for the most part we have compared our results to predictions based on a program, PERT2, developed by Morgan and Kobayashi<sup>6,7</sup> and on values calculated from the Antoine constants predicted by Kudchadker and Zwolinski<sup>8</sup> for  $n$ -alkanes up to  $C_{100}$ .

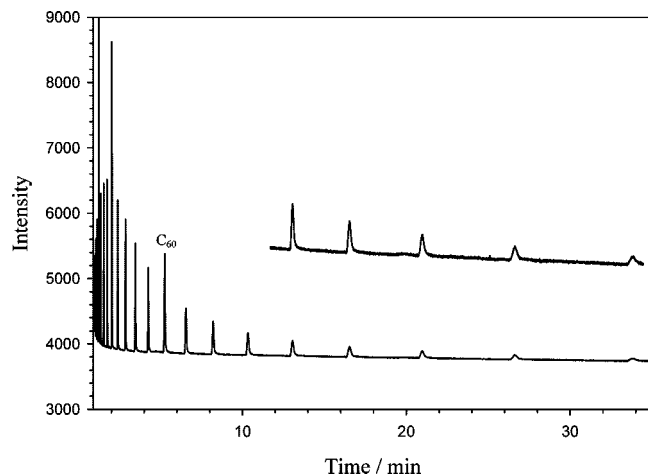
Morgan and Kobayashi extended Pitzer's CSP model to long chain molecules using vapor pressure and vaporization data on 10  $n$ -alkanes in the  $C_{10}$  to  $C_{28}$  range to predict vaporization enthalpies and vapor pressures for the  $n$ -alkanes up to  $C_{100}$ .<sup>11</sup> Our previous work on  $C_{21}$  to  $C_{38}$ , which was also based on extrapolation, was in very good agreement with most available experimental data and predictions of PERT2.<sup>1,2</sup> Kudchadker and Zwolinski used Kreglewski and Zwolinski's approach and developed power series expressions based on the normal boiling temperature to estimate the  $B$  and  $C$  constants of the Antoine equation. Using API Research Project 44 selected values for  $C_3$  to  $C_{17}$ , they also report Antoine constants for the  $n$ -alkanes up to  $C_{100}$ .<sup>8</sup> Antoine constants for the  $n$ -alkanes up to  $C_{100}$  along with their range of applicability have also been reported by Stephenson and Malanowski.<sup>12</sup> While the constants are numerically different from those reported by Kudchadker and Zwolinski,<sup>8</sup> identical vapor pressures are calculated. It is not clear how Stephenson and Malanowski arrived at the range of applicability of these constants, which are presumably derived from the work of Kudchadker and Zwolinski, but the limits reported by Stephenson and Malanowski were adhered to in this work.

This study reports the vapor pressures and vaporization enthalpies evaluated for the even  $n$ -alkanes from  $C_{40}$  to  $C_{76}$  from  $T = 298.15$  K to  $T = 540$  K. The study also addresses the predictions of a model developed from empirical data which predicts that vaporization enthalpy measured at the boiling

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**Figure 1.** GC trace of a mixture of Polywax 655 and Polywax 1000 spiked with *n*-alkanes C<sub>42</sub>, C<sub>50</sub>, and C<sub>60</sub> at *T* = 648 K (run 8). The solvent peak is not shown.

temperature approaches a maximum value and then begins to decrease as the size of the *n*-alkane continues increasing.<sup>13</sup>

## Experimental

All the *n*-alkanes up to C<sub>38</sub> were commercial samples purchased from Aldrich and Fluka, and their composition has been previously described.<sup>1</sup> *n*-Alkanes were also purchased as a mixture from Restek Corporation, D2887 Calibration Mix, containing 17 compounds which included tetracontane and tetratetracontane. Dotetracontane and octatetracontane (>99 %) were purchased from Fluka, and pentacosane and hexacosane were obtained from Supelco. The remaining *n*-alkanes, dopenacontane, tetrapentacontane, hexapentacontane, and octapentacontane were identified from a mixture of alkanes present in Polywax 655 (Restek Corp., catalog # 36225) and Polywax 1000. Polywax 655 and 1000 are oligomers of polyethylene with an average molecular weight of 655 g·mol<sup>-1</sup> and 1000 g·mol<sup>-1</sup>, respectively. The material consists of a series of even hydrocarbons, which in the C<sub>30</sub> to C<sub>60</sub> region contained compounds with retention times identical to the *n*-alkanes purchased separately. A typical plot of the larger *n*-alkanes spiked with C<sub>42</sub>, C<sub>50</sub>, and C<sub>60</sub> is shown in Figure 1. The even *n*-alkanes from C<sub>52</sub> to C<sub>58</sub> were identified from their relative retention times and were the only peaks observed between the retention times of pentacontane and hexacontane. Correlation gas chromatography experiments were performed on an HP 5890 gas chromatograph equipped with a split/splitless capillary injection port and a flame ionization detector run at a split ratio of approximately 100/1. Retention times were rounded to three significant figures following the decimal point using HP software interfaced to a computer. The instrument was run isothermally using a high temperature Al clad silica capillary column (0.25 mm ID, 0.01 μm methyl silicone film thickness, Quadex Corp., Catalog # 400 1HT-15-0.1F). The injection and detector temperatures were maintained at different temperatures but at least 5 K above the highest temperature of a series of runs. Helium was used as the carrier gas. At the temperatures of the experiments, the retention time of the solvent used, CH<sub>2</sub>Cl<sub>2</sub> or octane, increased with increasing temperature. This is a consequence of the increase in viscosity of the carrier gas with temperature; it is the criterion used to confirm that the solvent is not being retained on the column. The retention times of the solvent were used to determine the dead volume of the column. Adjusted retention times, *t*<sub>a</sub>, were calculated by subtracting the

measured retention time of the solvent from the retention time of each analyte as a function of temperature over a 30 K range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke digital thermometer. Temperature was maintained constant by the gas chromatograph to ± 0.1 K. All plots of ln(*t*<sub>o</sub>/*t*<sub>a</sub>) vs 1/*T*, where *t*<sub>o</sub> = 1 min, were characterized with correlation coefficients, *r*<sup>2</sup>, > 0.99. The retention times measured for all analytes are reported as Supporting Information.

## Results

**Vaporization Enthalpies.** Experimental retention times are provided as Supporting Information in Tables S1 to S4 and S14 corresponding to Tables 1 to 4 and 14 described below. A plot of ln(*t*<sub>o</sub>/*t*<sub>a</sub>) versus 1/*T* resulted in linear plots whose slopes and intercepts are provided in Tables 1 to 4. Uncertainties in the slopes are reported in the Supporting Information. The second and third columns of each section of Tables 1 to 4 list the slopes and intercepts obtained from plots of ln(*t*<sub>o</sub>/*t*<sub>a</sub>) vs 1/*T* for duplicate or triplicate runs. Enthalpies of transfer from the stationary phase of the column to the gas phase, Δ<sub>sin</sub><sup>g</sup>*H*<sub>m</sub>, were obtained by multiplying the slopes by the gas constant, *R* = 8.314·10<sup>-3</sup> kJ·mol<sup>-1</sup>·K<sup>-1</sup>, column 4. Vaporization enthalpies reported previously for the *n*-alkanes tetracosane to octatriacontane<sup>1</sup> (exclusive of C<sub>25</sub> to C<sub>27</sub>, C<sub>29</sub> to C<sub>31</sub>, C<sub>33</sub> and C<sub>34</sub>) are reported in column 5 of Tables 1A and 1B. The last column reports the vaporization enthalpies for tetracontane and tetratetracontane calculated from the correlation equation listed below each run (Tables 1A and 1B, eq 1 and eq 2. These values and their mean value, used in subsequent correlations, are summarized in Table 5.

The vaporization enthalpies of dotetracontane, hexatetracontane, and octatetracontane are evaluated in Table 2 using correlation eqs 3 and 4. The resulting values are also listed in Table 5 along with their mean value which was also used in subsequent correlations. Table 3, A to C summarizes the results obtained for dopenacontane, tetrapentacontane, hexapentacontane, and hexacontane. Correlation eqs 5 through 7 were generated as a result. Vaporization enthalpies are similarly summarized in Table 5. Results on the remaining *n*-alkanes, dohexacontane to hexaheptacontane, evaluated in a similar fashion, resulting in correlation eqs 8 and eqs 9, are reported in Table 4 and summarized in Table 5. The uncertainties reported in Tables 1 to 4 are standard errors calculated from the uncertainty associated with the slopes and intercepts of eq 1 to eq 9.<sup>14</sup> The uncertainties reported in Table 5 are two standard deviations of the mean. The former represents the uncertainty in the value and the latter represents the reproducibility.

The vaporization enthalpies of all *n*-alkanes in the literature<sup>1,2,15</sup> along with the results of these sets of extrapolations are summarized in Table 6 and illustrated in Figure 2. This figure plots the vaporization enthalpies at *T* = 298.15 K of pentane on through to hexaheptacontane as a function of the number of carbon atoms, *N*. The results for pentane through to hexacontane appear quite linear as suggested by the linear correlation equation, eq 10, reported in the caption of Figure 2. However, some curvature is observed above C<sub>60</sub>. The coefficient of the quadratic equation, eq 11, used to fit all the data is also reported in the caption of Figure 2. At this point, it is not possible to determine whether the observed curvature is simply due to extensive extrapolation or is a consequence of the structure of the compounds. Since there are no experimental data to compare with, as noted above,

**Table 1. Enthalpies of Transfer and Vaporization Enthalpies Obtained for Tetracontane and Tetratetracontane**

(A) run 1	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(571 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	(T/K)	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1} (\text{lit.})^1$	$\text{kJ}\cdot\text{mol}^{-1} (\text{calcd})$
tetracosane	-8388	16.529	69.73	121.9	122.2
octacosane	-9446	17.683	79.35	141.9	142.0
dotriacontane	-10740	18.93	89.29	162.5	162.5
pentatriacontane	-11535	19.693	95.90	178.1	176.2
hexatriacontane	-11921	20.168	99.11	182.9	182.8
heptatriacontane	-12277	20.59	102.07	187.6	188.9
octatriacontane	-12523	20.816	104.11	192.7	193.1
tetracontane	-13136	21.484	109.21		203.6 ± 3.9
tetratetracontane	-14337	22.790	119.19		224.2 ± 4.2

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (2.061 \pm 0.034)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(571 \text{ K}) - (21.538 \pm 1.07) r^2 = 0.9986 \quad (1)$$

(B) run 2	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(570 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	(T/K)	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1} (\text{lit.})^1$	$\text{kJ}\cdot\text{mol}^{-1} (\text{calcd})$
tetracosane	-7821.4	15.524	65.02	121.9	122.0
octacosane	-9101.6	16.906	75.68	141.9	142.0
dotriacontane	-10405	18.352	86.50	162.5	162.4
pentatriacontane	-11342	19.372	94.29	178.1	177.1
hexatriacontane	-11707	19.812	97.33	182.9	182.8
heptatriacontane	-12052	20.215	100.20	187.6	188.2
octatriacontane	-12363	20.556	102.78	192.7	193.0
tetracontane	-13024	21.311	108.28		203.4 ± 1.9
tetratetracontane	-14298	22.75	118.87		223.3 ± 2.0

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.881 \pm 0.016)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(570 \text{ K}) - (0.27 \pm 0.56) r^2 = 0.9996 \quad (2)$$

**Table 2. Enthalpies of Transfer and Vaporization Enthalpies Obtained for Dotetracontane, Hexatetracontane, Octatetracontane, and Pentacontane**

(A) run 3	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(572 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	(T/K)	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1} (\text{lit.})$	$\text{kJ}\cdot\text{mol}^{-1} (\text{calcd})$
pentatriacontane	-12134	20.995	100.88	178.1	177.6
hexatriacontane	-12458	21.359	103.57	182.9	182.8
heptatriacontane	-12785	21.728	106.29	187.6	188.0
octatriacontane	-13109	22.091	108.98	192.7	193.2
tetracontane	-13750	22.812	114.31	203.5 <sup>a</sup>	203.4
dotetracontane	-14384	23.522	119.58		213.5 ± 2.5
tetratetracontane	-15013	24.228	124.81	223.7 <sup>a</sup>	223.5
hexatetracontane	-15624	24.904	129.89		233.3 ± 2.7
octatetracontane	-16230	25.575	134.93		242.9 ± 2.8
pentacontane	-16822	26.227	139.85		252.4 ± 2.9

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.918 \pm 0.021)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(572 \text{ K}) - (15.83 \pm 0.41) r^2 = 0.9995 \quad (3)$$

(B) run 4	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(570 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	(T/K)	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1} (\text{lit.})^1$	$\text{kJ}\cdot\text{mol}^{-1} (\text{calcd})$
dotriacontane	-10775	19.261	89.58	162.5	162.1
triacontane	-11114	19.647	92.40	167.6	167.5
tetratriacontane	-11441	20.013	95.12	172.7	172.7
pentatriacontane	-11768	20.381	97.84	178.1	177.9
hexatriacontane	-12079	20.724	100.42	182.9	182.9
heptatriacontane	-12416	21.11	103.22	187.6	188.3
octatriacontane	-12729	21.455	105.82	192.7	193.3
tetracontane	-13359	22.161	111.06	203.5 <sup>a</sup>	203.3
dotetracontane	-13996	22.876	116.36		213.5 ± 1.7
tetratetracontane	-14614	23.568	121.50	223.7 <sup>a</sup>	223.3
hexatetracontane	-15239	24.265	126.69		233.3 ± 1.9
octatetracontane	-15853	24.953	131.80		243.1 ± 1.9
pentacontane	-16453	25.623	136.78		252.6 ± 2.0

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.918 \pm 0.014)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(570 \text{ K}) + (9.7 \pm 0.4) r^2 = 0.9996 \quad (4)$$

<sup>a</sup> See Table 5.

**Table 3. Enthalpies of Transfer and Vaporization Enthalpies Obtained for Dopentacontane, Tetrapentacontane, Hexapentacontane, Octapentacontane, and Hexacontane**

(A) run 5	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(614 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	(T/K)	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (this work)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
heptatriacontane	-11097	18.594	92.26	187.6 <sup>1</sup>	187.7
octatriacontane	-11584	19.222	96.31	192.7 <sup>1</sup>	194.9
tetracontane	-12127	19.789	100.82	203.5	203.0
dotetracontane	-12745	20.475	106.06	213.5	212.2
tetratetracontane	-13405	21.231	111.44	223.7	222.0
hexatetracontane	-14138	22.108	117.54	233.0	232.9
octatetracontane	-14835	22.927	123.33	242.7	243.3
pentacontane	-15531	23.75	129.12	252.0	253.7
dopentacontane	-16160	24.463	134.35		263.0 ± 5.5
tetrapentacontane	-16780	25.163	139.50		272.3 ± 5.7
hexapentacontane	-17337	25.762	144.13		280.6 ± 5.9
octapentacontane	-17908	26.386	148.88		289.1 ± 6.1

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.791 \pm 0.040)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(614 \text{ K}) + (22.46 \pm 1.37) r^2 = 0.9971 \quad (5)$$

(B) run 6	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(623 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	(T/K)	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (this work)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
hexatriacontane	-10684	18.203	88.82	182.9 <sup>1</sup>	182.7
octatricacontane	-11302	18.884	93.96	192.7 <sup>1</sup>	193.2
tetracontane	-11902	19.539	98.95	203.5	203.3
dotetracontane	-12530	20.237	104.17	213.5	213.9
tetratetracontane	-13085	20.825	108.78	223.7	223.3
hexatetracontane	-13669	21.458	113.64	233.3	233.1
octatetracontane	-14243	22.078	118.41	243.0	242.8
pentacontane	-14840	22.735	123.37	252.5	252.9
dopentacontane	-15377	23.302	127.84		262.0 ± 1.5
tetrapentacontane	-15930	23.893	132.44		271.3 ± 1.5
hexapentacontane	-16466	24.46	136.89		280.3 ± 1.6
octapentacontane	-17014	25.047	141.45		289.6 ± 1.6
hexacontane	-17566	25.642	146.04		298.9 ± 1.7

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (2.031 \pm 0.012)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(623 \text{ K}) + (2.35 \pm 0.38) r^2 = 0.9998 \quad (6)$$

(C) run 7	slope		$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(623 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	(T/K)	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (this work)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
dotetracontane	-12740	20.807	105.915	213.5	214.0
tetratetracontane	-13305	21.411	110.613	223.7	223.2
hexatetracontane	-13910	22.077	115.642	233.3	233.2
octatetracontane	-14493	22.711	120.489	243.0	242.8
pentacontane	-15106	23.391	125.585	252.5	252.8
dopentacontane	-15571	23.845	129.451		260.5 ± 3.8
tetrapentacontane	-16117	24.427	133.990		269.4 ± 3.9
hexapentacontane	-16650	24.987	138.422		278.2 ± 4.0
octapentacontane	-17166	25.524	142.711		286.7 ± 4.1
hexacontane	-18029	26.609	149.886		300.9 ± 4.3

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.976 \pm 0.029)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(623 \text{ K}) + (4.64 \pm 0.45) r^2 = 0.9994 \quad (7)$$

we have compared our results to predictions based on PERT2, developed by Morgan and Kobayashi,<sup>6,7</sup> and predictions from the Antoine Constants reported by Kudchadker and Zwolinski<sup>8</sup> as compiled by Stephensen and Malanowski.<sup>12</sup> These predictions are listed in Table 10. Discussion of this comparison follows the section on vapor pressures.

**Vapor Pressures.** In addition to their usefulness in obtaining vaporization enthalpies, the slopes and intercepts provided in Tables 1 to 4 can also be used to evaluate vapor pressures,  $p$ ,

when used in combination with experimental data. The use of the retention time data to provide vapor pressure data has been described previously.<sup>1,2</sup> The equations associated with the slopes and intercepts of each compound relate the temperature dependence of the vapor pressure of the solute ( $t_{\text{o}}/t_{\text{a}}$ ) above the stationary phase of the column over a narrow temperature range. Although these equations would not be expected to be accurate in predicting vapor pressures by themselves, when used in combination with a series of standards with known vapor

**Table 4. Enthalpies of Transfer and Vaporization Enthalpies Obtained for the Even *n*-Alkanes from Dohexacontane to Hexaheptacontane**

(A) run 8	slope		$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(653 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	( <i>T</i> /K)	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (this work)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
dotetracontane	-11790	19.069	98.02	213.5	213.3
tetratetracontane	-12378	19.708	102.91	223.7	223.3
hexatetracontane	-12965	20.347	107.79	233.3	233.3
octatetracontane	-13532	20.955	112.50	243.0	242.9
pentacontane	-14106	21.577	117.27	252.5	252.7
dopentacontane	-14651	22.155	121.80	261.8	261.9
tetrapentacontane	-15197	22.736	126.34	270.9	271.2
hexapentacontane	-15734	23.304	130.81	279.6	280.3
octapentacontane	-16260	23.857	135.18	288.3	289.3
hexacontane	-16782	24.403	139.52	299.9	298.1
dohexacontane	-17288	24.93	143.73		306.7 ± 2.8
tetrahexacontane	-17804	25.472	148.02		315.5 ± 2.9
hexahexacontane	-18324	26.02	152.34		324.3 ± 3.0
octahexacontane	-18769	26.457	156.04		331.9 ± 3.0
heptacontane	-19259	26.963	160.11		340.2 ± 3.1
doheptacontane	-19736	27.451	164.08		348.3 ± 3.2
tetraheptacontane	-20187	27.899	167.83		356.0 ± 3.2
hexaheptacontane	-20656	28.377	171.73		363.9 ± 3.3

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (2.043 \pm 0.019)\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(653 \text{ K}) + (13.10 \pm 0.80) r^2 = 0.9993 \quad (8)$$

(B) run 9	slope		$\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(653 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
	( <i>T</i> /K)	intercept	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$ (lit.)	$\text{kJ}\cdot\text{mol}^{-1}$ (calcd)
dotetracontane	-11539	18.722	95.93	213.5	213.4
tetratetracontane	-12125	19.355	100.80	223.7	223.2
hexatetracontane	-12716	19.999	105.72	233.3	233.2
octatetracontane	-13296	20.627	110.54	243.0	242.9
pentacontane	-13881	21.262	115.40	252.5	252.8
dopentacontane	-14431	21.848	119.97	261.8	262.1
tetrapentacontane	-14979	22.43	124.53	270.9	271.3
hexapentacontane	-15519	23.002	129.02	279.6	280.4
octapentacontane	-16040	23.548	133.35	288.3	289.1
hexacontane	-16571	24.107	137.77	299.9	298.1
dohexacontane	-17082	24.64	142.01		306.7 ± 2.8
tetrahexacontane	-17586	25.163	146.20		315.2 ± 2.9
hexahexacontane	-18080	25.672	150.31		323.5 ± 3.0
octahexacontane	-18576	26.186	154.43		331.8 ± 3.0
heptacontane	-19066	26.691	158.51		340.1 ± 3.1
doheptacontane	-19547	27.184	162.51		348.2 ± 3.2
tetraheptacontane	-20027	27.679	166.50		356.2 ± 3.3
hexaheptacontane	-20511	28.179	170.52		364.4 ± 3.3

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (2.025 \pm 0.019)\Delta_{\text{sin}}^{\text{g}}H_{\text{m}}(653 \text{ K}) + (19.14 \pm 0.80) r^2 = 0.9993 \quad (9)$$

**Table 5. Summary of Evaluated Vaporization Enthalpies**

	$\text{kJ}\cdot\text{mol}^{-1}$									average <sup>a</sup>
	run 1	run 2	run 3	run 4	run 5	run 6	run 7	run 8	run 9	
tetracontane	203.6	203.4								203.5 ± 0.2
dotetracontane			213.5	213.5						213.5
tetratetracontane	224.2	223.3								223.7 ± 0.9
hexatetracontane			233.3	233.3						233.3
octatetracontane			242.9	243.1						243.0 ± 0.2
pentacontane			252.4	252.6						252.5 ± 0.2
dopentacontane					263.0	262.0	260.5			261.8 ± 1.5
tetrapentacontane					272.3	271.3	269.4			271.0 ± 1.7
hexapentacontane					280.6	280.3	278.2			279.7 ± 1.5
octapentacontane					289.1	289.6	286.7			288.5 ± 1.8
hexacontane						298.9	300.9			299.9 ± 2.0
dohexacontane								306.8	306.7	306.8 ± 0.1
tetrahexacontane								315.6	315.2	315.4 ± 0.4
hexahexacontane								324.5	323.5	324.0 ± 1.0
octahexacontane								332	331.8	331.9 ± 0.2
heptacontane								340.4	340.1	340.3 ± 0.3
doheptacontane								348.5	348.2	348.4 ± 0.3
tetraheptacontane								356.1	356.2	356.2 ± 0.1
hexaheptacontane								364.1	364.4	364.3 ± 0.3

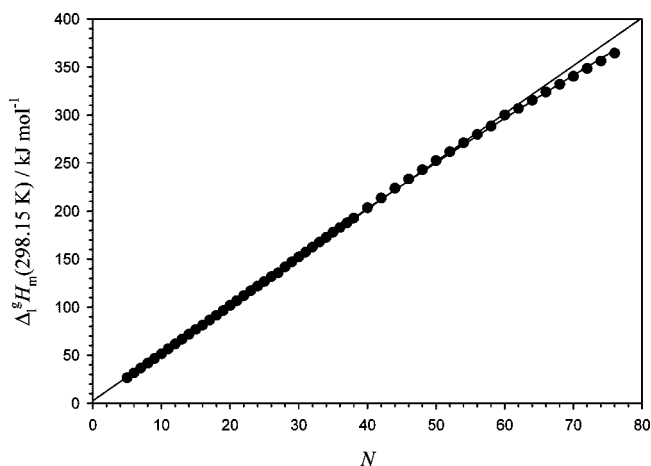
<sup>a</sup> The uncertainty represents two standard deviations of the mean.



**Table 6.** Vaporization Enthalpies of the *n*-Alkanes at  $T = 298.15$  K as a Function of the Number of Carbon Atoms,  $N^a$ 

$\Delta_1^g H_m(298.15 \text{ K})$		$\Delta_1^g H_m(298.15 \text{ K})$		$\Delta_1^g H_m(298.15 \text{ K})$		$\Delta_1^g H_m(298.15 \text{ K})$	
$N$	$\text{kJ}\cdot\text{mol}^{-1}$	$N$	$\text{kJ}\cdot\text{mol}^{-1}$	$N$	$\text{kJ}\cdot\text{mol}^{-1}$	$N$	$\text{kJ}\cdot\text{mol}^{-1}$
5	26.42	19	96.44	32	162.5	52	261.8
6	31.52	20	101.81	33	167.6	54	271.0
7	36.57	21	106.8	34	172.7	56	279.7
8	41.56	22	111.9	35	178.1	58	288.3
9	46.55	23	117.0	36	182.9	60	299.9
10	51.42	24	121.9	37	187.6	62	306.8
11	56.58	25	126.8	38	192.7	64	315.4
12	61.52	26	131.7	40	203.5	66	324.0
13	66.68	27	135.6	42	213.5	68	331.9
14	71.73	28	141.9	44	223.7	70	340.3
15	76.77	29	147.1	46	233.3	72	348.4
16	81.35	30	152.3	48	243.0	74	356.2
17	86.47	31	157.3	50	252.5	76	364.3
18	91.44						

<sup>a</sup> Values for  $N = 5$  to  $N = 20$  from ref 15.



**Figure 2.** Vaporization enthalpies of the *n*-alkanes at  $T = 298.15$  K from pentane to hexaheptacontane as a function of the number of carbon atoms,  $N$ . Vaporization enthalpies up to  $C_{20}$  are from ref 15, and all others are from ref 1 and this work. The equation of the line obtained from a linear regression of compounds from pentane to hexacontane is given by:

$$\Delta_1^g H_m(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (5.00 \pm 0.01)N + (1.87 \pm 1.02) \quad r^2 = 0.9998 \quad (10)$$

The following second order equation was used to fit pentane to hexaheptacontane:

$$\Delta_1^g H_m(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (-7.36 \pm 0.54) \cdot 10^{-3} N^2 + (5.431 \pm 0.044)N - (2.864 \pm 0.72) \quad r^2 = 0.9998 \quad (11)$$

pressures at the temperatures of interest, the results obtained by correlation have been shown to be quite satisfactory.<sup>2</sup> Vapor pressure equations for heneicosane to octatriacontane have previously been reported in the form of eq 12.<sup>1,2</sup> The  $A$ ,  $B$ ,  $C$ , and  $D$  coefficients of this equation are reported in Table 7.  $T/K$  represents the temperature and  $p_o = 101325$  Pa.

$$\ln(p/p_o) = A(T/K)^{-3} + B(T/K)^{-2} + C(T/K)^{-1} + D \quad (12)$$

Values of  $\ln(p/p_o)$  for the standards were calculated using eq 12 at each temperature over the temperature range (298.15 to 540) K at 30 K intervals. In the first correlation,  $\ln(p/p_o)$  values using eq 12 and the constants of Table 7 were calculated for the *n*-alkane standards in Table 1 up to  $C_{38}$ . The results were correlated with the corresponding  $\ln(t_o/t_a)$  values calculated from the slopes and intercepts in Table 1 for both the standards and

**Table 7.**  $A$ ,  $B$ ,  $C$ , and  $D$  Coefficients of Equation 12 for Tetracosane to Octatriacontane<sup>a</sup>

	$A$	$B$	$C$	$D$
tetracosane	250720000	-3528600	530.15	6.2817
pentacosane	267380000	-3730700	741.19	6.1496
hexacosane	282440000	-3919300	910.53	6.0704
heptacosane	300920000	-4125300	1198.8	5.8109
octacosane	313890000	-4312000	1279.4	5.8835
nonacosane	328710000	-4504300	1431.2	5.8413
triacontane	344040000	-4699800	1601.6	5.7696
hentriacontane	360370000	-4900200	1791.2	5.679
dotriacontane	375240000	-5092100	1947.2	5.63
tritriacontane	389830000	-5280900	2098	5.585
tetracontane	404350000	-5467900	2249.5	5.537
pentatriacontane	417460000	-5648000	2363.8	5.5436
hexatriacontane	433200000	-5843200	2553.2	5.447
heptatriacontane	448900000	-6037000	2743.2	5.347
octatriacontane	463300000	-6223000	2891.9	5.304

<sup>a</sup> Note that the Antoine constants,  $A$ ,  $B$ , and  $C$  are different from the  $A$ ,  $B$ ,  $C$  constants of eq 12 and the  $A$ ,  $B$ ,  $C$ ,  $D$  constants from refs 1 and 2.

**Table 8.** Evaluation of the Vapor Pressures of Tetracontane and Tetratetracontane at  $T = 298.15$  K

$T = 298.15$ K	slope		$\ln(p/p_o)$		$\ln(p/p_o)$
	( $T/K$ )	intercept	$\ln(t_o/t_a)$	lit. <sup>1</sup>	
tetracosane	-7821.4	15.52	-10.71	-22.18	-22.16
octacosane	-9101.6	16.91	-13.62	-26.49	-26.55
dotriacontane	-10405	18.35	-16.55	-30.96	-30.97
pentatriacontane	-11342	19.37	-18.67	-34.31	-34.17
hexatriacontane	-11707	19.81	-19.45	-35.38	-35.36
heptatriacontane	-12052	20.22	-20.21	-36.43	-36.5
octatriacontane	-12363	20.56	-20.91	-37.52	-37.56
tetracontane	-13024	21.31	-22.37		-39.76
tetratetracontane	-14298	22.75	-25.21		-44.04

$$\ln(p/p_o)_{\text{calcd}} = (1.51 \pm 0.008) \ln(t_o/t_a) - (5.99 \pm 0.77) \quad r^2 = 0.9998 \quad (13)$$

for tetracontane and tetratetracontane. The results of this correlation are illustrated in Table 8 for run 2 at  $T = 298.15$  K and by eq 13. Similar correlations were repeated at 30 K intervals. From the linear correlations obtained, it was possible to calculate  $\ln(p/p_o)_{\text{calcd}}$  values for tetracontane and tetratetracontane at each temperature. The two  $\ln(p/p_o)$  values calculated for tetracontane (runs 1 and 2) at a given temperature from Tables 1A and B were averaged, and then the average value of  $\ln(p/p_o)$  was plotted against  $1/T$  and the results fit to a third order polynomial. A similar procedure was also followed for tetratetracontane. The constants obtained for eq 12 for

**Table 9.** *A, B, C, and D* Coefficients for Equation 12 Evaluated in This Work<sup>a</sup>

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
tetracontane	492892989	-6606544	3183.30	5.27
dotetracontane	514705019	-6922387	3348.86	5.29
tetratetracontane	550113379	-7346741	3778.56	5.12
hexatetracontane	564508533	-7599158	3810.60	5.22
octatetracontane	589075146	-7932516	4039.56	5.19
pentaccontane	613301019	-8260161	4268.30	5.14
dopentacontane	487086616	-7408666	1564.80	7.46
tetrapentacontane	509586695	-7716664	1772.35	7.41
hexapentacontane	532133326	-8019154	1997.20	7.33
octapentacontane	554464295	-8320276	2215.70	7.25
hexacontane	730610097	-9844804	5365.41	4.96
dohexacontane	611971593	-9029780	2863.74	7.0
tetrahexacontane	620513044	-9221534	2812.09	7.15
hexahexacontane	629047724	-9412553	2761.70	7.29
octahexacontane	637712295	-9596396	2731.45	7.4
heptacontane	646223779	-9783335	2688.59	7.53
doheptacontane	654726322	-9967694	2650.72	7.65
tetraheptacontane	663246355	-10149129	2619.62	7.75
hexaheptacontane	671651325	-10332047	2580.78	7.87

<sup>a</sup> The Antoine constants *A*, *B*, and *C* are different from the *A*, *B*, *C* constants of eq 12.

these two *n*-alkanes are provided in Table 9. This process was repeated using  $\ln(p/p_0)$  values for the alkanes in Tables 2A and 2B, now also using calculated  $\ln(p/p_0)$  values for tetracontane and tetratetracontane as standards. This provided corresponding  $\ln(p/p_0)$  values for dotetracontane, hexatetracontane, octatetracontane, and pentacontane. The resulting  $\ln(p/p_0)$  values were also averaged, and the average values were plotted against  $1/T$  and fit to a third order polynomial. This process was repeated for the compounds in Table 3A to C and Table 4A and B to provide the coefficients for the third order polynomial for the even *n*-alkanes from dopentacontane to hexaheptacontane. Values of  $\ln(p/p_0)$  and  $\ln(t_0/t_a)$  were always highly correlated. The coefficients for eq 12 obtained for all the *n*-alkanes of this study are summarized in Table 9.

As noted above, there are no experimental values of vapor pressure and vaporization enthalpy available to our knowledge with which to compare these results. Carothers et al.<sup>5</sup> reported a rough calculation of the order of magnitude of the vapor pressure of heptacontane at  $T = 300$  °C. Their calculations suggested a vapor pressure of less than 1.3 Pa at this temperature; the parameters for heptacontane in Table 9 predict a vapor pressure of 0.5 Pa. As a consequence of the lack of other experimental data, we have compared vapor pressures and vaporization enthalpies at  $T = 298.15$  K with those predicted by PERT2 and vapor pressures at temperatures at which the Antoine Constants estimated by Kudchadker and Zwolinski and PERT2 were applicable. These comparisons are summarized in Table 10. Both vapor pressures and vaporization enthalpies calculated at  $T = 298.15$  K by PERT2 (columns 3 and 5, respectively) are in good agreement with the results of this work (columns 2 and 4) up to about  $C_{60}$ . Above hexacontane, the two results begin to diverge. Vaporization enthalpy values calculated by PERT2 above  $C_{60}$  increase more slowly, and as a consequence, higher vapor pressures are predicted in comparison to the gas chromatographic results.

Column 6 of Table 10 reports the temperature that was used in conjunction with the Antoine constants. Each temperature is 15 K within the range deemed applicable by Stephenson and Malanowski.<sup>12</sup> At the temperature indicated in this column, each of the *n*-alkanes is predicted to have a similar vapor pressure (column 8 of Table 10). A similar trend in  $\ln(p/p_0)$  at  $T_m$  as

observed with the values calculated by PERT2 is observed between the results of this work and the estimated values of Kudchadker and Zwolinski (comparison between columns 7 and 8).

The vaporization enthalpies of column 9 were calculated using the constants in Table 9 to calculate vapor pressures over a 30 K range at each mean temperature reported in column 6. A  $\ln(p/p_0)$  versus  $1/(T/K)$  treatment of the resulting vapor pressures was followed by numerical evaluation of the product of the slope and gas constant, *R*. The vaporization enthalpies in column 10 were calculated from the Antoine constants at each mean temperature using eq 14:

$$\Delta_1^g H_m(T_m)/\text{kJ} \cdot \text{mol}^{-1} = 2.303RB[T_m/\text{K}/(T_m/\text{K} + C)]^2/1000 \quad (14)$$

The terms in eq 14 are defined as follows: *R* is the gas constant and *B* and *C* are the constants of the Antoine equation as reported by Stephenson and Malanowski.<sup>12</sup>  $\log(p/\text{kPa}) = A - B/(T/K + C)$ . The vaporization enthalpies in the last column were calculated by the program PERT2, automatically, once the temperature,  $T_m$ , was defined.<sup>7</sup>

Comparison of the vaporization enthalpies calculated at each mean temperature shows a similar divergence with molecular size. At the higher temperatures, the vaporization enthalpies estimated from the Antoine constants predicted by Kudchadker and Zwolinski as reported by Stephenson and Malanowski appear to be in closer agreement to the values obtained in this work than those predicted by PERT2, falling roughly halfway between the results of this work and those predicted by PERT2.

**Do Vaporization Enthalpies of *n*-Alkanes Vary Linearly With Carbon Number?** The results illustrated in Figure 2 suggest that the relationship between vaporization enthalpy and carbon number, up to  $C_{60}$ , is quite linear. Is the curvature observed for the larger *n*-alkanes an artifact of the gas chromatographic method or is there any basis for expecting the vaporization enthalpy of the larger *n*-alkanes and other homologous series to show curvature?

Recently, we observed linear relationships between the vaporization enthalpy measured at the boiling temperature and the corresponding entropy of vaporization for several homologous series including the *n*-alkanes.<sup>13</sup> These relationships are summarized in Table 11. A few of the smallest members of some series fell significantly off the line and were not included in the analysis. The number of data points that were used are entered in the last column of the table. Substituting  $\Delta_1^g H_m(T_B)/T_B$  for  $\Delta_1^g S_m(T_B)$  and solving for  $T_B$  resulted in eq 15. Here *m* represents the slope of the lines reported in Table 10 and *b* is the intercept. If it is assumed that  $\Delta_1^g H_m(T_B)$  continues to increase with an increasing number of methylene groups, *M*, then eq 14 is the equation of a hyperbola that asymptotically approaches the slope of the line, *m*, as  $M \rightarrow \infty$ . Examination of the slopes of the lines in Table 10 suggested a limiting value of  $T_B$  of approximately 3000 K.<sup>13</sup>

$$T_B = m\Delta_1^g H_m(T_B)/(\Delta_1^g H_m(T_B) - b) \quad (15)$$

An analysis of the behavior of boiling temperatures and critical temperatures of several homologous series as a function of chain length led to the conclusion that both critical temperatures and boiling temperatures behave hyperbolically and converge at approximately  $(1217 \pm 246)$  K.<sup>13</sup> This conclusion was arrived at as a result of studies in which plots

Table 10. Comparison of Vaporization Enthalpies and Vapor Pressures With Estimated Values

	ln( $p/p_0$ )		$\Delta_1^{\text{g}}H_m(298\text{ K})$		$T_m/\text{K}$	ln( $p/p_0$ )		$\Delta_1^{\text{g}}H_m(T_m/\text{K})$		
	$T = 298.15\text{ K}$		$\text{kJ}\cdot\text{mol}^{-1}$			$T = T_m/\text{K}$		$\text{kJ}\cdot\text{mol}^{-1}$		
	This work	PERT2	This work	PERT2		This work	ref 8	This work	ref 8	PERT2
tetracontane	-39.8	-39.7	203.5	207.7	572	-6.7	-6.6	128.1	132.2	128.7
dotetracontane	-41.9	-41.9	213.5	218	582	-6.8	-6.6	132.1	136	132.7
tetratetracontane	-44.1	-43.9	223.7	228.1	592	-6.9	-6.6	135.9	139.3	136.4
hexatetracontane	-46.2	-46	233.3	238.2	601	-6.9	-6.6	139.7	142.8	140.2
octatetracontane	-48.3	-48.1	243	248.2	610	-7.0	-6.6	143.2	145.9	143.8
pentacontane	-50.3	-50.1	252.5	258.1	618	-7.0	-6.6	146.8	149	147.4
dopentacontane	-52.3	-50.8	261.8	260	626	-7.0	-6.6	152.8	152	147.5
tetrapentacontane	-54.2	-52.6	270.9	268.4	633	-7.1	-6.6	156.3	155	150.5
hexapentacontane	-56.1	-54.2	279.6	276.1	640	-7.2	-6.6	159.4	157.8	153.0
octapentacontane	-58	-55.8	288.3	283.9	647	-7.3	-6.6	162.4	160.3	155.5
hexacontane	-60.2	-57.3	299.9	290.8	653	-7.3	-6.6	163.4	163	157.8
dohexacontane	-61.9	-59	306.7	299	660	-7.3	-6.6	168.7	165.2	160.4
tetrahexacontane	-63.7	-60.3	315.3	305.2	665	-7.4	-6.6	172.3	168.3	162.4
hexahexacontane	-65.6	-61.8	323.9	312.5	671	-7.4	-6.6	175.5	170	164.7
octahexacontane	-67.3	-63.1	331.9	319	676	-7.5	-6.6	178.6	172.3	166.7
heptacontane	-69.1	-64.5	340.1	325.5	681	-7.6	-6.6	180.6	174.4	168.8
doheptacontane	-70.9	-65.7	348.2	331	686	-7.6	-6.6	184.9	176.4	170.3
tetraheptacontane	-72.6	-66.8	356.1	336.6	691	-7.7	-6.6	187.8	178.2	171.8
hexaheptacontane	-74.4	-68.0	364.2	342.3	695	-7.8	-6.6	192.2	180.4	173.6

Table 11. Correlation Equations Obtained by Plotting  $\Delta_1^{\text{g}}H_m(T_B)$  Versus  $\Delta_1^{\text{g}}S_m(T_B)$ 

enthalpy ( $\text{J}\cdot\text{mol}^{-1}$ )—entropy relationships ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )			
		corr. coeff.	data points
<i>n</i> -alkanes	$\Delta_1^{\text{g}}H_m(T_B) = (3190.7 \pm 22.6), \Delta_1^{\text{g}}S_m(T_B) - (240583 \pm 350)$	$r^2 = 0.9992$	18
<i>n</i> -alkylbenzenes	$\Delta_1^{\text{g}}H_m(T_B) = (2469.3 \pm 119), \Delta_1^{\text{g}}S_m(T_B) - (169585 \pm 951)$	$r^2 = 0.9806$	12
<i>n</i> -alkylcyclohexanes	$\Delta_1^{\text{g}}H_m(T_B) = (3370.5 \pm 37.3), \Delta_1^{\text{g}}S_m(T_B) - (247174 \pm 296)$	$r^2 = 0.9985$	14
<i>n</i> -alkylcyclopentanes	$\Delta_1^{\text{g}}H_m(T_B) = (3028.8 \pm 97.4), \Delta_1^{\text{g}}S_m(T_B) - (220567 \pm 926)$	$r^2 = 0.9877$	14
1-alkenes	$\Delta_1^{\text{g}}H_m(T_B) = (3717.8 \pm 87.3), \Delta_1^{\text{g}}S_m(T_B) - (284890 \pm 999)$	$r^2 = 0.9918$	17
<i>n</i> -alkanethiols	$\Delta_1^{\text{g}}H_m(T_B) = (2268.7 \pm 163), \Delta_1^{\text{g}}S_m(T_B) - (161693 \pm 1728)$	$r^2 = 0.9558$	11

Table 12. Summary of Limiting Values of  $T_B(\infty)$  and  $T_C(\infty)$  Obtained by Plotting  $1/[1 - T_M/T(\infty)]$  versus the Number of Repeat Units,  $M$ , of a Series of Homologous Compounds By Treating  $T_B(\infty)$  and  $T_C(\infty)$  as Variables

polyethylene series	$T_B(\infty)/\text{K}$	$\pm \sigma/\text{K}$	data points	$T_C(\infty)/\text{K}$	$\pm \sigma/\text{K}$	# of data points
<i>n</i> -alkanes	1076	0.9	18	1050	1.7	16
2-methyl- <i>n</i> -alkanes	1110	0.2	8	950	0.6	5
<i>n</i> -alk-1-enes	1090	0.4	17	1035	0.3	8
<i>n</i> -alkylcyclopentanes	1140	0.6	15			
<i>n</i> -alkylcyclohexanes	1120	0.1	13			
<i>n</i> -alkylbenzenes	1140	1.1	15			
1-amino- <i>n</i> -alkanes	1185	3.4	15			
1-chloro- <i>n</i> -alkanes	1125	0.3	13			
1-bromo- <i>n</i> -alkanes	1125	1.0	12			
1-fluoro- <i>n</i> -alkanes	1075	0.4	9			
1-hydroxy- <i>n</i> -alkanes	1820	0.8	12	1045	3.6	11
2-hydroxy- <i>n</i> -alkanes	1055	1.8	7			
<i>n</i> -alkanals	910	1.4	7	1070	1.0	8
2-alkanones	1440	1.6	8	1105	1.3	11
3-alkanones				1185	1.3	10
<i>n</i> -alkane-1-thiols	1090	0.2	14			
sym <i>n</i> -dialkyl disulfides	1190	0.4	9			
<i>n</i> -alkylnitriles	1855	2.6	11			
<i>n</i> -alkanoic acids	1185	1.3	16	1105	3.7	31
methyl <i>n</i> -alkanoates	1395	2.6	10			

of  $1/[1 - T_X(M)/T_X(\infty)]$  against the number of methylene groups of the homologous series,  $M$ , resulted in good linear correlations.  $T_X(\infty)$  in this treatment represented either the limiting boiling temperature,  $T_B(\infty)$ , or the critical temperature,  $T_C(\infty)$ ; both  $T_C(\infty)$  and  $T_B(\infty)$  were treated as variables in independent correlations. The limiting temperature,  $T_X(\infty)$ , was allowed to vary until plots of  $1/[1 - T_X(M)/T_X(\infty)]$  versus  $M$  became linear. Limiting  $T_B$  and  $T_C$  values were found to converge. These limiting temperatures obtained for various series are summarized in columns 2 and 5 of Table 12. The value of  $(1217 \pm 246)$  K, obtained by averaging all the boiling temperatures, fit both boiling and critical temperatures quite well and was used as the limiting value.<sup>13</sup> The average

standard deviation of a total of 229 boiling temperatures distributed over 19 homologous series was  $\pm 2.2$  K; for 8 homologous series, the average standard deviation in critical temperature was  $\pm 4.1$  K.

An immediate consequence of the convergence of both boiling and critical temperature at large  $M$  is that the vaporization enthalpy of the homologous series must also approach zero as  $M$  approaches infinity, since the vaporization enthalpy at the critical temperature is equal to zero. Hence the assumption that  $\Delta_1^{\text{g}}H_m(T_B)$  continues to increase with increasing size is questionable. If the limiting boiling temperature is  $(1217 \pm 246)$  K, then solving for the maximum value of  $\Delta_1^{\text{g}}H_m(T_B)$ ,  $\Delta_1^{\text{g}}H_m(T_B)_{\text{max}}$  in eq 15 results in eq 16.<sup>16</sup>



**Table 13. Summary of Values of the Parameters of  $a_H$  and  $b_H$  Generated in Fitting  $\Delta_1^g H_m(T_B)$  of Several Homologous Series Using Equation 17 and a Value of  $\Delta_1^g H_m(T_B)_{\max} = (154.5 \pm 18.5) \text{ kJ} \cdot \text{mol}^{-1}$**

	$a_H$	$b_H$	$\pm 2\sigma/\text{kJ} \cdot \text{mol}^{-1}$	data points
<i>n</i> -alkanes	0.02690	1.120	1.0	18
<i>n</i> -alkylbenzenes	0.02496	1.268	1.0	15
<i>n</i> -alkylcyclohexanes	0.02457	1.260	0.4	15
<i>n</i> -alkylcyclopentanes	0.02575	1.234	0.4	15
<i>n</i> -alk-1-enes	0.02576	1.149	1.0	17
<i>n</i> -alkane-1-thiols	0.02914	1.176	0.8	13

$$\Delta_1^g H_m(T_B)_{\max} = b_H / (T_B - m) \quad (16)$$

Substituting for the limiting boiling temperature in eq 16 and using the slopes and intercepts provided in Table 11 resulted in an average value for  $\Delta_1^g H_m(T_B)_{\max}$  of  $(154.5 \pm 18.5) \text{ kJ} \cdot \text{mol}^{-1}$ .<sup>17</sup> Since this treatment suggested that the vaporization enthalpy at the boiling temperature approaches a maximum value at some values of  $M$ , while decreasing to zero in the limit,  $\Delta_1^g H_m(T_B)$  at small  $M$  could also be modeled by a hyperbolic function. A nonlinear least-squares fit of  $[1/(1 - \Delta_1^g H_m(T_B)/\Delta_1^g H_m(T_B)_{\max})]$  versus the number of methylene groups using  $\Delta_1^g H_m(T_B)_{\max} = 154.5 \text{ kJ} \cdot \text{mol}^{-1}$  resulted in linear fits; the results are summarized in Table 13. The terms  $a_H$  and  $b_H$  represent the slope and intercept of the linear fits, respectively. Rearranging this linear relationship and solving for  $\Delta_1^g H_m(T_B)$  in terms of  $\Delta_1^g H_m(T_B)_{\max}$ ,  $M$ , and the slope and intercept results in the hyperbolic function, eq 17. The standard deviation associated with the fit is well within the experimental uncertainty of the data ( $2\sigma \leq 1 \text{ kJ} \cdot \text{mol}^{-1}$ ).

$$\Delta_1^g H_m(T_B) = \Delta_1^g H_m(T_B)_{\max} (1 - 1/(a_H M + b_H)) \quad (17)$$

The behavior of vaporization enthalpy as a function of chain size was explained as follows. If vaporization enthalpy at the boiling temperature is a measure of the energy necessary to break attractive intermolecular forces, an increasing chain of repeat units, provided the chain is flexible, will coil back on itself as it becomes larger.<sup>13</sup> The proportion of intramolecular interactions will eventually increase at the expense of the intermolecular ones once the molecule gets large enough. In the limit, the ratio of intramolecular/intermolecular interactions will approach zero.

While vaporization enthalpy at the boiling temperature may increase to some maximum value and then begin to decrease for the *n*-alkanes as molecular size continues to increase, the behavior of vaporization enthalpy at temperatures below the boiling temperature as a function of size is expected to behave somewhat differently. Equation 18 summarizes the relationship between the vaporization enthalpy measured at the boiling temperature and at temperature,  $T$ .

$$\Delta_1^g H_m(T) = \Delta_1^g H_m(T_B) + \int_T^{T_B} \Delta C p_1^g dT \quad (18)$$

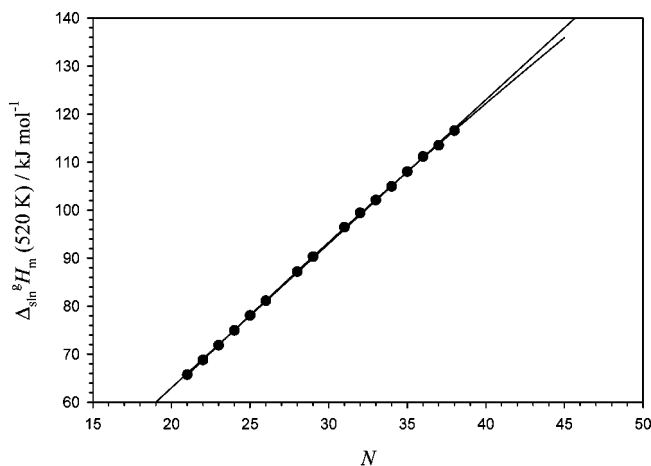
As the linear molecule gets larger and the proportion of intramolecular interactions increases at the expense of the intermolecular ones, the contribution of each successive methylene group to  $\Delta_1^g H_m(T)$  will be attenuated. Similarly, the contribution of  $\int \Delta C p_1^g dT$  should also be attenuated since as  $T \rightarrow 1217 \text{ K}$ ,  $dT \rightarrow 0$ . This assumes a relatively constant contribution of each successive  $\text{CH}_2$  group to  $\Delta C p_1^g$ . The conclusion of this empirical model is that vaporization enthalpies at temperatures other than at boiling, including  $T = 298.15 \text{ K}$ , are not necessarily likely to vanish with increasing chain length but should show some curvature. This model predicts that curvature should be more pronounced at higher temperatures,

provided that vaporization enthalpy comparisons with chain length are made at the same temperature.

Current methods of measuring vaporization enthalpies depend directly or indirectly on the vapor pressure of the material. The direct measurement of vapor pressure of molecules of the size necessary for this study is difficult if not presently impossible. Correlation gas chromatography is an indirect method. This technique measures the enthalpy of transfer of an analyte from the stationary phase of the column to the gas phase. It is related to the vaporization enthalpy through the following thermodynamic cycle:

$$\Delta_{\text{sln}}^g H_m(T) = \Delta_1^g H_m(T) + \Delta_{\text{sln}}^g H_m(T) \quad (19)$$

The  $\Delta_{\text{sln}}^g H_m(T)$  term represents the enthalpy of interaction of the analyte on the column and is the smaller of the two terms in eq 19. As noted above, this technique relies on the use of standards to obtain vaporization enthalpies and vapor pressures. Vaporization enthalpies and vapor pressures of suitable standards of the size necessary for this study are not available, hence the need for extrapolation. However, it is possible to measure enthalpies of transfer of larger molecules by gas chromatography. If the model described above regarding how the ratio of intermolecular to intramolecular interactions varies with size is correct, then both vaporization enthalpy as well as the enthalpy of interaction of the analyte on the column should be attenuated in the same manner as a function of the size of the homologous series.



**Figure 3.** Correlation between enthalpies of transfer,  $\Delta_{\text{sln}}^g H_m(520 \text{ K})$ , and the number of carbon atoms,  $N$ , of the *n*-alkanes from heneicosane to octatriacontane. The equation of the line obtained by a linear regression analysis is given by:

$$\Delta_{\text{sln}}^g H_m(520 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = (3.00 \pm 0.013)N + (3.039 \pm 0.286) \quad r^2 = 0.9997 \quad (20)$$

The equation of the line fit by a second order polynomial is given by:

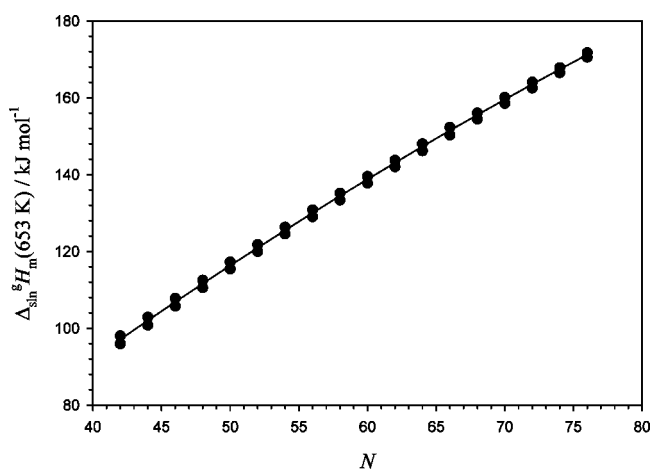
$$\Delta_{\text{sln}}^g H_m(520 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = (-9.865 \pm 1.5)10^{-3}N^2 + (3.58 \pm 0.09)N - (5.224 \pm 1.27) \quad r^2 = 0.9999 \quad (21)$$

It has been demonstrated, repeatedly, that enthalpies of transfer of homologous series correlate linearly with vaporization enthalpies.<sup>1,2,18–20</sup> Figure 2 illustrates the linear correlation of vaporization enthalpy of the *n*-alkanes (at least up to 60 carbons) observed as a function of the number of carbon atoms,  $N$ . Therefore, enthalpies of transfer should also correlate linearly

**Table 14. Enthalpies of Transfer of Some *n*-Alkanes from Hencosane to Octatriacontane**

	slope	intercept	$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(520 \text{ K})$	$\Delta_{\text{v}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{v}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$
			$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}(\text{lit.})$	$\text{kJ}\cdot\text{mol}^{-1}(\text{calcd})$
hencosane	-7904.8	16.389	65.717	106.8	106.2
docosane	-8273.8	16.816	68.785	111.9	111.4
tricosane	-8641.7	17.243	71.844	117.0	116.6
tetracosane	-9012.8	17.679	74.929	121.9	121.8
pentacosane	-9390.4	18.128	78.068	126.8	127.1
hexacosane	-9756.1	18.556	81.108	131.7	132.2
octacosane	-10488	19.417	87.193	141.9	142.5
nonacosane	-10862	19.868	90.302	147.1	147.7
hentriacontane	-11597	20.744	96.413	157.3	158.0
dotriacontane	-11958	21.171	99.414	162.5	163.1
triacontane	-12280	21.52	102.091	167.6	167.6
tetracontane	-12621	21.909	104.926	172.7	172.4
pentatriacontane	-12993	22.364	108.019	178.0	177.6
hexatriacontane	-13370	22.83	111.153	182.8	182.9
heptatriacontane	-13651	23.107	113.489	187.5	186.9
octatriacontane	-14019	23.557	116.548	192.7	192.0

$$\Delta_{\text{v}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.689 \pm 0.008)\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(520 \text{ K}) - (4.81 \pm 0.52) \quad r^2 = 0.9997 \quad (22)$$



**Figure 4.** Plot of  $\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(653 \text{ K})$  against the number of carbon atoms,  $N$ , for runs 8 and 9. The equation of the straight line (not shown) obtained by a linear regression of both runs is given by:

$$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(653 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (2.175 \pm 0.013)N + (7.215 \pm 0.286) \quad r^2 = 0.9971 \quad (23)$$

The equation of the line fit for both runs (shown) by a second order polynomial is given by:

$$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(653 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (-8.54 \pm 1.63)10^{-3}N^2 + (3.18 \pm 0.193)N - (21.6 \pm 5.6) \quad r^2 = 0.9984 \quad (24)$$

with carbon number. Table 14 summarizes the results of measuring the enthalpies of transfer of hencosane to octatriacontane simultaneously at a mean temperature  $T_{\text{m}} = 520 \text{ K}$ . The enthalpies of transfer are plotted against the number of carbon atoms in Figure 3. The first of the two equations at the bottom of the Figure 3, eq 20, illustrates the fit using a linear relationship while eq 21 describes the fit using a second order polynomial. The results suggest that the parabolic fit is slightly better based on the value of the correlation coefficient. Also included in the last two columns of Table 14 are the enthalpies of vaporization calculated by correlating enthalpies of transfer with vaporization enthalpies reported previously, eq 22.<sup>1</sup> It should be pointed out that the literature values in this table were also obtained by correlation gas chromatography in a series of

four separate correlations involving other standards.<sup>2</sup> Despite measurements under different experimental conditions, the two sets of values are related quite linearly according to the correlation coefficient,  $r^2$ .

If the improvement in fit using a second order polynomial is not simply an artifact, then similar and perhaps more pronounced curvature should also be exhibited in correlations of larger *n*-alkanes. Figure 4 illustrates how enthalpies of transfer, measured at a mean temperature,  $T_{\text{m}} = 653 \text{ K}$ , correlate with the number of carbon atoms,  $N$ , for dotetracontane to hexaheptacontane. Treating the data in runs 8 and 9 in a linear fashion results in eq 23 reported below the figure (line not shown). The line drawn in the figure was obtained by treating the data with a second order polynomial and also represents the average of runs 8 and 9. The second order polynomial clearly gives the best fit as suggested by the correlation coefficients. The curvature obtained in this study is somewhat less than that predicted by PERT2 and the estimated Antoine constants of Kudchadker and Zwolinski, but appears qualitatively consistent with the estimation results. An examination of the magnitude and uncertainty of the second order term in eqs 21 and 24 suggests that the curvature is reproducible in these two cases. It should be emphasized, however, that since enthalpies of transfer are dependent on two thermodynamic terms (eq 19), it is not presently clear how much of the curvature observed in Figures 3 and Figures 4 is due to each respective term.

## Summary

The vaporization enthalpies and vapor pressures of the even *n*-alkanes from tetracontane to hexaheptacontane are evaluated through a process of extrapolation by correlation—gas chromatography. The vaporization enthalpies of all these hydrocarbons are measurements of the subcooled liquid and as such are hypothetical properties. The results are compared to two sets of estimated values. The results are generally in good agreement up to approximately hexacontane. Above hexacontane, the estimated and measured values begin to diverge. Both experimental and estimation methods are in qualitative agreement with a model that predicts vaporization enthalpies of the *n*-alkanes at temperatures below boiling and will show some curvature with increasing size.

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## Supporting Information Available:

Tables including the experimental retention times described in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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