

# Vapor Pressures and Vaporization Enthalpies of the *n*-Alkanes from C<sub>31</sub> to C<sub>38</sub> at *T* = 298.15 K by Correlation Gas Chromatography

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The temperature dependence of gas-chromatographic retention times for hentriacontane to octatriacontane is reported. These data are used in combination with other literature values to evaluate the vaporization enthalpies and vapor pressures of these *n*-alkanes from *T* = 298.15 to 575 K. The vapor pressure and vaporization enthalpy results obtained are compared with existing literature data where possible and found to be internally consistent. The vaporization enthalpies and vapor pressures obtained for the *n*-alkanes are also tested directly and through the use of thermochemical cycles using literature values for several polyaromatic hydrocarbons. Sublimation enthalpies are also calculated for hentriacontane to octatriacontane by combining vaporization enthalpies with temperature adjusted fusion enthalpies.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are important environmental contaminants, many of which exhibit very low vapor pressures. In the gas phase, they exist mainly sorbed to aerosol particles. The partitioning process between the condensed and gas phases is often described by an empirical relationship based on the subcooled vapor pressure of the liquid phase.<sup>1</sup> Subcooled vapor pressures of liquid PAHs have been calculated using the corresponding vapor pressure of the solid, gas-chromatographic retention times, and various other thermochemical properties.<sup>2</sup> This article describes an alternative gas chromatographic method.

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>3,4</sup> Recently we have reported the vaporization enthalpies of the hydrocarbons heneicosane to triacontane (C<sub>21</sub> to C<sub>30</sub>) and described a protocol that can be used to evaluate the subcooled liquid vapor pressure values of these materials.<sup>5</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 *n*-alkanes is related to the fact that the *n*-alkanes can serve as excellent standards in the evaluation of vaporization enthalpies and liquid vapor pressures of other hydrocarbons such as the PAHs. The *n*-alkanes are readily available, relatively inert, and non-toxic, and vapor pressures are presently available over a considerable temperature and pressure range.

Many of the PAHs of environmental interest are less volatile than the C<sub>21</sub> to C<sub>30</sub> *n*-alkanes studied previously. Since studies using correlation gas chromatography work best when the standards bracket the retention times of compounds of interest, it has been necessary to extend the procedure used to evaluate the vapor pressures and

vaporization enthalpies of C<sub>21</sub> to C<sub>30</sub> to include C<sub>31</sub> to C<sub>38</sub>. The vapor pressures and vaporization enthalpies of these larger *n*-alkanes 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 unavailable. Therefore it has been necessary to use the properties of the *n*-alkanes: C<sub>21</sub> to C<sub>30</sub> evaluated previously as standards for these studies. This method has been referred to previously as a stepladder approach and is essentially based on extrapolation. The use of such an extrapolation is quite risky since any errors present in early correlations can be amplified in subsequent ones. Consequently both the vaporization enthalpies and the vapor pressures resulting from this study need to be independently confirmed.

This study reports the vapor pressures and vaporization enthalpies evaluated for C<sub>31</sub> to C<sub>38</sub> from *T* = 298.15 K to *T* = 575 K and compares the results to vapor pressures and vaporization enthalpies available in the literature for these compounds at elevated temperatures. Recommended vaporization enthalpies of pentane to eicosane at *T* = 298.15 K are correlated to the number of methylene groups, and this correlation is extended to include C<sub>21</sub> to C<sub>30</sub> measured recently<sup>5</sup> and C<sub>31</sub> to C<sub>38</sub> measured in this study. The vaporization enthalpies at *T* = 298.15 K of several *n*-alkanes are also used to evaluate the vaporization enthalpies of some solid reference PAHs, whose vaporization enthalpies could be confirmed independently by means of a thermochemical cycle. The vaporization enthalpies and subcooled vapor pressure results of the PAHs of this study are also compared to results reported by Lei et al.<sup>2</sup>

## Experimental Section

The following alkanes: C<sub>32</sub> (97+); C<sub>34</sub> (98+); C<sub>36</sub> (98+), were purchased from Aldrich Chemical Co. All the remaining *n*-alkanes (>99.5%) were purchased from Fluka; the purity of C<sub>38</sub> as analyzed by gas chromatography was >98%. All were used without any further purification. Correlation gas chromatography experiments were performed on an HP 5890A Series II Gas Chromatograph

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**B** *Journal of Chemical and Engineering Data*

**Table 1. Gas Chromatographic Retention Times for the *n*-Alkanes from C<sub>28</sub> to C<sub>38</sub>**

	<i>t</i> /min at the following values of <i>T</i> /K						
	534.4	539.5	544.6	549.65	554.8	559.9	564.9
	C <sub>28</sub> to C <sub>33</sub>						
methylene chloride	0.415	0.419	0.418	0.415	0.415	0.413	0.413
octacosane	9.269	7.870	6.680	4.885	4.885	4.218	3.650
nonacosane	11.892	10.003	8.433	6.070	6.070	5.200	4.461
triacontane	15.275	12.740	10.667	7.560	7.560	6.432	5.473
hentriacontane	19.575	16.215	13.470	9.419	9.419	7.949	6.727
dotriacontane	25.169	20.677	17.052	11.763	11.763	9.865	8.285
tritriacontane	32.293	26.362	21.570	14.690	14.690	12.236	10.206
	C <sub>28</sub> to C <sub>34</sub>						
methylene chloride	0.416	0.425	0.426	0.423	0.424	0.425	0.425
octacosane	6.650	5.739	4.935	4.254	3.700	3.241	2.855
nonacosane	8.377	7.173	6.123	5.238	4.518	3.925	3.431
triacontane	10.657	9.035	7.643	6.486	5.557	4.792	4.155
hentriacontane	13.369	11.290	9.492	8.004	6.800	5.822	5.015
dotriacontane	16.942	14.201	11.852	9.928	8.380	7.125	6.093
tritriacontane	21.455	17.850	14.799	12.321	10.320	8.715	7.405
tetracontane	27.187	22.450	18.488	15.301	12.736	10.688	9.025
	C <sub>31</sub> to C <sub>38</sub>						
methylene chloride	0.264	0.265	0.268	0.268	0.265	0.269	0.267
hentriacontane	6.080	5.114	4.343	3.722	3.210	2.790	2.436
dotriacontane	7.607	6.344	5.350	4.554	3.902	3.365	2.918
tritriacontane	9.473	7.864	6.589	5.571	4.744	4.065	3.500
tetracontane	11.849	9.768	8.130	6.830	5.780	4.921	4.212
pentatriacontane	14.835	12.145	10.043	8.382	7.058	5.967	5.075
hexatriacontane	18.492	15.067	12.389	10.287	8.604	7.237	6.117
heptatriacontane	23.053	18.694	15.295	12.630	10.495	8.787	7.383
octatriacontane	28.770	23.195	18.874	15.489	12.814	10.652	8.913

95 equipped with a split/splitless capillary injection port and  
 96 a flame-ionization detector run at a split ratio of 100/1.  
 97 Retention times were recorded to three significant figures  
 98 following the decimal point on an HP 3989A Integrator.  
 99 The instrument was run isothermally using a 15-m SPB-5  
 100 capillary column. Helium was used as the carrier gas. At  
 101 the temperatures of the experiments, the retention time  
 102 of the solvent, CH<sub>2</sub>Cl<sub>2</sub> or CCl<sub>4</sub>, increased with increasing  
 103 temperature. This is a consequence of the increase in  
 104 viscosity of the carrier gas with temperature; it is the  
 105 criterion used to confirm that the solvent is not being  
 106 retained on the column. The retention times of the solvent  
 107 were used to determine the dead volume of the column.  
 108 Adjusted retention times, *t*<sub>a</sub>, were calculated by subtracting  
 109 the measured retention time of the solvent from the  
 110 retention time of each analyte as a function of temperature  
 111 over a 30-K range. Column temperatures were controlled  
 112 by the gas chromatograph and were monitored independ-  
 113 ently by using a Fluke digital thermometer. Temperature  
 114 was maintained constant by the gas chromatograph to ±0.1  
 115 K.

116 The sample of 1,3,5-triphenylbenzene (97%, Aldrich  
 117 Chemical Co.) used to measure fusion enthalpy was  
 118 analyzed by gas chromatography and found to be 99.6%  
 119 pure. The fusion enthalpy was measured on a Perkin-Elmer  
 120 DSC 7. The instrument was standardized using indium,  
 121 and the standardization was checked using zinc, benzoic  
 122 acid, and naphthalene.<sup>6</sup> The results are listed in Table 11.

**Results**

123 **A. Vaporization Enthalpies.** Experimental retention  
 124 times are presented in Table 1. A plot of ln(1/*t*<sub>a</sub>) vs 1/*T*  
 125 resulted in linear plots whose slopes and intercepts are  
 126 provided in Table 2. The top of Table 3 lists the enthalpies  
 127 of transfer from solution to the gas phase, Δ<sub>sln</sub><sup>v</sup>*H*<sub>m</sub>/*R*,  
 128 measured for octacosane to triacontane (column 2) along  
 129 with the vaporization enthalpies reported previously for  
 130 octacosane to triacontane (column 3).<sup>5</sup> The last column  
 131 reports the vaporization enthalpies calculated from the  
 132 correlation equation listed below the table. In the second  
 133 correlation of Table 3, octacosane–triacontane were used  
 134

**Table 2. Equations for the Temperature Dependence of ln(1/*t*<sub>a</sub>)<sup>a</sup>**

	<i>T</i> <sub>m</sub> = 549.7 K	Δ <sub>sln</sub> <sup>v</sup> <i>H</i> <sub>m</sub> / <i>R</i>	intercept	<i>r</i> <sup>2</sup>
	C <sub>28</sub> to C <sub>33</sub>			
octacosane	-9956.9 ± 24.6	16.45 ± 0.002	0.9999	
nonacosane	-10304 ± 30.4	16.84 ± 0.003	0.9999	
triacontane	-10648 ± 34.1	17.23 ± 0.003	0.9999	
hentriacontane	-10979 ± 31.2	17.59 ± 0.003	0.9999	
dotriacontane	-11324 ± 35	17.98 ± 0.003	0.9999	
tritriacontane	-11666 ± 34	18.37 ± 0.003	0.9999	
	C <sub>28</sub> to C <sub>34</sub>			
octacosane	-9831.6 ± 46	16.218 ± 0.004	0.9999	
nonacosane	-10164 ± 48.8	16.583 ± 0.004	0.9999	
triacontane	-10528 ± 37.1	17.002 ± 0.003	0.9999	
hentriacontane	-10829 ± 50.9	17.317 ± 0.004	0.9999	
dotriacontane	-11163 ± 47.8	17.688 ± 0.004	0.9999	
tritriacontane	-11508 ± 46.9	18.080 ± 0.004	0.9999	
tetracontane	-11839 ± 42.1	18.447 ± 0.004	0.9999	
	C <sub>31</sub> to C <sub>38</sub>			
hentriacontane	-10781 ± 65.4	17.676 ± 0.005	0.9998	
dotriacontane	-11129 ± 69.2	18.072 ± 0.006	0.9998	
tritriacontane	-11440 ± 63.1	18.404 ± 0.005	0.9998	
tetracontane	-11774 ± 67.1	18.776 ± 0.005	0.9998	
pentatriacontane	-12113 ± 70.1	19.160 ± 0.006	0.9998	
hexatriacontane	-12420 ± 65.3	19.448 ± 0.005	0.9998	
heptatriacontane	12723 ± 62.2	19.811 ± 0.005	0.0008	
octatriacontane	-13047 ± 61.8	20.169 ± 0.005	0.9998	

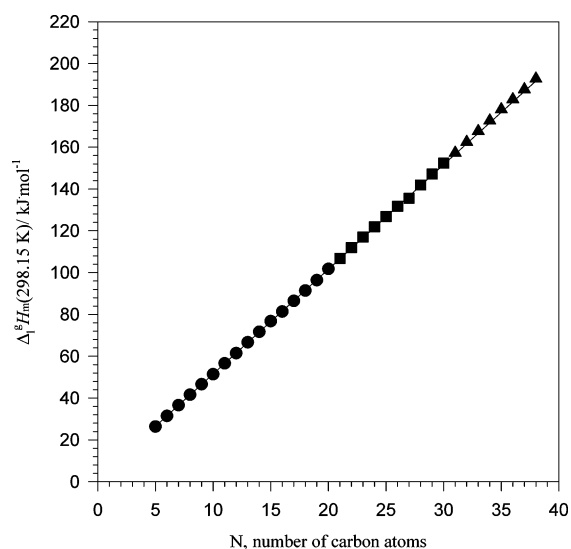
<sup>a</sup> ln(1/*t*<sub>a</sub>) = Δ<sub>sln</sub><sup>v</sup>*H*<sub>m</sub>/*R* + intercept.

to evaluate the vaporization enthalpy of tetracontane. 135  
 The last set of entries in Table 3 uses the vaporization 136  
 enthalpies of hentriacontane–tetracontane to evaluate 137  
 the vaporization enthalpies of pentatriacontane–octatria- 138  
 contane. 139

The results of these extrapolations are illustrated in 140  
 Figure 1. This figure plots the vaporization enthalpies at 141  
*T* = 298.15 K of pentane on through to octatriacontane. 142  
 The values of pentane through to eicosane represent 143  
 recommended literature values.<sup>7</sup> Vaporization enthalpies 144  
 from heneicosane through to triacontane represent values 145  
 previously evaluated;<sup>5</sup> these values were evaluated using 146  
 heptadecane to eicosane as standards. The values of 147  
 hentriacontane through to octatriacontane are results of 148  
 this study using octacosane–triacontane as standards. 149

**Table 3. Vaporization Enthalpies of the *n*-Alkanes (kJ·mol<sup>-1</sup>)**

	$\Delta_{\text{sln}}^{\text{v}}H_{\text{m}}(549.7 \text{ K})$	$\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (lit)	$\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (calc)
		<b>C<sub>28</sub> to C<sub>33</sub></b>	
octacosane	82.78	141.9	141.9 ± 0.6
nonacosane	85.66	147.1	147.1 ± 0.6
triacontane	88.52	152.3	152.3 ± 0.6
hentriacontane	91.28		157.3 ± 0.6
dotriacontane	94.14		162.5 ± 0.7
tritriacontane	96.99		167.6 ± 0.7
	$\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.8101 \pm 0.0148)\Delta_{\text{sln}}^{\text{v}}H_{\text{m}}(T_{\text{m}}) - (7.929 \pm 0.0036); r^2 = 0.9999$		
		<b>C<sub>28</sub> to C<sub>34</sub></b>	
octacosane	81.74	141.9	141.9 ± 2.5
nonacosane	84.5	147.1	147.0 ± 2.5
triacontane	87.53	152.3	152.6 ± 2.6
hentriacontane	90.03	157.3	157.2 ± 2.7
dotriacontane	92.8	162.5	162.3 ± 2.8
tritriacontane	95.67	167.6	167.6 ± 2.8
tetratriacontane	98.42		172.7 ± 3.0
	$\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.8493 \pm 0.015)\Delta_{\text{sln}}^{\text{v}}H_{\text{m}}(T_{\text{m}}) - (9.2802 \pm 0.169); r^2 = 0.9998$		
		<b>C<sub>31</sub> to C<sub>38</sub></b>	
hentriacontane	51.3	157.2	157.2 ± 4.1
dotriacontane	53.9	163.2	162.7 ± 4.2
tritriacontane	57.2	167.6	167.5 ± 4.3
tetratriacontane	60.3	172.7	172.7 ± 4.4
pentatriacontane	63.3		178.0 ± 4.6
hexatriacontane	66.3		182.8 ± 4.7
heptatriacontane	69.2		187.5 ± 4.8
octatriacontane			192.6 ± 4.9
	$\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.8749 \pm 0.0226)\Delta_{\text{sln}}^{\text{v}}H_{\text{m}}(T_{\text{m}}) - (10.815 \pm 0.14); r^2 = 0.9997$		



**Figure 1.** The vaporization enthalpies of the *n*-alkanes at  $T = 298.15 \text{ K}$ . ●, recommended vaporization enthalpies from the literature; ■, vaporization enthalpies previously evaluated by correlation-gas chromatography;<sup>4</sup> ▲, are the results of this study. The line was calculated using recommended literature vaporization enthalpies<sup>5</sup> of  $C_5$  to  $C_{20}$  by a linear regression analysis and extrapolated to include all the data points.

150 Recommended values of Ruzicka and Majer<sup>7</sup> as well as the  
 151 values evaluated in this and in a previous publication<sup>5</sup> are  
 152 summarized in Table 4. The line through the data in Figure  
 153 1 was calculated using the recommended literature values  
 154 for  $C_5$  to  $C_{20}$  by a linear regression analysis. The line was  
 155 then extrapolated to include  $C_{21}$  to  $C_{38}$ . The equation of  
 156 the line is given by eq 1. Use of all the data to derive the  
 157 equation results in eq 2

$$\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (5.004 \pm 0.008)N_{\text{C}} + (1.507 \pm 0.144) \quad r^2 = 0.9999 \quad (1)$$

$$\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (5.038 \pm 0.006)N_{\text{C}} + (1.07 \pm 0.348) \quad r^2 = 0.9999 \quad (2)$$

**Table 4. Summary of Recommended Vaporization Enthalpies ( $C_5$  to  $C_{20}$ ) and Vaporization Enthalpies Evaluated by Correlation Gas Chromatography (kJ·mol<sup>-1</sup>)**

<i>n</i> -alkane	$N_{\text{C}}$	$\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})_{\text{calcd}}^a$
pentane	5	26.4 <sup>b</sup>	26.5
hexane	6	31.5 <sup>b</sup>	31.5
heptane	7	36.6 <sup>b</sup>	36.5
octane	8	41.6 <sup>b</sup>	41.5
nonane	9	46.6 <sup>b</sup>	46.5
decane	10	51.4 <sup>b</sup>	51.5
undecane	11	56.6 <sup>b</sup>	56.6
dodecane	12	61.5 <sup>b</sup>	61.6
tridecane	13	66.7 <sup>b</sup>	66.6
tetradecane	14	71.7 <sup>b</sup>	71.6
pentadecane	15	76.8 <sup>b</sup>	76.6
hexadecane	16	81.4 <sup>b</sup>	81.6
heptadecane	17	86.5 <sup>b</sup>	86.8
octadecane	18	91.4 <sup>b</sup>	91.6
nonadecane	19	96.4 <sup>b</sup>	96.6
tricosane	20	101.8 <sup>b</sup>	101.6
hencicosane	21	106.8 <sup>c</sup>	106.6
docosane	22	111.9 <sup>c</sup>	111.6
tricosane	23	117.0 <sup>c</sup>	116.6
tetracosane	24	121.9 <sup>c</sup>	121.6
pentacosane	25	126.8 <sup>c</sup>	126.6
hexacosane	26	131.7 <sup>c</sup>	131.6
heptacosane	27	135.6 <sup>c</sup>	136.6
octacosane	28	141.9 <sup>c</sup>	141.6
nonacosane	29	147.1 <sup>c</sup>	146.6
triacontane	30	152.3 <sup>c</sup>	151.6
hentriacontane	31	157.3 <sup>d</sup>	156.6
dotriacontane	32	162.5 <sup>d</sup>	161.6
tritriacontane	33	167.6 <sup>d</sup>	166.6
tetratriacontane	34	172.7 <sup>d</sup>	171.6
pentatriacontane	35	178.0 <sup>d</sup>	176.6
hexatriacontane	36	182.8 <sup>d</sup>	181.7
heptatriacontane	37	187.5 <sup>d</sup>	186.7
octatriacontane	38	192.6 <sup>d</sup>	191.7

<sup>a</sup> Calculated using  $C_5$  to  $C_{20}$  according to eq 1. <sup>b</sup> Recommended values, ref 7. <sup>c</sup> Reference 5. <sup>d</sup> This work.

Despite the linear fit observed between  $\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$  158 and the number of carbon atoms,  $N_{\text{C}}$ , the extent of 159 extrapolation is significant; these values need to be tested 160

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**Table 5. Previously Evaluated Coefficients for Calculating  $\ln(p/p_0)$  Using Eq 3<sup>5</sup>**

compounds	A (10 <sup>-8</sup> )	B (10 <sup>-6</sup> )	C	D
heneicosane	1.9989	-2.9075	-98.135	6.6591
docosane	2.1713	-3.1176	110.72	6.5353
tricosane	2.3386	-3.3220	310.77	6.4198
tetracosane	2.5072	-3.5286	530.15	6.2817
pentacosane	2.6738	-3.7307	741.19	6.1496
hexacosane	2.8244	-3.9193	910.53	6.0704
heptacosane	3.0092	-4.1253	1198.8	5.8109
octacosane	3.1389	-4.3120	1279.4	5.8835
nonacosane	3.2871	-4.5043	1431.2	5.8413
triacontane	3.4404	-4.6998	1601.6	5.7696

**Table 6. Coefficients for Calculating  $\ln(p/p_0)$  Using Eq 3, This Work**

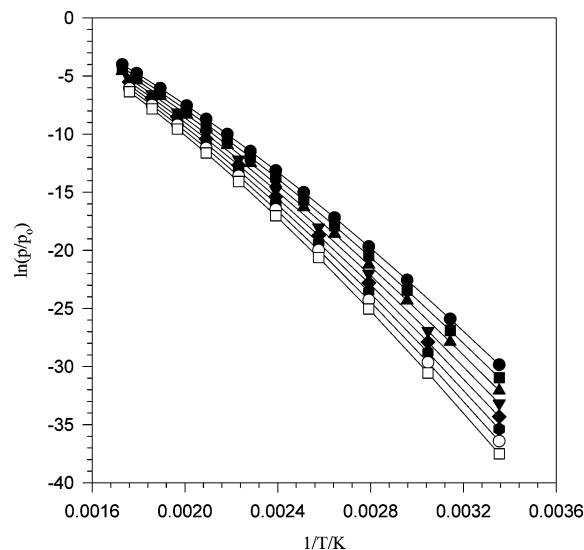
compounds	A (10 <sup>-8</sup> )	B (10 <sup>-6</sup> )	C	D
hentriacontane	3.6037	-4.9002	1791.2	5.6790
dotriacontane	3.7524	-5.0921	1947.2	5.6300
tritriacontane	3.8983	-5.2809	2098.0	5.5850
tetratriacontane	4.0435	-5.4679	2249.5	5.5370
pentatriacontane	4.1746	-5.6480	2363.8	5.5436
hexatriacontane	4.3320	-5.8432	2553.2	5.4470
heptatriacontane	4.4890	-6.0370	2743.2	5.3470
octatriacontane	4.6330	-6.2230	2891.9	5.3040

161 and confirmed by some independent means. This is dis-  
162 cussed in further detail below.

163 **B. Vapor Pressures.** In addition to their usefulness in  
164 obtaining vaporization enthalpies, the equations in Table  
165 2 can also be used to evaluate vapor pressures,  $p$ , when  
166 used in combination with experimental data. The use of  
167 these correlation equations to provide vapor pressure data  
168 has been described previously.<sup>5</sup> These equations relate the  
169 temperature dependence of the vapor pressure of the solute  
170 ( $1/t_a$ ) above the stationary phase of the column over a  
171 narrow temperature range. Although these equations  
172 would not be expected to be accurate in predicting vapor  
173 pressures by themselves, when used with a series of  
174 standards with known vapor pressures at the temperature  
175 of interest, the results obtained through a process of  
176 correlation have been shown to be quite satisfactory. Vapor  
177 pressure equations for heneicosane to triacontane have  
178 previously been reported in the form of eq 3.<sup>5</sup> The  $A$ ,  $B$ ,  $C$ ,  
179 and  $D$  coefficients of this equation are reported in Table 5;  
180  $T$  represents the temperature and  $p_0 = 101325$  Pa

$$\ln(p/p_0) = AT^{-3} + BT^{-2} + CT^{-1} + D \quad (3)$$

181 Values of  $\ln(p/p_0)$  for the standards were calculated using  
182 eq 3 at each temperature over the temperature range  
183 298.15 K to 575 K at roughly 30 K intervals. In the first  
184 correlation,  $\ln(p/p_0)$  values calculated for  $C_{28}$  to  $C_{30}$  from  
185 Table 4 were correlated with the corresponding  $\ln(1/t_a)$   
186 values calculated from the equations in Table 2,  $C_{28}$  to  $C_{33}$ ,  
187 at each temperature. The equations describing the linear  
188 correlation observed between  $\ln(p/p_0)$  and  $\ln(1/t_a)$  for the  
189 standards ( $C_{28}$  to  $C_{30}$ ) were then used to calculate  $\ln(p/p_0)$   
190 values for  $C_{31}$  to  $C_{33}$  at each temperature interval over the  
191 temperature range  $T = 298.15$  K to  $T = 575$  K. These  $\ln$ -  
192 ( $p/p_0$ ) values were then fit to eq 3. The  $A$ ,  $B$ ,  $C$ , and  $D$   
193 coefficients that resulted from the fit are reported as the  
194 first three entries in Table 6. This process was then  
195 repeated by correlating  $\ln(p/p_0)$  values for  $C_{28}$  to  $C_{33}$   
196 calculated from eq 3 with values of  $\ln(1/t_a)$  calculated from  
197 Table 2,  $C_{28}$  to  $C_{34}$ . The values of  $\ln(1/t_a)$  for  $C_{28}$  to  $C_{34}$   
198 were used to evaluate  $\ln(p/p_0)$  values for  $C_{34}$  over the same  
199 temperature range. The resulting values were also fit to  
200 eq 3. Finally in the last correlation,  $\ln(p/p_0)$  values calcu-  
201 lated for  $C_{31}$  to  $C_{34}$  from the appropriate equations in Table



**Figure 2.** A plot of  $\ln(p/p_0)$  vs  $1/T$  for the  $n$ -alkanes from  $T = 298.15$  K to  $T = 570$  K (from top to bottom). ●, hentriacontane; ■, dotriacontane; ▲, tritriacontane; ▼, tetratriacontane; ◆, pentatriacontane; ●, hexatriacontane; ○, heptatriacontane; □, octatriacontane.

6 were correlated against the  $\ln(1/t_a)$  values calculated from  
the last correlation in Table 2,  $C_{31}$  to  $C_{38}$ . This resulted in  
 $\ln(p/p_0)$  values for  $C_{35}$  to  $C_{38}$  summarized by the constants  
given as the last 4 entries in Table 6. In summary, values  
of  $\ln(p/p_0)$  for  $C_{28}$  to  $C_{30}$  were used to evaluate the corre-  
sponding values for  $C_{31}$  to  $C_{38}$ . The temperature depen-  
dence of  $\ln(p/p_0)$  over the temperature range  $T = 298.15$  K  
to  $T = 575$  K for  $C_{31}$  to  $C_{38}$  is illustrated in Figure 2 in  
the form of a  $\ln(p/p_0)$  vs  $1/T$  plot. As with the vaporization  
enthalpies described above, because of the nature and  
extent of the extrapolation, the validity of the equations  
reported in Table 6 needs to be independently verified.

**C. Comparison of Results.** Experimental vapor pres-  
sures and vaporization enthalpies for  $C_{31}$  to  $C_{38}$  are  
available. Some of the experimental data are quite old,<sup>8,9</sup>  
and the quality of the most recent data from Piacente  
et al.<sup>10</sup> has been questioned.<sup>5,11</sup> Morgan and Kobayashi  
have extended Pitzer's CSP model for vapor pressures and  
enthalpy of vaporization to long-chain molecules.<sup>12</sup> The  
model, PERT2,<sup>13</sup> has been developed in combination with  
new vapor pressure and enthalpy of vaporization measure-  
ments on 10  $n$ -alkanes in the  $C_{10}$  to  $C_{28}$  range.<sup>14</sup> This  
model is capable of accurately predicting a variety of physical  
properties of the  $n$ -alkanes from which it has been derived.  
These properties include vapor pressure and vaporization  
enthalpies as a function of temperature. In view of the  
paucity of experimental data, most of which are available  
at elevated temperatures, we have also included compar-  
isons using PERT2.

Table 7 compares vapor pressures and vaporization  
enthalpies calculated from literature data, the predictions  
of PERT2, and the results obtained using the equations in  
Table 6 at various temperatures, including predictions at  
 $T = 298.15$  K. The results reported by Piacente et al.<sup>10</sup>  
are also included for the purpose described below. Column 2  
defines the temperature of the comparison, columns 3 and  
6 provide literature values, and columns 4 and 7 are the  
values calculated as a result of this work. Differences  
between literature values and this work are provided in  
columns 4 and 8.

The vapor pressures and vaporization enthalpies results  
reported by Mazee<sup>9</sup> are in good agreement with those

**Table 7. Literature and Calculated Values of  $\Delta_1^g H(T_m)$  and  $\ln(p/p_0)$  at  $T = T_m$  ( $\text{kJ}\cdot\text{mol}^{-1}$ )**

	$T_m/\text{K}$	$\Delta_1^g H(T_m)^a$	$\Delta_1^g H(T_m)^b$	$\Delta\Delta_1^g H(T_m)$	$\ln(p/p_0)^a$	$\ln(p/p_0)^b$	$\Delta\ln(p/p_0)$
Triacontane							
Mazee <sup>9</sup>	535.5	100.0	102.5	-2.5	-5.34	-5.39	0.05
PERT2 <sup>12,c</sup>	535.5	103.3	102.5	0.8	-5.34	-5.39	0.05
Francis and Wood <sup>8</sup>	549.7	102.6	100.9	1.7	-4.53	-4.80	0.27
PERT2 <sup>12,c</sup>	549.7	101.0	100.9	-0.9	-4.75	-4.80	0.05
Piacente et al. <sup>10</sup>	454	143.2	117.2	26.0	-9.6	-9.82	0.27
PERT2 <sup>12,c</sup>	298.15	155.4	152.3	3.1	-28.9	-28.8	-0.10
Hentriacontane							
Mazee <sup>9</sup>	535.7	105.0	105.9	-0.90	-5.69	-5.71	0.02
PERT2 <sup>12,c</sup>	535.7	106.6	105.9	0.7	-5.65	-5.71	0.06
Piacente et al. <sup>10</sup>	450	146.0	121.8	24.2	-10.4	-10.64	0.24
PERT2 <sup>12,c</sup>	298.15	160.6	157.3	3.3	-30.0	-29.8	-0.20
Dotriacontane							
Piacente et al. <sup>10</sup>	456	147.1	124.5	22.6	-10.2	-10.6	0.42
PERT2 <sup>12,c</sup>	456	125.0	124.5	0.5	-10.58	-10.6	0.02
PERT2 <sup>12,c</sup>	298.15	165.9	162.5	3.4	-31.1	-31.0	-0.10
Trtriacontane							
Piacente et al. <sup>10</sup>	458	148.0	128.0	20.0	-10.6	-10.95	0.34
PERT2 <sup>12,c</sup>	458	128.4	128.0	0.4	-10.89	-10.95	0.06
PERT2 <sup>12,c</sup>	298.15	171.2	167.6	3.6	-32.2	-32.1	-0.1
Tetracontane							
Mazee <sup>9</sup>	548.2	107.9	113.6	-5.7	-5.9	-6.1	0.16
PERT2 <sup>12,c</sup>	548.2	114.3	113.6	0.7	-6.0	-6.1	0.1
Francis and Wood <sup>8</sup>	584.4	140.2	107.6	32.60	-4.38	-4.31	-0.07
PERT2 <sup>12,c</sup>	584.4	107.9	107.6	0.3	-4.5	-4.38	0.12
Piacente et al. <sup>10</sup>	471	152.0	128.9	23.1	-10.1	-10.5	0.40
PERT2 <sup>12,c</sup>	298.15	176.4	172.7	3.7	-33.3	-33.2	-0.1
Pentatriacontane							
Mazee <sup>9</sup>	561.3	111.5	114.6	-3.1	-5.66	-5.81	0.15
PERT2 <sup>12,c</sup>	561.3	115.2	114.6	0.6	-5.70	-5.81	0.11
PERT2 <sup>12,c</sup>	298.15	181.7	178.0	3.7	-34.4	-34.3	-0.1
Hexatriacontane							
Mazee <sup>9</sup>	557.7	114.9	118.3	-3.4	-6.17	-6.26	0.091
PERT2 <sup>12,c</sup>	557.7	119.0	118.3	0.7	-6.14	-6.26	0.12
Piacente et al. <sup>10</sup>	484	157.0	133.4	23.6	-9.98	-10.4	-0.42
PERT2 <sup>12,c</sup>	298.15	186.9	182.8	4.1	-35.4	-35.4	-0.1
Heptatriacontane							
Piacente et al. <sup>10</sup>	491	155.0	135.2	19.8	-9.88	-10.3	-0.42
PERT2 <sup>12,c</sup>	491	136.0	135.2	0.8	-10.2	-10.3	0.1
PERT2 <sup>12,c</sup>	298.15	192.1	187.5	4.6	-36.5	-36.4	-0.1
Octatriacontane							
Piacente et al. <sup>10</sup>	491	160.0	138.8	21.2	-10.3	-10.7	-0.4
PERT2 <sup>12,c</sup>	491	139.6	138.8	0.8	10.58	-10.7	0.12
PERT2 <sup>12,c</sup>	298.15	197.3	192.6	4.7	-37.6	-37.5	-0.1

<sup>a</sup> Literature value. <sup>b</sup> This work. <sup>c</sup> Calculated using PERT2.

244 obtained from the equation in Table 6 and with the  
 245 predictions of PERT2. The vaporization enthalpies reported  
 246 by Mazee are slightly lower, by roughly  $3 \text{ kJ}\cdot\text{mol}^{-1}$ , than  
 247 our results and the predictions of PERT2. Differences in  
 248  $\ln(p/p_0)$  values were also small but differed consistently by  
 249 an average of 0.09. The experimental results of Mazee  
 250 suggest slightly higher vapor pressures than do the predic-  
 251 tions of the equations of Table 6. The results of Francis  
 252 and Wood<sup>8</sup> are mixed. Agreement for  $C_{30}$  is quite good;  
 253  $\Delta_1^g H_m(T_m)$  results for  $C_{34}$  are poor. The best agreement in  
 254  $\Delta_1^g H_m(T_m)$ , ( $C_{30}$ ), gives the poorest agreement in  $\ln(p/p_0)$ ,  
 255 while the best agreement in  $\ln(p/p_0)$  gives the poorest  
 256 agreement in  $\Delta_1^g H_m(T_m)$  ( $C_{34}$ ). As noted above, the results  
 257 of Piacente et al.<sup>10</sup> give the poorest overall agreement.  
 258 However it is interesting to note that they are consistently  
 259 off by an average of  $(22.5 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}$  in  $\Delta_1^g H_m(T_m)$  and  
 260  $(0.37 \pm 0.08)$  in  $\ln(p/p_0)$ . This suggests the presence of some  
 261 systematic error(s) in their measurements. Nearly all the  
 262 experimental results suggest vapor pressures that are  
 263 slightly higher than those calculated by the equations in  
 264 Table 5. PERT2 predicts vaporization enthalpies that are

265 slightly larger than those calculated by the equations in  
 266 Table 6.

267 Comparisons of the predictions of PERT2 with the  
 268 results of this work at  $T = 298.15 \text{ K}$  are also informative.  
 269 The vaporization enthalpies at  $T = 298.15 \text{ K}$  predicted by  
 270 PERT2 are consistently higher by at least  $3 \text{ kJ}\cdot\text{mol}^{-1}$ , and  
 271 the differences appear to be slowly increasing with increas-  
 272 ing number of methylene groups. Vapor-pressure predic-  
 273 tions at the temperatures investigated, on the other hand,  
 274 are almost identical. The results of these comparisons  
 275 suggest that vapor pressures and vaporization enthalpies  
 276 can be reliably predicted using the equations in Table 6.  
 277 The fact that predictions by these equations and PERT2  
 278 were developed through an independent protocol using  
 279 experimental data is particularly reassuring.

280 As another independent test of the reliability of the  
 281 predictions made by the equations in Table 6, a number of  
 282 experiments were conducted using the *n*-alkanes as stan-  
 283 dards and polyaromatic hydrocarbons (PAHs) as un-  
 284 knowns. Many of the PAHs of environmental concern have  
 285 retention times similar to the *n*-alkanes of this study; most

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**Table 8. Retention Times (min) for Some *n*-Alkanes and PAHs**

<i>T</i> /K	398.2	403.2	408.2	413.2	418.2	423.2	428.2
methylene chloride	2.83	2.839	2.851	2.862	2.874	2.886	2.9
decane	4.217	4.033	3.884	3.76	3.66	3.575	3.514
dodecane	7.471	6.731	6.135	5.654	5.264	4.938	4.685
naphthalene	7.656	6.96	6.388	5.92	5.538	5.21	4.955
biphenyl	16.115	13.9	12.111	10.68	9.622	8.542	7.808
tetradecane	17.402	14.716	12.594	10.928	9.622	8.542	7.711
pentadecane	28.148	23.196	19.334	16.336	13.993	12.089	10.644
<i>T</i> /K	532.5	537.5	542.6	547.5	552.6	557.6	562.6
methylene chloride	0.262	0.261	0.261	0.26	0.262	0.265	0.25
hexacosane	3.601	3.088	2.676	2.331	2.04	1.803	1.598
octacosane	5.87	4.954	4.221	3.615	3.113	2.703	2.355
benzo[ <i>a</i> ]pyrene	7.615	6.595	5.757	5.043	4.436	3.923	3.541
1,3,5-triphenylbenzene	8.62	7.325	6.276	5.404	4.68	4.111	3.541
<i>T</i> /K	528.9	534	539.1	544.2	549.3	554.4	559.5
triacontane	9.657	8.022	6.735	5.68	4.83	4.111	3.541
carbon tetrachloride	0.373	0.359	0.36	0.413	0.406	0.403	0.395
octacosane	10.775	9.135	7.7	6.546	5.577	4.784	4.13
perylene	14.307	12.472	10.781	9.359	8.147	7.122	6.291
triacontane	18.105	15.056	12.49	10.436	8.767	7.405	6.291
hentriacontane	23.403	19.323	15.905	13.192	11.002	9.227	7.795
1,2:3,4-dibenzanthracene	27.615	23.465	19.895	16.935	14.532	12.49	10.808
dotriacontane	30.292	24.804	20.27	16.709	13.824	11.516	9.669
trtriacontane	39.178	31.825	25.81	21.123	17.375	14.392	12.002
<i>T</i> /K	528.9	534	539.1	544.2	549.2	554.4	559.5
carbon tetrachloride	0.405	0.408	0.403	0.395	0.392	0.39	0.382
octacosane	10.831	9.115	7.65	6.484	5.535	4.755	4.105
perylene	14.38	12.412	10.693	9.27	8.08	7.08	6.26
triacontane	18.122	14.995	12.401	10.352	8.705	7.364	6.26
hentriacontane	23.413	19.231	15.798	13.092	10.933	9.183	7.758
1,2:5,6-dibenzanthracene	27.433	23.276	19.709	16.815	14.432	12.437	10.766
dotriacontane	30.275	24.64	20.112	16.57	13.735	11.463	9.619
trtriacontane	39.103	31.618	25.598	20.95	17.265	14.33	11.941

are solids with values of  $\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$  that are hypothetical. Two PAHs, naphthalene and biphenyl, were chosen primarily to test the effectiveness of using vapor pressures of the *n*-alkanes as standards in determining the vapor pressures of PAHs. The vapor pressures and vaporization, fusion, and sublimation enthalpies of these two compounds are well known.<sup>6</sup> Other PAHs chosen are compounds with available fusion and sublimation enthalpy values. In addition, two of the PAHs, perylene<sup>3</sup> and 1,3,5-triphenylbenzene,<sup>4</sup> are compounds whose vaporization enthalpies have previously been evaluated by correlation gas chromatography using earlier  $\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$  values for the *n*-alkanes as standards.<sup>15</sup> This study affords an opportunity to adjust earlier values using the new  $\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$  values for the *n*-alkanes used as standards; the new values are believed to be more accurate.

The reliability of the  $\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$  values obtained using the *n*-alkanes of this study as standards can be tested by direct comparison and by means of the thermochemical cycle described by eq 4

$$\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(298.15 \text{ K}) - \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(298.15 \text{ K}) \quad (4)$$

Table 8 reports the retention times of four mixtures containing various PAHs together with various *n*-alkanes exhibiting similar retention times. The temperature dependence of  $\ln(1/t_{\text{a}})$  of these mixtures is provided in Table 9, and a summary of the vaporization enthalpies calculated for the PAHs in these mixtures is given in Table 10. The equation correlating  $\Delta_{\text{sln}}^{\text{v}}H_{\text{m}}(T_{\text{m}})$  with  $\Delta_{\text{I}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$  is provided at the bottom of each mixture.

**Table 9. Equations for the Temperature Dependence of  $\ln(1/t_{\text{a}})$  of Some *n*-Alkanes and PAHs<sup>a</sup>**

	$\Delta_{\text{sln}}^{\text{v}}H_{\text{m}}/R$	intercept	$r^2$
Naphthalene, Biphenyl, $T_{\text{m}} = 413.2 \text{ K}$			
decane	$-4651.5 \pm 38$	$11.36 \pm 0.01$	0.9996
naphthalene	$-4862.0 \pm 41$	$10.64 \pm 0.01$	0.9996
dodecane	$-5439.5 \pm 39$	$12.13 \pm 0.01$	0.9974
biphenyl	$-5659.1 \pm 52$	$11.63 \pm 0.01$	0.9958
tetradecane	$-6306.2 \pm 49$	$13.17 \pm 0.01$	0.9996
pentadecane	$-6744.1 \pm 50$	$13.72 \pm 0.01$	0.9997
Benzo[ <i>a</i> ]pyrene, 1,3,5-Triphenylbenzene, $T_{\text{m}} = 547.6 \text{ K}$			
hexacosane	$-9051.9 \pm 83$	$15.80 \pm 0.007$	0.9996
octacosane	$-9761.8 \pm 71$	$16.614 \pm 0.006$	0.9997
benzo[ <i>a</i> ]pyrene	$-8072.4 \pm 116$	$13.172 \pm 0.010$	0.9990
1,3,5-triphenylbenzene	$-9212.2 \pm 70$	$15.182 \pm 0.006$	0.9997
triacontane	$-10448 \pm 67$	$17.387 \pm 0.006$	0.9998
dotriacontane	$-11141 \pm 60$	$18.180 \pm 0.005$	0.9998
Perylene, 1,2:5,6-Dibenzanthracene, $T_{\text{m}} = 544.2 \text{ K}$			
octacosane	$-10001 \pm 67$	$16.568 \pm 0.006$	0.9998
perylene	$-8434 \pm 71$	$13.312 \pm 0.006$	0.9996
triacontane	$-10706 \pm 70$	$17.372 \pm 0.006$	0.9998
hentriacontane	$-11041 \pm 73$	$17.744 \pm 0.007$	0.9998
1,2:5,6-dibenzanthracene	$-9288 \pm 55$	$14.266 \pm 0.005$	0.9998
dotriacontane	$-11381 \pm 77$	$18.126 \pm 0.007$	0.9998
trtriacontane	$-11715 \pm 83$	$18.499 \pm 0.008$	0.9997
Perylene, 1,2:3,4-Dibenzanthracene, $T_{\text{m}} = 544.2 \text{ K}$			
octacosane	$-9963.2 \pm 36$	$16.492 \pm 0.003$	0.9999
perylene	$-8397.1 \pm 31$	$13.237 \pm 0.003$	0.9999
triacontane	$-10680 \pm 39$	$17.316 \pm 0.004$	0.9999
hentriacontane	$-11013 \pm 40$	$17.686 \pm 0.004$	0.9999
1,2:3,4-dibenzanthracene	$-9327.7 \pm 34$	$14.332 \pm 0.003$	0.9999
dotriacontane	$-11357 \pm 42$	$18.075 \pm 0.004$	0.9999
trtriacontane	$-11693 \pm 43$	$18.452 \pm 0.004$	0.9999

<sup>a</sup>  $\ln(1/t_{\text{a}}) = \Delta_{\text{sln}}^{\text{v}}H_{\text{m}}/R + \text{intercept}$ .

Equation 4 relates sublimation and fusion enthalpies with vaporization enthalpies at  $T = 298.15 \text{ K}$ . The subli-

**Table 10. Vaporization Enthalpies of Some PAHs (kJ·mol<sup>-1</sup>)**

	$\Delta_{\text{sln}}^{\text{v}}H_{\text{m}}(413.2 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (lit)	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (calc)
decane	38.67	51.4	52.5 ± 2.4
dodecane	45.22	61.5	61.7 ± 2.8
naphthalene	40.42		54.9 ± 2.5
biphenyl	47.05		64.3 ± 2.9
tetradecane	52.43	71.7	72.0 ± 3.3
pentadecane	56.07	76.8	77.1 ± 3.5
$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K}) = (1.419 \pm 0.062) \Delta_{\text{sln}}^{\text{g}}H_{\text{m}}(T_{\text{m}}) - (2.42 \pm 0.93); r^2 = 0.9925$			
	$\Delta_{\text{sln}}^{\text{v}}H_{\text{m}}(547.6 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (lit)	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (calc)
hexacosane	75.25	131.7	131.6 ± 0.9
octacosane	81.16	141.9	142.1 ± 1.0
benzo[a]pyrene	67.11		117.1 ± 0.8
1,3,5-triphenylbenzene	76.59		134.0 ± 1.0
triacontane	86.86	152.3	152.2 ± 1.1
dotriacontane	92.62	162.5	162.5 ± 1.2
$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K}) = (1.779 \pm 0.0125) \Delta_{\text{sln}}^{\text{v}}H_{\text{m}}(T_{\text{m}}) - (2.218 \pm 0.161); r^2 = 0.9999$			
	$\Delta_{\text{sln}}^{\text{v}}H_{\text{m}}(544.2 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (lit)	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (calc)
octacosane	83.14	141.9	141.8 ± 0.8
perylene	70.12		118.3 ± 0.7
triacontane	89.01	152.3	152.4 ± 0.9
hentriacontane	91.79	157.3	157.4 ± 0.9
1,2:5,6-dibenzanthracene	77.22		131.1 ± 0.7
dotriacontane	94.62	162.5	162.5 ± 0.9
tritriacontane	97.39	167.6	167.5 ± 0.9
$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K}) = (1.803 \pm 0.01) \Delta_{\text{sln}}^{\text{v}}H_{\text{m}}(T_{\text{m}}) - (8.104 \pm 0.106); r^2 = 0.9999$			
	$\Delta_{\text{sln}}^{\text{v}}H_{\text{m}}(544.2 \text{ K})$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (lit)	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$ (calc)
octacosane	82.83	141.9	141.8 ± 1.0
perylene	69.81		118.5 ± 0.8
triacontane	88.79	152.3	152.4 ± 1.0
hentriacontane	91.56	157.3	157.4 ± 1.1
1,2:3,4 dibenzanthracene	77.55		132.3 ± 0.9
dotriacontane	94.42	162.5	162.5 ± 1.2
tritriacontane	97.21	167.6	167.5 ± 1.2
$(\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K}) = (1.788 \pm 0.0112) \Delta_{\text{sln}}^{\text{v}}H_{\text{m}}(T_{\text{m}}) - (6.275 \pm 0.131); r^2 = 0.9998$			

316 mation enthalpies of most of the PAHs in this comparison  
 317 have been measured at various temperatures; fusion enthalpies  
 318 are available at the melting temperature. To apply  
 319 eq 4, it was first necessary to adjust some of these literature  
 320 values to a common temperature,  $T = 298.15 \text{ K}$ . For  
 321 consistency, all sublimation, vaporization, and fusion enthalpies  
 322 reported in Table 11 were adjusted when necessary  
 323 using eqs 5, 6, and 7, respectively.<sup>4,16</sup>

$$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(T_{\text{m}}) + (0.75 + 0.15C_{\text{p,cr}})(T_{\text{m}} - 298.15)/1000 \quad (5)$$

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = \Delta_{\text{l}}^{\text{g}}H_{\text{m}}(T_{\text{m}}) + (10.58 + 0.26C_{\text{pl}})(T_{\text{m}} - 298.15)/1000 \quad (6)$$

$$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(T_{\text{fus}}) + (0.15C_{\text{p,cr}} - 0.26C_{\text{pl}} - 9.83)(T_{\text{fus}} - 298.15)/1000 \quad (7)$$

324 The  $C_{\text{p,cr}}$  and  $C_{\text{pl}}$  terms ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) refer to the heat  
 325 capacity of the crystal and liquid phase, respectively, and  
 326 all were estimated by group additivity; the values used are  
 327 listed as footnotes to Table 11.

328 Experimental values for naphthalene and biphenyl  
 329 deserve some comment. Both have been recommended for  
 330 use as reference standards for sublimation and fusion  
 331 enthalpy measurements.<sup>6</sup> The vaporization enthalpies of  
 332 naphthalene evaluated by eq 4 or measured directly are  
 333 in very good agreement with the value measured in this  
 334 work and that reported by Lei et al.<sup>2</sup> The results for  
 335 biphenyl are similar.

The sublimation enthalpy of benzo[a]pyrene has been  
 reported twice. The experimental values are listed in  
 column 1 of Table 11.<sup>17,18</sup> Adjusted to  $T = 298.15 \text{ K}$ , both  
 values are in good agreement. The experimental fusion  
 enthalpy is reported in column 4 of the table,<sup>19</sup> adjusted to  
 $T = 298.15 \text{ K}$  results in a fusion enthalpy of  $(8.4 \pm 3.5)$   
 $\text{kJ}\cdot\text{mol}^{-1}$ . The vaporization enthalpy calculated by eq 4,  
 $(114.1 \pm 3.9) \text{kJ}\cdot\text{mol}^{-1}$ , can be compared to a value of  $(117.1$   
 $\pm 1.6) \text{kJ}\cdot\text{mol}^{-1}$  reported in Table 11. As summarized, the  
 two numbers compare within the expressed uncertainties.

Literature values for 1,3,5-triphenylbenzene are provided  
 as the fourth entry in Table 11. The sublimation enthalpy  
 of 1,3,5-triphenylbenzene has been measured several times.  
 As shown in Table 11, agreement between the different  
 measurements is very good. Malaspina et al.<sup>20</sup> also report  
 a fusion enthalpy of  $(22.9 \pm 0.6) \text{kJ}\cdot\text{mol}^{-1}$  at  $T_{\text{fus}} = 448.5$   
 $\text{K}$ . Adjusting the fusion enthalpy to  $T = 298.15 \text{ K}$  and  
 applying eq 4 results in a vaporization enthalpy of  $(138.4$   
 $\pm 5.1) \text{kJ}\cdot\text{mol}^{-1}$  at this temperature. Agreement with the  
 results of this study seem poor.

The fusion enthalpy of 1,3,5-triphenylbenzene has also  
 been measured by Verevkin<sup>21</sup> and by Lebedev et al.<sup>22</sup> These  
 results, which are in good agreement with each other, are  
 at variance with the fusion enthalpy reported by Malaspina  
 et al.<sup>20</sup> We have also repeated this measurement and find  
 our results consistent with the results of Verevkin<sup>21</sup> and  
 Lebedev et al.<sup>21</sup> All three values are reported in Table 11.  
 Using an average sublimation enthalpy and the mean  
 fusion enthalpy at  $T = 298.15 \text{ K}$  of  $(20.4 \pm 3.6)$  reported in  
 Table 11 results in  $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}(298.15) = (129.2 \pm 4.3) \text{kJ}\cdot\text{mol}^{-1}$ .

As noted above, a vaporization enthalpy for 1,3,5-  
 triphenylbenzene was previously measured by correlation

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Table 11. Calculated Vaporization Enthalpies (kJ·mol<sup>-1</sup>) Using a Thermochemical Cycle

$\Delta_{cr}^g H_m(T_m)^a$	$T_m/K$	$\Delta_{cr}^g H_m$ (298.15K)	$\Delta_{cr}^l H_m$ ( $T_{fus}$ )	$T_{fus}/K$	$\Delta_{cr}^l H_m^a$ (298.15K)	$\Delta_{cr}^g H_m - \Delta_{cr}^l H_m$ (298.15 K)	$\Delta_l^g H_m$ (298.15 K)	ref
Naphthalene								
		72.6 ± 0.6	19.06 ± 0.08	353.4	16.9 ± 0.7	55.7 ± 1.0	55.7 ± 2.8	6
							56.1	2
summary <sup>d</sup>		72.6 ± 0.6			16.9 ± 0.7	55.7 ± 1.0	54.9 ± 2.5 <sup>b</sup> 54.9 ± 1.6 <sup>b</sup>	
Biphenyl								
		82.1 ± 2.1	18.57 ± 0.01	342.1	16.6 ± 0.6	65.5 ± 2.2	62.5	6
							64.3 ± 2.9 <sup>b</sup>	2
summary <sup>d</sup>		82.1 ± 2.1			16.6 ± 0.6	65.5 ± 2.2	64.3 ± 2.9 <sup>b</sup>	
Benzo[a]pyrene								
122.5	298.15	122.5						17
118.4 ± 1.4	394	122.4 ± 1.7						18
			19.1 ± 0.7 <sup>c</sup>	454	8.4 ± 3.5		117.1 ± 1.6 <sup>b</sup>	19
average/summary <sup>d</sup>		122.5 ± 0.2			8.4 ± 3.3	114.1 ± 3.3	117.1 ± 1.6 <sup>b</sup>	
1,3,5-Triphenylbenzene								
142.0 ± 2.9	427	149.2 ± 3.6	22.9 ± 0.6	448.5	10.8 ± 3.6	138.4 ± 5.1		20
		148.5						36
		148.8						37
145.6 ± 1.8	376	149.9 ± 2.2	32.6 ± 0.4	445.2	20.7 ± 3.6			21
			33.4	446	21.5 ± 3.6			22
			31.1 ± 1.0 <sup>b,e</sup>	447.9	18.9 ± 3.8			
average <sup>d</sup>		149.1 ± 1.2			20.4 ± 3.6	129.2 ± 4.3	132.7 ± 1.0 <sup>b</sup> 134.0 ± 2.0 <sup>b</sup> 133.4 ± 2.0 <sup>b</sup>	23
Perylene								
123.2	383	126.8 ± 1.1						16
132.6 ± 3.6	408	137.2 ± 3.9						30
137.6 ± 2.5	480	145.4 ± 3.4						31
139	418	144.1 ± 1.5						36
129.6 ± 2.1	415	134.6 ± 2.6						32
			31.9 ± 0.1	550.9	14.5 ± 5.2			33
			32.6 ± 0.3	551.3	15.3 ± 5.2			34
			31.8	553.9	14.3 ± 5.2			18
							89.9	2
							118.1 ± 1.7 <sup>b</sup>	3
							119.2 ± 1.4 <sup>b</sup>	3
							118.5 ± 0.8 <sup>b</sup>	
average/summary <sup>d</sup>		140.3 ± 10 <sup>f</sup>			14.8 ± 5.2	125.5 ± 11.3	118.6 ± 1.1 <sup>g</sup>	
1,2:3,4-Dibenzanthracene								
		135.0						16
139.1 ± 4.0	440	145.7 ± 4.6						35
			25.8 ± 0.1	553.5	6.9 ± 6.2			18
							97.5	2
summary <sup>d</sup>		145.9 ± 4.5			6.9 ± 6.2	139 ± 7.7	132.3 ± 1.8 <sup>b</sup> 132.3 ± 1.8 <sup>b</sup>	
1,2:5,6-Dibenzanthracene								
		134.1						16
140.8 ± 2	449.5	148 ± 3.1						35
141.8	457	149.4 ± 2.5						37
			31.2 ± 1.0	544.2	13.0 ± 6.1			18
							99.7	2
average/summary <sup>d</sup>	148.7 ± 2.0 <sup>h</sup>			13.0 ± 6.1	135.7 ± 6.4	131.1 ± 1.4 <sup>b</sup>		

<sup>a</sup> Where necessary, sublimation enthalpy and fusion enthalpies were adjusted to 298.15 K using eqs 5 and 7, respectively, and the following estimated heat capacities. Naphthalene:  $C_{pcr}$ , 157 J·mol<sup>-1</sup>·K<sup>-1</sup>;  $C_{pl}$ , 205 J·mol<sup>-1</sup>·K<sup>-1</sup>. Biphenyl:  $C_{pcr}$ , 192 J·mol<sup>-1</sup>·K<sup>-1</sup>;  $C_{pl}$ , 248.6 J·mol<sup>-1</sup>·K<sup>-1</sup>. Benzo[a]pyrene, perylene:  $C_{pcr}$ , 279.2 J·mol<sup>-1</sup>·K<sup>-1</sup>;  $C_{pl}$ , 385.4 J·mol<sup>-1</sup>·K<sup>-1</sup>. 1,3,5-Triphenylbenzene:  $C_{pcr}$ , 366 J·mol<sup>-1</sup>·K<sup>-1</sup>;  $C_{pl}$ , 484 J·mol<sup>-1</sup>·K<sup>-1</sup>. 1,2:3,4-Dibenz-anthracene, 1,2:5,6-dibenzanthracene:  $C_{pcr}$ , 313 J·mol<sup>-1</sup>·K<sup>-1</sup>,  $C_{pl}$ , 427.6 J·mol<sup>-1</sup>·K<sup>-1</sup>. References 3 and 38. <sup>b</sup> Results by correlation gas chromatography. <sup>c</sup> Sum of the fusion and transition enthalpy. <sup>d</sup> Uncertainties in  $\Delta_{cr}^g H_m(298.15K)$ ,  $\Delta_{cr}^l H_m(T_{fus})$ , and  $\Delta_l^g H_m(298.15 K)$  represent two standard deviations ( $\pm 2\sigma$ ); uncertainty in  $\Delta_{cr}^l H_m(298.15K)$  was calculated as  $((\pm 2\sigma)_{\text{measurement}}^2 + (\pm 2\sigma)_{\text{temperature adjustment}}^2)^{1/2}$ ; the uncertainty ( $\pm 2\sigma$ ) in the temperature adjustment was estimated as 0.3 of the total temperature adjustment. <sup>e</sup> Average of three determinations. <sup>f</sup> Average of last four entries. <sup>g</sup> Average of last three entries. <sup>h</sup> Average of last two entries.

368 gas chromatography using several large *n*-alkanes as  
 369 standards.<sup>4</sup> The value previously reported as 139.95 kJ·mol<sup>-1</sup>  
 370 should be changed as a result of new values for three of  
 371 the *n*-alkanes used as standards: C<sub>20</sub>,<sup>7</sup> C<sub>22</sub>, and C<sub>28</sub>.<sup>5,23</sup> Use  
 372 of the values reported in column 3 of Table 4 and the  
 373 equations describing the temperature dependence of ln(1/  
 374  $t_a$ )<sup>23</sup> results in a new  $\Delta_l^g H_m(298.15 K)$  value of (132.7 ±  
 375 1.0) kJ·mol<sup>-1</sup>. A comparison of the vaporization enthalpies  
 376 obtained in this study for 1,3,5-triphenylbenzene and the

value calculated by eq 4 results in two values that fall  
 within the range of the experimental uncertainty.

377  
 378  
 379 Examination of the sublimation enthalpies reported in  
 380 Table 11 for perylene at  $T = 298.15 K$  reveals substantial  
 381 scatter in the experimental data. The mean value of the  
 382 last four entries is (140.3 ± 9.1) kJ·mol<sup>-1</sup>. Agreement in  
 383 the experimental fusion enthalpies is good, and application  
 384 of eq 4 leads to a vaporization enthalpy at  $T = 298.15 K$  of  
 385 (125.5 ± 11.3) kJ·mol<sup>-1</sup>.

**Table 12. Parameters of the Cox and Wagner Equations Used in the Calculations of  $\ln(p/p_0)^a$**

	$T_b/K$	$A_0$	$A_1 (10^3)$	$A_2 (10^6)$
decane	447.269	2.9669	-1.932579	1.64463
dodecane	489.438	3.05854	-2.018454	1.60685
tetradecane	526.691	3.13624	-2.063853	1.54151
pentadecane	543.797	3.16774	-2.062348	1.48726
biphenyl <sup>b</sup>	528.422	2.93082	-1.44703	1.00381

	$T_c/K$	$p_c/kPa$	$A$	$B$	$C$	$D$
naphthalene <sup>c</sup>	748.4	4105	-7.79639	2.25115	-2.7033	-3.2266

<sup>a</sup> All data are from ref 7 unless otherwise noted. <sup>b</sup> Reference 24. <sup>c</sup> Reference 25.

386 Perylene is another compound whose vaporization enthalpy has been measured previously by correlation gas chromatography using  $C_{24}$ ,  $C_{26}$ , and  $C_{28}$  as standards. 387 Experimental values of  $(122.4 \pm 3.6)$  and  $(123.7 \pm 3.0)$  388  $\text{kJ}\cdot\text{mol}^{-1}$  were reported.<sup>3</sup> Using the new values reported 389 in Table 4 for these three *n*-alkanes results in changes to 390 values of  $(118.1 \pm 1.7)$  and  $(119.2 \pm 1.4)$   $\text{kJ}\cdot\text{mol}^{-1}$  for the 391 vaporization enthalpy of perylene at  $T = 298.15$  K. The 392 average of these values,  $(118.6 \pm 1.1)$   $\text{kJ}\cdot\text{mol}^{-1}$ , falls well 393 with the limits of uncertainty of the experimental mea- 394 surements. Lei et al.<sup>2</sup> have reported a vaporization en- 395 thalpy of perylene at  $T = 298.15$  K of  $89.9$   $\text{kJ}\cdot\text{mol}^{-1}$ . This 396 value was derived using pyrene and 1,2-benzanthracene 397 as standards. The value reported by Lei et al.<sup>2</sup> appears to 398 be small based on the value derived from eq 4. 399

400 Two values are reported for the sublimation enthalpy of 401 1,2:3,4-dibenzanthracene. Agreement between the two 402 entries is poor. Averaging these two values would result 403 in a vaporization enthalpy of  $133.6$   $\text{kJ}\cdot\text{mol}^{-1}$ , in very good 404 agreement with the results of this work. However, there 405 are few experimental details provided by the authors of 406 the first entry.<sup>17</sup> Disregarding the first entry, the vaporiza- 407 tion enthalpy calculated using only the second entry 408 provides a value that is still within the experimental 409 uncertainties of the measurements. 410

411 Three experimental measurements are reported for the 412 sublimation enthalpy of 1,2:5,6-dibenzanthracene; two of 413 the values are in good agreement. Averaging the last two 414 entries, adjusting their value to  $T = 298.15$  K, and 415 subtracting  $\Delta_{cr}^1 H_m(298.15 \text{ K})$  results in a vaporization 416 enthalpy of  $(135.7 \pm 6.4)$   $\text{kJ}\cdot\text{mol}^{-1}$ ; this value compares 417 favorably with the value of  $(131.1 \pm 1.4)$   $\text{kJ}\cdot\text{mol}^{-1}$  obtained 418 in this study. As with perylene, the vaporization enthalpies 419 at  $T = 298.15$  K reported for 1,2:3,4-dibenzanthracene and 420 1,2:5,6-dibenzanthracene by Lei et al.<sup>2</sup> appear to be too 421 small. 422

423 As noted above, naphthalene and biphenyl were included 424 in this study to validate the use of *n*-alkane vapor pressures 425 in evaluating the vapor pressures of the PAHs. The vapor 426 pressures of the *n*-alkane standards<sup>7</sup> were calculated with 427 the aid of the Cox equation (eq 8). The reference pressure 428 in the Cox equation,  $p_0$  (101.325 kPa), refers to the vapor 429 pressure at the normal boiling point,  $T_b$

$$\ln(p/p_0) = (1 - T_b/T) \exp(A_0 + A_1 T + A_2 T^2) \quad (8)$$

429 The  $T_b$  and  $A$  terms in eq 8 for the *n*-alkanes in question 430 are given in Table 12.

431 The literature vapor pressure for liquid biphenyl at  $T =$  432  $298.15$  K was also calculated by means of the Cox equation, 433 which has been shown to extrapolate with good precision 434 over the necessary temperature range of the extrapola- 435 tion.<sup>24</sup> The literature vapor pressure for liquid naphthalene 436 was calculated with the aid of the Wagner equation (eq 9).<sup>25</sup>

**Table 13. Correlation of  $\ln(1/t_a)$  with Experimental Vapor Pressures at 298.15 K**

	$\ln(1/t_a)$	$\ln(p/p_0)_{\text{expt}}$	$\ln(p/p_0)_{\text{calc}}$
decane	-4.24	-6.32	-6.30
naphthalene	-5.66		-8.07
dodecane	-6.11	-8.63	-8.63
biphenyl	-7.35		-10.17
tetradecane	-7.98	-10.94	-10.96
pentadecane	-8.90	-12.08	-12.11

$\ln(p/p_0)_{\text{calc}} = (1.246 \pm 0.020) \ln(1/t_a) - 1.013 \pm 0.078;$   
 $r^2 = 0.9990$

**Table 14. Comparison of Subcooled Liquid Vapor Pressures with Literature Values at  $T = 298.15$  K**

	$\ln(p/p_0)_{\text{calc}}^a$	$\ln(p/p_0)_{\text{lit}}^b$
$C_{10}H_8$ naphthalene	-8.07	-7.98, <sup>c</sup> -7.91
$C_{12}H_{10}$ biphenyl	-10.17	-10.28, <sup>d</sup> -10.2
$C_{20}H_{12}$ perylene	-24.05, -24.14	-21.5
$C_{20}H_{12}$ benzo[a]pyrene	-23.3	
$C_{22}H_{14}$ 1,2:3,4-dibenzanthracene	-26.6	26.4
$C_{22}H_{14}$ 1,2:5,6-dibenzanthracene	-26.4	-26.7
$C_{24}H_{18}$ 1,3,5-triphenylbenzene	-26.0	
$C_{24}H_{18}$ 1,3,5-triphenylbenzene	-10.0 (475 K)	-8.2 (475 K) <sup>e</sup>

<sup>a</sup> This work. <sup>b</sup> Reference 2 unless otherwise noted. <sup>c</sup> Reference 25. <sup>d</sup> Reference 24. <sup>e</sup> Reference 20.

The parameters used for this calculation are also included 437

$$\ln(p/p_c) = 1/T/T_c [A(1 - T/T_c) + B(1 - T/T_c)^{1.5} + C(1 - T/T_c)^{2.5} + D(1 - T/T_c)^5] \quad (9)$$

438 in Table 12. The reference pressure in the Wagner equation 439 is the critical pressure. In this instance, it was necessary 440 to evaluate  $p$  at  $T = 298.15$  K and then convert back to 441  $\ln(p/p_0)$ .

442 The equations in Table 9 to were used to calculate  $\ln-$  443  $(1/t_a)$  values at  $T = 298.15$  K for naphthalene, biphenyl, 444 and the appropriate *n*-alkanes used in the mixture; the 445 results are listed in the second column of Table 13 next to 446  $\ln(p/p_0)_{\text{expt}}$  values for the *n*-alkanes derived from the Cox 447 equation. The equation derived from the correlation of  $\ln-$  448  $(p/p_0)_{\text{expt}}$  with  $\ln(1/t_a)$  is given at the bottom of Table 13. 449 Vapor pressures for naphthalene and biphenyl reported in 450 the third column of Table 14 were calculated with the aid 451 of this equation.

452 A comparison of the vapor pressures of subcooled liquid 453 naphthalene, biphenyl, and the other PAHs studied at  $T =$  454  $298.15$  K with literature values is provided in Table 14. 455 Comparison of the results for naphthalene and biphenyl 456 is very good. The vapor pressures of the other PAHs were 457 obtained from similar correlations of  $\ln(1/t_a)$  (derived from 458 the appropriate equations in Table 9) with  $\ln(p/p_0)$  values 459 calculated for  $T = 298.15$  K (calculated for the *n*-alkanes 460 using the equations in Tables 5 and 6). The equations 461 generated from the correlations were then used to calculate 462  $\ln(p/p_0)$  for the PAHs (equations not shown). The values 463 are compared when available to literature values calculated 464 by other thermochemical schemes.<sup>2</sup> Agreement between the 465 two values is in most cases quite good.

466 **D. Sublimation Enthalpies.** All the *n*-alkanes  $C_{21}$  to 467  $C_{38}$  are solids at  $T = 298.15$  K. Recently we reported 468 sublimation enthalpies for  $C_{21}$  to  $C_{30}$  by combining vapor- 469 ization enthalpies at  $T = 298.15$  K with enthalpy changes 470 associated with phase changes occurring between  $T =$  471  $298.15$  K and the liquid at  $T = T_{\text{fus}}$ . Recently Briard et al.<sup>26</sup> 472 have reported additional measurements of both fusion and 473 solid-solid-phase transitions. We have averaged the total 474 phase change enthalpies from  $T = 298.15$  to  $T = T_{\text{fus}}$  for 475 the *n*-alkanes  $C_{21}$  to  $C_{38}$  measured by Briard et al.<sup>26,27</sup> and

**Table 15. Vaporization, Solid–Liquid Phase Change, and Sublimation Enthalpies (kJ·mol<sup>-1</sup>) at T = 298.15 K**

	$\Delta_{\text{v}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})$	$\Delta_{\text{tpce}}H_{\text{m}}^{\text{c}}$	$T_{\text{fus}}/\text{K}^{\text{c}}$	$\Delta_{\text{tpce}}H_{\text{m}}(298.15 \text{ K})^{\text{d}}$	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})^{\text{e}}$	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(298.15 \text{ K})^{\text{f}}$
heneicosane	106.8 ± 2.5 <sup>a</sup>	63.4 ± 2.1	313.2	61.9 ± 2.1	168.7 ± 3.3	
docosane	111.9 ± 2.7 <sup>a</sup>	77.1 ± 2.1	316.8	75.2 ± 2.2	187.6 ± 3.5	
tricosane	117 ± 2.8 <sup>a</sup>	75.5 ± 3.9	320.4	73.1 ± 4.0	190.1 ± 4.9	
tetracosane	121.9 ± 2.8 <sup>a</sup>	86.1 ± 3.6	323.6	83.3 ± 3.7	205.2 ± 4.6	
pentacosane	126.8 ± 2.9 <sup>a</sup>	84.4 ± 3.0	326.3	81.2 ± 3.2	208.0 ± 4.3	
hexacosane	131.7 ± 3.2 <sup>a</sup>	93.9 ± 4.4	329.2	90.2 ± 4.5	221.9 ± 5.6	
heptacosane	135.6 ± 3.3 <sup>a</sup>	89.5 ± 7.1	331.7	85.4 ± 7.2	221.0 ± 7.9	
octacosane	141.9 ± 4.9 <sup>a</sup>	100.3 ± 3.8	334.2	95.7 ± 4.0	237.6 ± 6.4	
nonacosane	147.1 ± 5.1 <sup>a</sup>	97.9 ± 3.3	336.2	92.9 ± 3.6	240.6 ± 6.3	
triacontane	152.3 ± 5.3 <sup>a</sup>	105.1 ± 6.7	338.2	99.6 ± 6.9	251.9 ± 8.7	
hentriacontane	157.3 ± 1.2 <sup>b</sup>	109.9	341.1	103.9	261.1	
dotriacontane	162.5 ± 1.4 <sup>b</sup>	117.7 ± 4.8	342.5	111.3 ± 5.2	273.7 ± 5.4	271.1 ± 2.5
tritriacontane	167.6 ± 1.4 <sup>b</sup>	113.5 ± 8.8	344.3	106.6 ± 9.0	274.2 ± 9.1	
tetracontane	172.7 ± 6 <sup>b</sup>	127.4 ± 6.3	345.6	120.1 ± 6.7	292.8 ± 9.0	
pentatriacontane	178.1 ± 9.2 <sup>b</sup>	129.0 ± 4.3	347.7	121.2 ± 4.9	299.2 ± 10.4	
hexatriacontane	182.9 ± 9.4 <sup>b</sup>	128.8 ± 9.6	348.9	120.6 ± 9.9	303.5 ± 13.7	
heptatriacontane	187.6 ± 9.6 <sup>b</sup>	137	349.8	128.4	316.0	
octatriacontane	192.7 ± 9.8 <sup>b</sup>	136.7	351.7	127.6	320.3	

<sup>a</sup> Reference 4. <sup>b</sup> This work. <sup>c</sup> The sum of the phase-change enthalpies from  $T = 298.15 \text{ K}$  to  $T = T_{\text{fus}}$ , averaged from literature values cited in ref 26 and ref 28. <sup>d</sup> Total phase-change enthalpies adjusted to  $T = 298.15 \text{ K}$  using eq 7; heat capacities were estimated using group additivity and the following group values:  $\text{CH}_{3(\text{l})}$ , 34.9;  $\text{CH}_{3(\text{cr})}$ , 36.6;  $\text{CH}_{2(\text{l})}$ , 31.9;  $\text{CH}_{2(\text{cr})}$ , 26.9; see ref 38. <sup>e</sup> Calculation of the uncertainties are discussed in footnote d of Table 11. <sup>f</sup> Estimated value Ref 29.

476 the literature values cited by Dirand et al.<sup>28</sup> to generate  
477 some statistics for these solid–liquid phase changes. The  
478 uncertainties represent  $\pm 2\sigma$ ; uncertainties are reported for  
479 averages of three or more values. The results are listed in  
480 column 3 of Table 15; the melting temperature is provided  
481 in column 4. Column 5 reports the total phase-change  
482 enthalpy adjusted to  $T = 298.15 \text{ K}$  using eq 7. The group  
483 values used in calculating the heat capacities of the  
484 condensed phases are given in footnote d of Table 15. The  
485 sublimation enthalpy was calculated as the sum of the  
486 vaporization enthalpy at  $T = 298.15 \text{ K}$ , (column 2), and  
487 the total phase-change enthalpy was adjusted to  $T = 298.15$   
488 K. Sublimation enthalpies for the  $n$ -alkanes  $\text{C}_{21}$  to  $\text{C}_{30}$   
489 in this table differ slightly from values published recently.<sup>5</sup>  
490 This is due to the use of average values for the solid–liquid  
491 phase change enthalpies; previous results used only a  
492 single value. We are aware of only one sublimation en-  
493 thalpy value in the literature, that for dotriacontane,<sup>29</sup> and  
494 it is an estimated value; agreement with the results of this  
495 work is very good. Values for the even  $n$ -alkanes from  $\text{C}_{20}$   
496 to  $\text{C}_{38}$  have previously been reported by Piacente et al.<sup>9</sup>  
497 However these workers also calculated sublimation en-  
498 thalpies as the sum of the fusion and vaporization enthalpy.  
499 As discussed above, the vaporization enthalpies used in the  
500 calculations seem highly suspect and are not included in  
501 the comparison.

## 502 Conclusions

503 A series of equations are reported in Tables 5 and 6 that  
504 describe the temperature dependence of corrected retention  
505 time for  $\text{C}_{20}$  to  $\text{C}_{38}$ . These equations also provide vaporiza-  
506 tion enthalpy and vapor pressure data for these  $n$ -alkanes  
507 as a function of temperature. These equations are applic-  
508 able within the temperatures range  $T = 298.15 \text{ K}$  to  $T$   
509  $= 575 \text{ K}$ . The vapor pressures of the  $n$ -alkanes in conjunc-  
510 tion with gas chromatographic retention times appear  
511 useful in evaluating the vapor pressures of other types of  
512 hydrocarbons.

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## List of Symbols

$C_{\text{cr}}$	heat capacity of the solid	517
$C_{\text{pl}}$	heat capacity of the liquid	518
$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}(T)$	sublimation enthalpy at temperature $T$	519
$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(T_{\text{fus}})$	enthalpy of fusion at the melting temperature	520 521
$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}(298.15 \text{ K})$	fusion enthalpy of the crystal adjusted to $T = 298.15 \text{ K}$ from $T_{\text{fus}}$	522 523
$\Delta_{\text{v}}^{\text{g}}H_{\text{m}}(T_{\text{m}})$	enthalpy of vaporization at mean temperature $T_{\text{m}}$	525 526
$\Delta_{\text{sln}}^{\text{g}}H_{\text{m}}$	enthalpy of transfer from solution (GC column) to the vapor	527 528
$\Delta_{\text{sln}}H_{\text{m}}$	enthalpy of solution or adsorption on a GC column	529 530
$N_{\text{c}}$	number of carbon atoms	531
$p, p_0$	vapor pressure, 101.325 kPa	532
$\sigma$	standard deviation	533
$t_{\text{a}}$	time an analyte spends absorbed on a GC column	534 535
$T_{\text{b}}$	normal boiling temperature	536
$T_{\text{fus}}$	melting temperature	537

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