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Vapor Pressures and Vaporization Enthalpies of the *n*-Alkanes from C_{31} to C_{38} 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.[1] 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.[2] 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.[3,4] Recently we have reported the vaporization enthalpies of the hydrocarbons heneicosane to triacontane (C_{21} to C_{30}) and described a protocol that can be used to evaluate the subcooled liquid vapor pressure values of these materials.[5] 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 nontoxic, 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_{21} to C_{30} *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_{21} to C_{30} to include C_{31} to C_{38}. 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_{21} to C_{30} 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_{31} to C_{38} 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_{21} to C_{30} measured recently[5] and C_{31} to C_{38} 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.[2]

Experimental Section

The following alkanes: C_{32} (97+%); C_{34} (98+%); C_{36} (98+%), were purchased from Aldrich Chemical Co. All the remaining *n*-alkanes (>99.5%) were purchased from Fluka; the purity of C_{38} 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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Table 1. Gas Chromatographic Retention Times for the *n*-Alkanes from C_{28} to C_{38}

	t/min at the following values of T/K						
	534.4	539.5	544.6	549.65	554.8	559.9	564.9
			C_{28} to C_{33}				
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_{28} to C_{34}				
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
tetratriacontane	27.187	22.450	18.488	15.301	12.736	10.688	9.025
			C_{31} to C_{38}				
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
tetratriacontane	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

Table 2. Equations for the Temperature Dependence of $\ln(1/t_{\mathrm{a}})$[a]

$T_{\mathrm{m}} = 549.7$ K	$\Delta_{\mathrm{sln}}{}^{\mathrm{v}}H_{\mathrm{m}}/R$	intercept	r^2
	C_{28} to C_{33}		
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_{28} to C_{34}		
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
tetratriacontane	-11839 ± 42.1	18.447 ± 0.004	0.9999
	C_{31} to C_{38}		
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
tetratriacontane	-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	0.9998
octatriacontane	-13047 ± 61.8	20.169 ± 0.005	0.9998

[a] $\ln(1/t_{\mathrm{a}}) = \Delta_{\mathrm{sln}}{}^{\mathrm{v}}H_{\mathrm{m}}/R + \text{intercept}$.

equipped with a split/splitless capillary injection port and a flame-ionization detector run at a split ratio of 100/1. Retention times were recorded to three significant figures following the decimal point on an HP 3989A Integrator. The instrument was run isothermally using a 15-m SPB-5 capillary column. Helium was used as the carrier gas. At the temperatures of the experiments, the retention time of the solvent, CH_2Cl_2 or CCl_4, 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_{a}, 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.

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

Results

A. Vaporization Enthalpies. Experimental retention times are presented in Table 1. A plot of $\ln(1/(t_{\mathrm{a}}))$ vs $1/T$ resulted in linear plots whose slopes and intercepts are provided in Table 2. The top of Table 3 lists the enthalpies of transfer from solution to the gas phase, $\Delta_{\mathrm{sln}}{}^{\mathrm{v}}H_{\mathrm{m}}/R$, measured for octacosane to triacontane (column 2) along with the vaporization enthalpies reported previously for octacosane to triacontane (column 3).[5] The last column reports the vaporization enthalpies calculated from the correlation equation listed below the table. In the second correlation of Table 3, octacosane−tritriacontane were used to evaluate the vaporization enthalpy of tetratriacontane. The last set of entries in Table 3 uses the vaporization enthalpies of hentriacontane−tetratriacontane to evaluate the vaporization enthalpies of pentatriacontane−octatriacontane.

The results of these extrapolations are illustrated in Figure 1. This figure plots the vaporization enthalpies at $T = 298.15$ K of pentane on through to octatriacontane. The values of pentane through to eicosane represent recommended literature values.[7] Vaporization enthalpies from heneicosane through to triacontane represent values previously evaluated;[5] these values were evaluated using heptadecane to eicosane as standards. The values of hentriacontane through to octatriacontane are results of this study using octacosane−triacontane as standards.

Table 3. Vaporization Enthalpies of the *n*-Alkanes ($kJ·mol^{-1}$)

	$\Delta_{sln}{}^{v}H_m$(549.7 K)	$\Delta_l{}^{g}H_m$(298.15 K) (lit)	$\Delta_l{}^{g}H_m$(298.15 K) (calc)
C_{28} to C_{33}			
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
$\Delta_l{}^{g}H_m(298.15\ K)/kJ·mol^{-1} = (1.8101 \pm 0.0148)\Delta_{sln}{}^{v}H_m(T_m) - (7.929 \pm 0.0036);\ r^2 = 0.9999$			
C_{28} to C_{34}			
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
$\Delta_l{}^{g}H_m(298.15\ K)/\ kJ·mol^{-1} = (1.8493 \pm 0.015)\Delta_{sln}{}^{v}H_m(T_m) - (9.2802 \pm 0.169);\ r^2 = 0.9998$			
C_{31} to C_{38}			
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
$\Delta_l{}^{g}H_m(298.15\ K)/\ kJ·mol^{-1} = (1.8749 \pm 0.0226)\Delta_{sln}{}^{v}H_m(T_m) - (10.815 \pm 0.14);\ r^2 = 0.9997$			

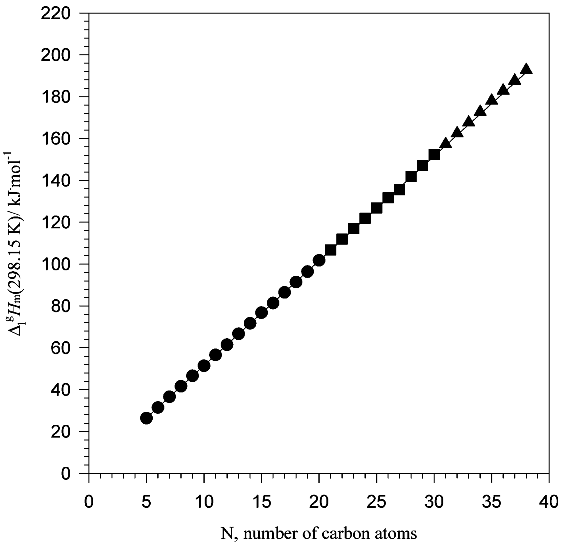

Figure 1. The vaporization enthalpies of the *n*-alkanes at T = 298.15 K. ●, recommended vaporization enthalpies from the literature; ■, vaporization enthalpies previously evaluated by correlation-gas chromatography;[4] ▲, are the results of this study. The line was calculated using recommended literature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

Recommended values of Ruzicka and Majer[7] as well as the values evaluated in this and in a previous publication[5] are summarized in Table 4. The line through the data in Figure 1 was calculated using the recommended literature values for C_5 to C_{20} by a linear regression analysis. The line was then extrapolated to include C_{21} to C_{38}. The equation of the line is given by eq 1. Use of all the data to derive the equation results in eq 2

$$\Delta_l{}^{g}H_m(298.15\ K)/kJ·mol^{-1} = (5.004 \pm 0.008)N_C + (1.507 \pm 0.144)\quad r^2 = 0.9999\quad (1)$$

$$\Delta_l{}^{g}H_m(298.15\ K)/kJ·mol^{-1} = (5.038 \pm 0.006)N_C + (1.07 \pm 0.348)\quad r^2 = 0.9999\quad (2)$$

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

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

[a] Calculated using C_5 to C_{20} according to eq 1. [b] Recommended values, ref 7. [c] Reference 5. [d] This work.

Despite the linear fit observed between $\Delta_l{}^{g}H_m$(298.15 K) and the number of carbon atoms, N_C, the extent of extrapolation is significant; these values need to be tested

Table 5. Previously Evaluated Coefficients for Calculating $\ln(p/p_o)$ Using Eq 3[5]

compounds	A (10^{-8})	B (10^{-6})	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 $\ln(p/p_o)$ Using Eq 3, This Work

compounds	A (10^{-8})	B (10^{-6})	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

and confirmed by some independent means. This is discussed in further detail below.

B. Vapor Pressures. In addition to their usefulness in obtaining vaporization enthalpies, the equations in Table 2 can also be used to evaluate vapor pressures, p, when used in combination with experimental data. The use of these correlation equations to provide vapor pressure data has been described previously.[5] These equations relate the temperature dependence of the vapor pressure of the solute ($1/t_a$) 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 with a series of standards with known vapor pressures at the temperature of interest, the results obtained through a process of correlation have been shown to be quite satisfactory. Vapor pressure equations for heneicosane to triacontane have previously been reported in the form of eq 3.[5] The A, B, C, and D coefficients of this equation are reported in Table 5; T represents the temperature and $p_o = 101325$ Pa

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

Values of $\ln(p/p_o)$ for the standards were calculated using eq 3 at each temperature over the temperature range 298.15 K to 575 K at roughly 30 K intervals. In the first correlation, $\ln(p/p_o)$ values calculated for C_{28} to C_{30} from Table 4 were correlated with the corresponding $\ln(1/t_a)$ values calculated from the equations in Table 2, C_{28} to C_{33}, at each temperature. The equations describing the linear correlation observed between $\ln(p/p_o)$ and $\ln(1/t_a)$ for the standards (C_{28} to C_{30}) were then used to calculate $\ln(p/p_o)$ values for C_{31} to C_{33} at each temperature interval over the temperature range $T = 298.15$ K to $T = 575$ K. These $\ln(p/p_o)$ values were then fit to eq 3. The A, B, C, and D coefficients that resulted from the fit are reported as the first three entries in Table 6. This process was then repeated by correlating $\ln(p/p_o)$ values for C_{28} to C_{33} calculated from eq 3 with values of $\ln(1/t_a)$ calculated from Table 2, C_{28} to C_{34}. The values of $\ln(1/t_a)$ for C_{28} to C_{34} were used to evaluate $\ln(p/p_o)$ values for C_{34} over the same temperature range. The resulting values were also fit to eq 3. Finally in the last correlation, $\ln(p/p_o)$ values calculated for C_{31} to C_{34} from the appropriate equations in Table 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 $\ln(p/p_o)$ values for C_{35} to C_{38} summarized by the constants given as the last 4 entries in Table 6. In summary, values of $\ln(p/p_o)$ for C_{28} to C_{30} were used to evaluate the corresponding values for C_{31} to C_{38}. The temperature dependence of $\ln(p/p_o)$ 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 $\ln(p/p_o)$ 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.

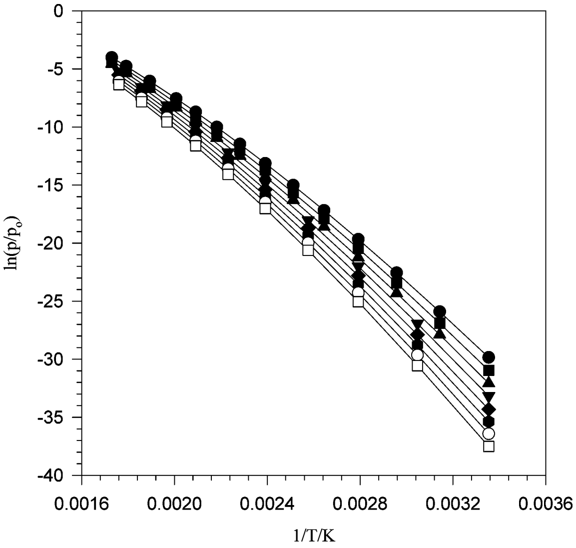

Figure 2. A plot of ln (p/p_o) vs $1/T$ for the n-alkanes from $T = 298.15$ K to $T = 570$ K (from top to bottom). ●, hentriacontane; ■, dotriacontane; ▲, tritriacontane; ▼, tetratriacontane; ◆, pentatriacontane; ⬢, hexatriacontane; ○, heptatriacontane; □, octatriacontane.

C. Comparison of Results. Experimental vapor pressures and vaporization enthalpies for C_{31} to C_{38} are available. Some of the experimental data are quite old,[8,9] and the quality of the most recent data from Piacente et al.[10] has been questioned.[5,11] Morgan and Kobayashi have extended Pitzer's CSP model for vapor pressures and enthalpy of vaporization to long-chain molecules.[12] The model, PERT2,[13] has been developed in combination with new vapor pressure and enthalpy of vaporization measurements on 10 n-alkanes in the C_{10} to C_{28} range.[14] 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 comparisons 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.[10] 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[9] are in good agreement with those

Table 7. Literature and Calculated Values of $\Delta_l{}^gH(T_m)$ and $\ln(p/p_o)$ at $T = T_m$ (kJ·mol^{-1})

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

[a] Literature value. [b] This work. [c] Calculated using PERT2.

obtained from the equations in Table 6 and with the predictions of PERT2. The vaporization enthalpies reported by Mazee are slightly lower, by roughly 3 kJ·mol^{-1}, than our results and the predictions of PERT2. Differences in $\ln(p/p_o)$ values were also small but differed consistently by an average of 0.09. The experimental results of Mazee suggest slightly higher vapor pressures than do the predictions of the equations of Table 6. The results of Francis and Wood[8] are mixed. Agreement for C_{30} is quite good; $\Delta_l{}^gH_m(T_m)$ results for C_{34} are poor. The best agreement in $\Delta_l{}^gH_m(T_m)$, (C_{30}), gives the poorest agreement in $\ln(p/p_o)$, while the best agreement in $\ln(p/p_o)$ gives the poorest agreement in $\Delta_l{}^gH_m(T_m)$ (C_{34}). As noted above, the results of Piacente et al.[10] give the poorest overall agreement. However it is interesting to note that they are consistently off by an average of (22.5 ± 2.1) kJ·mol^{-1} in $\Delta_l{}^gH_m(T_m)$ and (0.37 ± 0.08) in $\ln(p/p_o)$. This suggests the presence of some systematic error(s) in their measurements. Nearly all the experimental results suggest vapor pressures that are slightly higher than those calculated by the equations in Table 6. PERT2 predicts vaporization enthalpies that are slightly larger than those calculated by the equations in Table 6.

Comparisons of the predictions of PERT2 with the results of this work at $T = 298.15$ K are also informative. The vaporization enthalpies at $T = 298.15$ K predicted by PERT2 are consistently higher by at least 3 kJ·mol^{-1}, and the differences appear to be slowly increasing with increasing number of methylene groups. Vapor-pressure predictions at the temperatures investigated, on the other hand, are almost identical. The results of these comparisons suggest that vapor pressures and vaporization enthalpies can be reliably predicted using the equations in Table 6. The fact that predictions by these equations and PERT2 were developed through an independent protocol using experimental data is particularly reassuring.

As another independent test of the reliability of the predictions made by the equations in Table 6, a number of experiments were conducted using the *n*-alkanes as standards and polyaromatic hydrocarbons (PAHs) as unknowns. Many of the PAHs of environmental concern have retention times similar to the *n*-alkanes of this study; most

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

T/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
T/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[*a*]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
T/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
heneicosane	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
tritriacontane	39.178	31.825	25.81	21.123	17.375	14.392	12.002
T/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
heneicosane	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
tritriacontane	39.103	31.618	25.598	20.95	17.265	14.33	11.941

are solids with values of $\Delta_l^gH_m$(298.15 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.[6] Other PAHs chosen are compounds with available fusion and sublimation enthalpy values. In addition, two of the PAHs, perylene[3] and 1,3,5-triphenylbenzene,[4] are compounds whose vaporization enthalpies have previously been evaluated by correlation gas chromatography using earlier $\Delta_l^gH_m$(298.15 K) values for the *n*-alkanes as standards.[15] This study affords an opportunity to adjust earlier values using the new $\Delta_l^gH_m$(298.15 K) values for the *n*-alkanes used as standards; the new values are believed to be more accurate.

The reliability of the $\Delta_l^gH_m$(298.15 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

$$\Delta_l^gH_m(298.15\ \text{K})/\text{kJ}{\cdot}\text{mol}^{-1} = \Delta_{cr}^{\ g}H_m(298.15\ \text{K}) - \Delta_{cr}^{\ l}H_m(298.15\ \text{K}) \quad (4)$$

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 $\ln(1/t_a)$ 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 $\Delta_{sln}^{\ v}H_m(T_m)$ with $\Delta_l^gH_m$(298.15 K) is provided at the bottom of each mixture.

Table 9. Equations for the Temperature Dependence of $\ln(1/t_a)$ of Some *n*-Alkanes and PAHs[a]

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

[a] $\ln(1/t_a) = \Delta_{sln}^{\ v}H_m/R$ + intercept.

Equation 4 relates sublimation and fusion enthalpies with vaporization enthalpies at T = 298.15 K. The subli-

Table 10. Vaporization Enthalpies of Some PAHs ($kJ \cdot mol^{-1}$)

	$\Delta_{sln}{}^{v}H_m$(413.2 K)	$\Delta_l{}^gH_m$ (298.15 K) (lit)	$\Delta_l{}^gH_m$ (298.15 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

$\Delta_l{}^gH_m$ (298.15 K) = (1.419 ± 0.062) $\Delta_{sln}{}^gH_m(T_m)$ − (2.42 ± 0.93); r^2 = 0.9925

	$\Delta_{sln}{}^{v}H_m$(547.6 K)	$\Delta_l{}^gH_m$ (298.15 K) (lit)	$\Delta_l{}^gH_m$ (298.15 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

$\Delta_l{}^gH_m$ (298.15 K) = (1.779 ± 0.0125) $\Delta_{sln}{}^vH_m(T_m)$ − (2.218 ± 0.161); r^2 = 0.9999

	$\Delta_{sln}{}^{v}H_m$(544.2 K)	$\Delta_l{}^gH_m$ (298.15 K) (lit)	$\Delta_l{}^gH_m$ (298.15 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

$\Delta_l{}^gH_m$ (298.15 K) = (1.803 ± 0.01) $\Delta_{sln}{}^vH_m(T_m)$ − (8.104 ± 0.106); r^2 = 0.9999

	$\Delta_{sln}{}^{v}H_m$(544.2 K)	$\Delta_l{}^gH_m$ (298.15 K) (lit)	$\Delta_l{}^gH_m$ (298.15 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

($\Delta_l{}^gH_m$ (298.15 K) = (1.788 ± 0.0112) $\Delta_{sln}{}^vH_m(T_m)$ − (6.275 ± 0.131); r^2 = 0.9998

mation enthalpies of most of the PAHs in this comparison have been measured at various temperatures; fusion enthalpies are available at the melting temperature. To apply eq 4, it was first necessary to adjust some of these literature values to a common temperature, T = 298.15 K. For consistency, all sublimation, vaporization, and fusion enthalpies reported in Table 11 were adjusted when necessary using eqs 5, 6, and 7, respectively[4,16]

$$\Delta_{cr}{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ \cdot mol^{-1}} = \Delta_{cr}{}^{g}H_m(T_m) + (0.75 + 0.15C_{p_{cr}})(T_m - 298.15)/1000 \quad (5)$$

$$\Delta_{l}{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ \cdot mol^{-1}} = \Delta_{l}{}^{g}H_m(T_m) + (10.58 + 0.26C_{p_l})(T_m - 298.15)/1000 \quad (6)$$

$$\Delta_{cr}{}^{l}H_m(298.15\ \mathrm{K})/\mathrm{kJ \cdot mol^{-1}} = \Delta_{cr}{}^{l}H_m(T_{fus}) + (0.15C_{p_{cr}} - 0.26C_{p_l} - 9.83)(T_{fus} - 298.15)/1000 \quad (7)$$

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

Experimental values for naphthalene and biphenyl in Table 11 deserve some comment. Both have been recommended for use as reference standards for sublimation and fusion enthalpy measurements.[6] The vaporization enthalpies of naphthalene evaluated by eq 4 or measured directly are in very good agreement with the value measured in this work and that reported by Lei et al.[2] The results for 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.[17,18] Adjusted to T = 298.15 K, both values are in good agreement. The experimental fusion enthalpy is reported in column 4 of the table,[19] adjusted to T = 298.15 K results in a fusion enthalpy of (8.4 ± 3.5) $kJ \cdot mol^{-1}$. The vaporization enthalpy calculated by eq 4, (114.1 ± 3.9) $kJ \cdot mol^{-1}$, can be compared to a value of (117.1 ± 1.6) $kJ \cdot mol^{-1}$ 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.[20] also report a fusion enthalpy of (22.9 ± 0.6) $kJ \cdot mol^{-1}$ at T_{fus} = 448.5 K. Adjusting the fusion enthalpy to T = 298.15 K and applying eq 4 results in a vaporization enthalpy of (138.4 ± 5.1) $kJ \cdot mol^{-1}$ 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[21] and by Lebedev et al.[22] These results, which are in good agreement with each other, are at variance with the fusion enthalpy reported by Malaspina et al.[20] We have also repeated this measurement and find our results consistent with the results of Verevkin[21] and Lebedev et al.[21] All three values are reported in Table 11. Using an average sublimation enthalpy and the mean fusion enthalpy at T = 298.15 K of (20.4 ± 3.6) reported in Table 11 results in $\Delta_l{}^gH_m(298.15)$ = (129.2 ± 4.3) $kJ \cdot mol^{-1}$.

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

Table 11. Calculated Vaporization Enthalpies (kJ·mol^{-1}) 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
							54.9 ± 2.5^{b}	
summary^{d}		72.6 ± 0.6			16.9 ± 0.7	55.7 ± 1.0	54.9 ± 1.6^{b}	
Biphenyl								
		82.1 ± 2.1	18.57 ± 0.01	342.1	16.6 ± 0.6	65.5 ± 2.2		6
							62.5	2
							64.3 ± 2.9^{b}	
summary^{d}		82.1 ± 2.1			16.6 ± 0.6	65.5 ± 2.2	64.3 ± 2.9^{b}	
Benzo[*a*]pyrene								
122.5	298.15	122.5						17
118.4 ± 1.4	394	122.4 ± 1.7						18
			19.1 ± 0.7^{c}	454	8.4 ± 3.5			19
							117.1 ± 1.6^{b}	
average/summary^{d}		122.5 ± 0.2			8.4 ± 3.3	114.1 ± 3.3	117.1 ± 1.6^{b}	
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^{b,e}	447.9	18.9 ± 3.8			
							132.7 ± 1.0^{b}	23
							134.0 ± 2.0^{b}	
average^{d}		149.1 ± 1.2			20.4 ± 3.6	129.2 ± 4.3	133.4 ± 2.0^{b}	
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^{b}	3
							119.2 ± 1.4^{b}	3
							118.5 ± 0.8^{b}	
average/summary^{d}		140.3 ± 10^{f}			14.8 ± 5.2	125.5 ± 11.3	118.6 ± 1.1^{g}	
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
							132.3 ± 1.8^{b}	
summary^{d}		145.9 ± 4.5			6.9 ± 6.2	139 ± 7.7	132.3 ± 1.8^{b}	
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
							131.1 ± 1.4^{b}	
average/summary^{d}	148.7 ± 2.0^{h}			13.0 ± 6.1	135.7 ± 6.4	131.1 ± 1.4^{b}		

[a] 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: $C_{p_{cr}}$, 157 J·mol^{-1}·K^{-1}; C_{p_l}, 205 J·mol^{-1}·K^{-1}. Biphenyl: $C_{p_{cr}}$, 192 J·mol^{-1}·K^{-1}; C_{p_l}, 248.6 J·mol^{-1}·K^{-1}. Benzo[*a*]pyrene, perylene: $C_{p_{cr}}$, 279.2 J·mol^{-1}·K^{-1}; C_{p_l}, 385.4 J·mol^{-1}·K^{-1}. 1,3,5-Triphenylbenzene: $C_{p_{cr}}$, 366 J·mol^{-1}·K^{-1}; C_{p_l}, 484 J·mol^{-1}·K^{-1}. 1,2:3,4-Dibenzanthracene, 1,2:5,6-dibenzanthracene: $C_{p_{cr}}$, 313 J·mol^{-1}·K^{-1}, C_{p_l}, 427.6 J·mol^{-1}·K^{-1}. References 3 and 38. [b] Results by correlation gas chromatography. [c] Sum of the fusion and transition enthalpy. [d] 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 $((\pm 2\sigma)^2_{\text{measurement}} + (\pm 2\sigma)^2_{\text{temperature adjustment}})1/2$; the uncertainty ($\pm 2\sigma$) in the temperature adjustment was estimated as 0.3 of the total temperature adjustment. [e] Average of three determinations. [f] Average of last four entries. [g] Average of last three entries. [h] Average of last two entries.

gas chromatography using several large *n*-alkanes as standards.[4] The value previously reported as 139.95 kJ·mol^{-1} should be changed as a result of new values for three of the *n*-alkanes used as standards: C_{20},[7] C_{22}, and C_{28}.[5,23] Use of the values reported in column 3 of Table 4 and the equations describing the temperature dependence of ln(1/t_a)[23] results in a new $\Delta_{l}{}^{g}H_m$(298.15 K) value of (132.7 ± 1.0) kJ·mol^{-1}. A comparison of the vaporization enthalpies 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.

Examination of the sublimation enthalpies reported in Table 11 for perylene at T = 298.15 K reveals substantial scatter in the experimental data. The mean value of the last four entries is (140.3 ± 9.1) kJ·mol^{-1}. Agreement in the experimental fusion enthalpies is good, and application of eq 4 leads to a vaporization enthalpy at T = 298.15 K of (125.5 ± 11.3) kJ·mol^{-1}.

Table 12. Parameters of the Cox and Wagner Equations Used in the Calculations of $\ln(p/p_o)$[a]

	T_b/K	A_o	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[b]	528.422	2.93082	−1.44703	1.00381

	T_c/K	p_c/kPa	A	B	C	D
naphthalene[c]	748.4	4105	−7.79639	2.25115	−2.7033	−3.2266

[a] All data are from ref 7 unless otherwise noted. [b] Reference 24. [c] Reference 25.

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

	$\ln(1/t_a)$	$\ln(p/p_o)_{\text{expt}}$	$\ln(p/p_o)_{\text{calc}}$
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

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

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

		$\ln(p/p_o)_{\text{calc}}$[a]	$\ln(p/p_o)_{\text{lit}}$[b]
$C_{10}H_8$	naphthalene	−8.07	−7.98,[c] −7.91
$C_{12}H_{10}$	biphenyl	−10.17	−10.28,[d] −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)[e]

[a] This work. [b] Reference 2 unless otherwise noted. [c] Reference 25. [d] Reference 24. [e] Reference 20.

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. Experimental values of (122.4 ± 3.6) and (123.7 ± 3.0) kJ·mol^{-1} were reported.[3] Using the new values reported in Table 4 for these three *n*-alkanes results in changes to values of (118.1 ± 1.7) and (119.2 ± 1.4) kJ·mol^{-1} for the vaporization enthalpy of perylene at T = 298.15 K. The average of these values, (118.6 ± 1.1) kJ·mol^{-1}, falls well within the limits of uncertainty of the experimental measurements. Lei et al.[2] have reported a vaporization enthalpy of perylene at T = 298.15 K of 89.9 kJ·mol^{-1}. This value was derived using pyrene and 1,2-benzanthracene as standards. The value reported by Lei et al.[2] appears to be small based on the value derived from eq 4.

Two values are reported for the sublimation enthalpy of 1,2:3,4-dibenzanthracene. Agreement between the two entries is poor. Averaging these two values would result in a vaporization enthalpy of 133.6 kJ·mol^{-1}, in very good agreement with the results of this work. However, there are few experimental details provided by the authors of the first entry.[17] Disregarding the first entry, the vaporization enthalpy calculated using only the second entry provides a value that is still within the experimental uncertainties of the measurements.

Three experimental measurements are reported for the sublimation enthalpy of 1,2:5,6-dibenzanthracene; two of the values are in good agreement. Averaging the last two entries, adjusting their value to T = 298.15 K, and subtracting $\Delta_{cr}{}^{l}H_m$(298.15 K) results in a vaporization enthalpy of (135.7 ± 6.4) kJ·mol^{-1}; this value compares favorably with the value of (131.1 ± 1.4) kJ·mol^{-1} obtained in this study. As with perylene, the vaporization enthalpies at T = 298.15 K reported for 1,2:3,4-dibenzanthracene and 1,2:5,6-dibenzanthracene by Lei et al.[2] appear to be too small.

As noted above, naphthalene and biphenyl were included in this study to validate the use of *n*-alkane vapor pressures in evaluating the vapor pressures of the PAHs. The vapor pressures of the *n*-alkane standards[7] were calculated with the aid of the Cox equation (eq 8). The reference pressure in the Cox equation, p_o (101.325 kPa), refers to the vapor pressure at the normal boiling point, T_b

$$\ln(p/p_o) = (1 - T_b/T)\exp(A_o + A_1T + A_2T^2) \qquad (8)$$

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

The literature vapor pressure for liquid biphenyl at T = 298.15 K was also calculated by means of the Cox equation, which has been shown to extrapolate with good precision over the necessary temperature range of the extrapolation.[24] The literature vapor pressure for liquid naphthalene was calculated with the aid of the Wagner equation (eq 9).[25] The parameters used for this calculation are also included

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

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

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

A comparison of the vapor pressures of subcooled liquid naphthalene, biphenyl, and the other PAHs studied at T = 298.15 K with literature values is provided in Table 14. Comparison of the results for naphthalene and biphenyl is very good. The vapor pressures of the other PAHs were obtained from similar correlations of $\ln(1/t_a)$ (derived from the appropriate equations in Table 9) with $\ln(p/p_o)$ values calculated for T = 298.15 K (calculated for the *n*-alkanes using the equations in Tables 5 and 6). The equations generated from the correlations were then used to calculate $\ln(p/p_o)$ for the PAHs (equations not shown). The values are compared when available to literature values calculated by other thermochemical schemes.[2] Agreement between the two values is in most cases quite good.

D. Sublimation Enthalpies. All the *n*-alkanes C_{21} to C_{38} are solids at T = 298.15 K. Recently we reported sublimation enthalpies for C_{21} to C_{30} by combining vaporization enthalpies at T = 298.15 K with enthalpy changes associated with phase changes occurring between T = 298.15 K and the liquid at $T = T_{\text{fus}}$. Recently Briard et al.[26] have reported additional measurements of both fusion and solid−solid phase transitions. We have averaged the total phase change enthalpies from T = 298.15 to $T = T_{\text{fus}}$ for the *n*-alkanes C_{21} to C_{38} measured by Briard et al.[26,27] and

Table 15. Vaporization, Solid−Liquid Phase Change, and Sublimation Enthalpies ($kJ\cdot mol^{-1}$) at $T = 298.15$ K

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

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

the literature values cited by Dirand et al.[28] to generate some statistics for these solid−liquid phase changes. The uncertainties represent $\pm 2\sigma$; uncertainties are reported for averages of three or more values. The results are listed in column 3 of Table 15; the melting temperature is provided in column 4. Column 5 reports the total phase-change enthalpy adjusted to $T = 298.15$ K using eq 7. The group values used in calculating the heat capacities of the condensed phases are given in footnote *d* of Table 15. The sublimation enthalpy was calculated as the sum of the vaporization enthalpy at $T = 298.15$ K, (column 2), and the total phase-change enthalpy was adjusted to $T = 298.15$ K. Sublimation enthalpies for the *n*-alkanes C_{21} to C_{30} in this table differ slightly from values published recently.[5] This is due to the use of average values for the solid−liquid phase change enthalpies; previous results used only a single value. We are aware of only one sublimation enthalpy value in the literature, that for dotriacontane,[29] and it is an estimated value; agreement with the results of this work is very good. Values for the even *n*-alkanes from C_{20} to C_{38} have previously been reported by Piacente et al.[9] However these workers also calculated sublimation enthalpies as the sum of the fusion and vaporization enthalpy. As discussed above, the vaporization enthalpies used in the calculations seem highly suspect and are not included in the comparison.

Conclusions

A series of equations are reported in Tables 5 and 6 that describe the temperature dependence of corrected retention time for C_{20} to C_{38}. These equations also provide vaporization enthalpy and vapor pressure data for these *n*-alkanes as a function of temperature. These equations are applicable within the temperatures range $T = 298.15$ K to $T = 575$ K. The vapor pressures of the *n*-alkanes in conjunction with gas chromatographic retention times appear useful in evaluating the vapor pressures of other types of hydrocarbons.

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List of Symbols

C_{cr}	heat capacity of the solid
C_{p_l}	heat capacity of the liquid
$\Delta_{cr}^g H_m(T)$	sublimation enthalpy at temperature T
$\Delta_{cr}^l H_m(T_{fus})$	enthalpy of fusion at the melting temperature
$\Delta_{cr}^l H_m$(298.15 K)	fusion enthalpy of the crystal adjusted to $T = 298.15$ K from T_{fus}
$\Delta_l^g H_m(T_m)$	enthalpy of vaporization at mean temperature T_m
$\Delta_{sln}^g H_m$	enthalpy of transfer from solution (GC column) to the vapor
$\Delta_{sln} H_m$	enthalpy of solution or adsorption on a GC column
N_c	number of carbon atoms
p, p_o	vapor pressure, 101.325 kPa
σ	standard deviation
t_a	time an analyte spends absorbed on a GC colum
T_b	normal boiling temperature
T_{fus}	melting temperature

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