Hypothetical Thermodynamic Properties. Subcooled Vaporization Enthalpies and Vapor Pressures of Polyaromatic Hydrocarbons

William Hanshaw, Marjorie Nutt, and James S. Chickos*

Department of Chemistry and Biochemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121

The vaporization enthalpies and liquid vapor pressures from $T = 298.15$ K to $T = 510$ K of a series of polyaromatic hydrocarbons have been measured by correlation—gas chromatography. The vaporization enthalpies measured in kJ·mol^{-1} include: biphenylene (66.4 ± 1.7), fluorene (72.4 ± 1.7), 1-methylfluorene (77.2 ± 3.6), 2-phenylindene (84.3 ± 0.7), 1-, 2-, 9-methylanthracene (87.0 ± 1.0, 84.5 ± 2.7, 88.1 ± 1.0, respectively), 1-methylphenanthrene (84.5 ± 1.4), 4*H*-cyclopenta(*def*)phenanthrene (83.4 ± 0.7), pyrene (92.4 ± 1.1), 9,10-dimethylanthracene (94.5 ± 0.2), 2-ethylanthracene (91.4 ± 1.1), 2,3-benzofluorene (97.5 ± 3.9), 1,2-benzanthracene (105.8 ± 1.9), 2,3-benzanthracene (106.2 ± 3.7), triphenylene (106.1 ± 3.9), *p*-terphenyl-d_{14} (99.5 ± 4.4), triphenylmethane (93.2 ± 2.2), benzo[*a*]pyrene (117.8 ± 1.0), benzo[*e*]pyrene (118.2 ± 0.3), benzo[*k*]fluoranthene (117.4 ± 1.1), 3,4-benzofluoranthene (116.8 ± 1.6), benzo[*ghi*]perylene (128.9 ± 1.5), and *p*-quaterphenyl (136.1 ± 1.6). Vaporization enthalpy comparisons are made with available literature values by means of a thermochemical cycle, and agreement is within the combined experimental uncertainties. Vapor pressures are compared with available experimental literature values at elevated temperatures. Good agreement is found for most compounds. Comparisons with subcooled vapor pressures at $T = 298.15$ K obtained using other protocols are also made, and agreement generally is quite good.

Introduction

Polyaromatic hydrocarbons (PAHs) are an important group of environmental contaminants that are produced by a variety of incomplete combustion processes. The volatility of these materials varies drastically depending on their size and structure. The larger PAHs are relatively nonvolatile and are often found adsorbed on particulate matter. The partitioning between adsorbed material and the vapor is frequently described empirically on the basis of the vapor pressure of the subcooled liquid.[1–5] Since the subcooled liquid states of most of the larger PAHs at ambient temperatures are inaccessible, indirect methods have been employed to estimate their vapor pressures.

Vaporization enthalpies of crystalline materials are also quite useful. Combined with fusion enthalpies, they can provide sublimation enthalpies of compounds that are too nonvolatile to be measured by conventional methods, but many can be put through a gas chromatograph.[5,6] Additionally, vaporization enthalpies combined with fusion enthalpies have been used to provide independent confirmation of the magnitude of a sublimation enthalpy measurement. Despite their usefulness, there is only a limited amount of such data available.[7]

Gas chromatography has been used in various ways to obtain both vaporization enthalpies and subcooled vapor pressures.[1–5] Our group has been promoting correlation—gas chromatography as a simple and reliable manner in which vapor pressures and vaporization enthalpies of the subcooled liquid can be derived.[5,6] Since each analyte gets adsorbed on the column and moves on the column according to its vapor pressure on the column, measurement of the temperature dependence of its elution time provides a convenient measure of the interaction of the analyte with the column. The magnitude of this interaction energy, referred to as the enthalpy of transfer from the stationary phase of the column to the gas phase,

$\Delta_{sln}{}^g H_m(T_m)$, is due mainly to the vaporization enthalpy of the compound. For hydrocarbons, $\Delta_{sln}{}^g H_m(T_m)$ has been found to correlate linearly with the vaporization enthalpy of each analyte, $\Delta_l{}^g H_m(T)$, regardless of structure, provided that the vaporization enthalpies are all referenced to the same temperature. By including a series of compounds with known vaporization enthalpies in the mixture, the vaporization enthalpies of those hydrocarbons that are unknown can be evaluated. A plot of $\ln(t_o/t_a)$ versus $1/T$ results in a linear relationship with the slope of the line equal to $\Delta_{sln}{}^g H_m(T_m)/R$, where R is the gas constant. The term t_o is a reference time, 1 min, and t_a represents the adjusted retention time. The adjusted retention time of an analyte on a column is evaluated as the difference between the actual retention time measured and the retention time of an unretained reference, usually the solvent. Additionally, $\ln(t_o/t_a)$ of each hydrocarbon analyte has also been found to correlate linearly with $\ln(p)$ where p is the vapor pressure of the liquid phase of each analyte at a given temperature.[5,6] Thus, the same series of experiments can be used to evaluate vapor pressures if the mixture contains components with known vapor pressures.

This study reports the vaporization enthalpy and temperature dependence of vapor pressure for a series of PAHs that have previously been reported at $T = 298.15$ K as well as new measurements for compounds that do not appear to have been studied previously. In cases where other experimental data are available, the results are compared. Thermodynamic cycles are also reported when possible as a test of the reliability of the data generated.

The method employed is illustrated in detail for a small and for a relatively large PAH, for which experimental data are available. These model calculations are intended to document both the method and the applicability of the standards used in providing reliable

* Corresponding author. E-mail: jsc@umsl.edu. Phone: 314 516 5377.

Table 1A. Retention Times for Run 1

	T/K						
	478.15	483.15	488.15	493.15	498.15	503.15	508.15
	t/min						
CH_2Cl_2	3.19	3.225	3.237	3.252	3.005	3.28	3.305
hexadecane	5.817	5.495	5.221	4.995	4.545	4.64	4.51
fluorene	6.38	6.028	5.725	5.47	4.994	5.06	4.904
octadecane	8.624	7.838	7.205	6.682	5.99	5.877	5.574
anthracene	9.682	8.856	8.181	7.608	6.865	6.701	6.347
eicosane	14.288	12.485	11.074	9.917	8.71	8.174	7.52
triphenylmethane	15.574	13.719	12.24	11.015	9.735	9.126	8.404

Table 1B. Vaporization Enthalpies Calculated by Correlation

	slope		$\Delta_{sln}^g H_m$ (449 K)	$\Delta_l^g H_m$(298.15 K) /kJ·mol^{-1}	
run 1	K	intercept	kJ·mol^{-1}	lit.	calcd
hexadecane	−6278.3	12.172	52.195	81.4[a]	81.7 ± 1.9
fluorene	−5562.8	10.48	46.247		72.4 ± 1.7[b]
octadecane	−7038.3	13.035	58.514	91.4[a]	91.6 ± 2.1
anthracene	−6108.8	10.912	50.786	79.0[c]	79.5 ± 1.9
eicosane	−7808.5	13.932	64.917	101.81[a]	101.9 ± 2.4
triphenylmethane	−7158.9	12.463	59.516		93.2 ± 2.2[d]

$$\Delta_l^g H_m(298.15\ \text{K})/\text{kJ·mol}^{-1} =$$
$$(1.567 \pm 0.035)\Delta_{sln}^g H_m(493\ \text{K}) - (0.076 \pm 0.40), (r^2 = 0.9989) \quad (1)$$

[a] Ref 10. [b] The vaporization enthalpy of fluorene based on the average of [(72.3 ± 1.1),[11] (71.2 ± 1.6),[8] and (72.9 ± 3.3)][12] kJ·mol^{-1} is (72.1 ± 2.0) kJ·mol^{-1}. [c] Ref 13. [d] The vaporization enthalpy of triphenylmethane from the literature based on the average of [(93.7 ± 2.8)[11] and (93.8 ± 2.1)][9] kJ mol^{-1} is (93.8 ± 2.5) kJ·mol^{-1}.

Table 2. Results of Correlating Literature ln(p/p$_o$) with ln(t$_o$/t$_a$) Values at T = 298.15 K

	slope			ln(p/p$_o$)	
T = 298.15 K	K	intercept	ln(t$_o$/t$_a$)	lit.	calcd
hexadecane	−6278.3	12.172	−8.886	−13.18[a]	−13.24
octadecane	−7038.3	13.035	−10.572	−15.43[a]	−15.47
anthracene	−6108.8	10.912	−9.577	−14.24[b]	−14.15
eicosane	−7808.5	13.932	−12.258	−17.70[a]	−17.70
triphenylmethane	−7158.9	12.463	−11.548		−16.76
fluorene	−5562.8	10.48	−8.178		−12.30

$$\ln(p/p_o)\text{calcd} = (1.323 \pm 0.03)\ln(t_o/t_a) -$$
$$(1.476 \pm 0.076); (r^2 = 0.9990) \quad (2)$$

[a] Ref 10. [b] Ref 13.

vapor pressures and vaporization enthalpies for compounds for which this data may be unavailable at T = 298.15 K. The two compounds chosen for this purpose are fluorene and triphenylmethane.[8,9] The vaporization enthalpies of both compounds at T = 298.15 K are available as are vapor pressure data at elevated temperatures. Using the temperature dependence of retention time of these two compounds along with those of the standards and the vapor pressures of the standards, it was also possible to compute the vapor pressure of these two materials as a function of temperature. The vapor pressure results from these correlations were then tested against experimental vapor pressures at elevated temperatures for which experimental data are available. Finally, a summary of the temperature dependence of vapor pressure and vaporization enthalpies of a series of PAHs for which little or no data are available is reported. Details regarding the experimental retention times are provided in Supporting Information. Also included in the Supporting Information are the references to some of the vaporization enthalpies used as standards not reported below.

Table 3A. Parameters of the Cox Equation (Equation 4)[a]

	A$_o$	10^{3}A$_1$	10^{6}A$_2$	T$_b$/K
tetradecane	3.136240	−2063853	1.541507	526.691
hexadecane	3.18271	−2.002545	1.384476	559.978
octadecane	3.24741	−2.048039	1.36245	590.023
eicosane	3.31181	−2.102218	1.34878	617.415
biphenyl[b]	2.93082	−1.447	1.0038	528.422
phenanthrene[c]	3.423726	−1.030247	0.677377	372.36
acenaphthene[c]	3.246001	−0.873359	0.53659254	366.535
pyrene[c]	3.293731	−0.62829208	0.2999404	423.775
benzo[a]pyrene[c]	3.517519	−0.76759	0.419169	449.6

[a] All parameters from ref 10 unless noted otherwise. [b] Ref 14. [c] Ref 15. The value in column 5 represents an arbitrary chosen reference temperature corresponding to the vapor pressure, p$_o$, of 28.70 Pa for phenanthrene, 198.0 Pa for acenaphthene, 69.5 Pa for pyrene, and 6.15 Pa for benzo[a]pyrene in eq 4.

Table 3B. Parameters of the Third-Order Polynomial (Equation 3) Used as Standards[a]

	10^{-8}A T^3	10^{-6}B T^2	C T	D
heneicosane	1.9989	−2.9075	−98.135	6.6591
docosane	2.1713	−3.1176	110.72	6.5353
tricosane	2.3386	−3.322	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	−4.312	1279.4	5.8835
nonacosane	3.2871	−4.5043	1431.2	5.8413
tricontane	3.4404	−4.6998	1601.6	5.7696
hentriacontane[b]	3.6037	−4.9002	1791.2	5.6790
dotriacontane[b]	3.7524	−5.0921	1947.2	5.630
tritriacontane[b]	3.8983	−5.2809	2098.0	5.585
anthracene[c]	0.957586	−1.413713	−3073.66	8.361
perylene[c]	3.356997	−4.269274	2557.59	2.961
p-terphenyl-d$_{14}$[c]	1.759086	−2.525730	−1277.36	7.319
chrysene[c]	2.474476	−3.233954	462.43	5.087

[a] Constants from ref 6 unless noted otherwise. [b] Ref 5. [c] Ref 13.

Table 3C. Parameters of the Wagner Equation (Equation 5)

	A$_W$	B$_W$	C$_W$	D$_W$	T$_c$/K	p$_c$/kPa	ref
naphthalene	−7.79639	2.25115	−2.7033	−3.2266	748.4	4105	16
diphenylmethane	−9.023973	3.839191	−4.94231	−3.42478	778	3280	28

Experimental

All PAHs used in this study were obtained from various commercial sources and used as is. All were analyzed by gas chromatography, and most were found to have purities of 99 %+. Since all were analyzed as mixtures, the initial purity of these materials is not as important as in studies where the thermochemical properties are highly dependent on purity. Correlation gas chromatography experiments were performed on two different HP 5890 Series II gas chromatographs equipped with split/splitless capillary injection ports and flame ionization detectors at a split ratio of approximately 100/1. Retention times are reported to three significant figures following the decimal point using an HP 3396 Series III integrator. The compounds were run isothermally mostly on a 30 m SPB 5 column. While

Table 3D. Parameters of the Antoine Equation[a]

	A	B	C	T/K range	ref
fluorene	7.94839	2641.73	230.963	383 to 428	8
triphenylmethane	7.38135	2368.761	171.71	343 to 462	9

[a] $\log(p/\text{Torr}) = A - B/(T/K - 273.15 + C)$.

Table 4. Parameters of the Third-Order Polynomial for Fluorene and Triphenylmethane Evaluated in This Work (Equation 3)

	$10^{-8}A$ T^3	$10^{-6}B$ T^2	C T	D
fluorene	2.81912268	−3.039484	2358.69	7.648
triphenylmethane	7.6236040	−1.7164648	−2378.221	3.348

enthalpies of transfer do depend on the nature of the column used, the results following the correlation remain independent of the nature of the column within the reproducibility of the results. Temperature was controlled to ± 0.5 K. Helium was used as the carrier gas. At the temperatures of the experiments, the retention time of methane or of the solvent used, CH_2Cl_2, increased with increasing temperature. This is a consequence of the increase in viscosity of the carrier gas with temperature: it is the criterion that has been used to confirm that the reference was not being retained on the column. The retention time of the reference was used to determine the dead volume of the column. Adjusted retention times, t_a, were calculated by subtracting the measured retention time of the nonretained reference from the retention time of each analyte as a function of temperature, generally over a 30 K range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke digital thermometer. Temperature maintained by the gas chromatograph was constant to ± 0.1 K. Enthalpies of transfer were calculated as the product of the slope of the line obtained by plotting $\ln(t_o/t_a)$ vs $1/T$ and the gas constant, R. All plots of $\ln(t_o/t_a)$ vs $1/T$, where $t_o = 1$ min, were characterized with correlation coefficients, r^2, > 0.99. Unless noted otherwise, $p_o = 101.325$ kPa. The retention times measured for all analytes are reported in the Supporting Information. The uncertainties (± σ) reported in the last column of these tables were calculated from the uncertainty in the slope and intercept of the equations listed at the bottom of each

respective table. These uncertainties reflect the potential error in the absolute value of the vaporization enthalpy.

The fusion enthalpy for biphenylene is also reported. The value was measured on a Perkin-Elmer DSC 7. The instrument was standardized using both indium and naphthalene. Details of the measurements are given in the Supporting Information

Results on Fluorene and Triphenylmethane

Fluorene and triphenylmethane were used as test cases to determine whether the *n*-alkanes are suitable standards to evaluate vaporization enthalpies of the PAHs whose vaporization enthalpies are unavailable. Anthracene was also included as a typical PAH. The retention times of these materials are provided in Table 1A. Plots of $\ln(t_o/t_a)$ where $t_o = 1$ min and t_a represents the difference in retention time of each analyte and the nonretained solvent, CH_2Cl_2, resulted in the slope and intercepts reported in Table 1B. Treating the vaporization enthalpies of fluorene and triphenylmethane as unknowns, correlation of the enthalpies of transfer, $\Delta_{sln}^g H_m(T_m)$, against vaporization enthalpy resulted in eq 1. The vaporization enthalpies calculated from this equation are provided in the last column of Table 1B. As indicated by both by the correlation coefficient and the uncertainty cited, the vaporization enthalpy of anthracene is suitably reproduced. The resulting values of [(72.2 ± 1.3) and (93.3 ± 1.6)] kJ·mol^{-1} for fluorene and triphenylmethane can be compared to average literature values of [(72.1 ± 2.0) and (93.8 ± 2.5)] kJ·mol^{-1}, respectively (Table 1B). These results suggest that the *n*-alkanes are suitable standards for evaluating vaporization enthalpies of PAHs. Literature vaporization enthalpy values for fluorene and triphenylmethane were used as known values in subsequent correlations.

To determine how suitable the *n*-alkanes are for evaluating vapor pressures of the PAHs, the slopes and intercepts reported in Table 1B were used to evaluate the vapor pressures of fluorene and triphenylmethane as a function of temperature. Literature values of $\ln(p/p_o)$ for hexadecane, anthracene, octadecane, and eicosane at $T = 298.15$ K were correlated with $\ln(t_o/t_a)$ values calculated for these compounds from the slopes and intercepts of Table 1B. The results are shown in Table 2. The correlation equation generated, eq 2, was used along with $\ln(t_o/t_a)$ values of fluorene and triphenylmethane, also calculated from their respective slopes and intercepts, to obtain $\ln(p/p_o)$ values for these two PAHs at $T = 298.15$ K. Repetition of this correlation over the temperature range $T = 298.15$ K to $T = 540$ K at $T = 30$ K intervals resulted in $\ln(p/p_o)$ values for fluorene and triphenylmethane as a function of temperature that were fit to the following third-order polynomial

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

The reference pressure, p_o, refers to 101.325 kPa. The parameters used to calculate experimental vapor pressures used as reference for comparisons for this and the other correlations reported in this article are provided in Tables 3A to 3C. The parameters in Table 3A were used in conjunction with the Cox equation

$$\ln(p/p_o) = (1 - T_b/T) \exp(A_o + A_1(T/K) + A_2(T/K)^2) \quad (4)$$

T_b refers to the normal boiling temperature. The parameters in Table 3B were used with eq 3, and the parameters in Table 3C were used with the Wagner equation, eq 5

$$\ln(p/p_c) = (1/T_r)[A_W(1 - T_r) + B_W(1 - T_r)^{1.5} + C_W(1 - T_r)^{2.5} + D_W(1 - T_r)^5] \quad (5)$$

$T_r = T/T_c$. Table 4 reports the coefficients for eq 3 that were obtained for fluorene and triphenylmethane. As mentioned
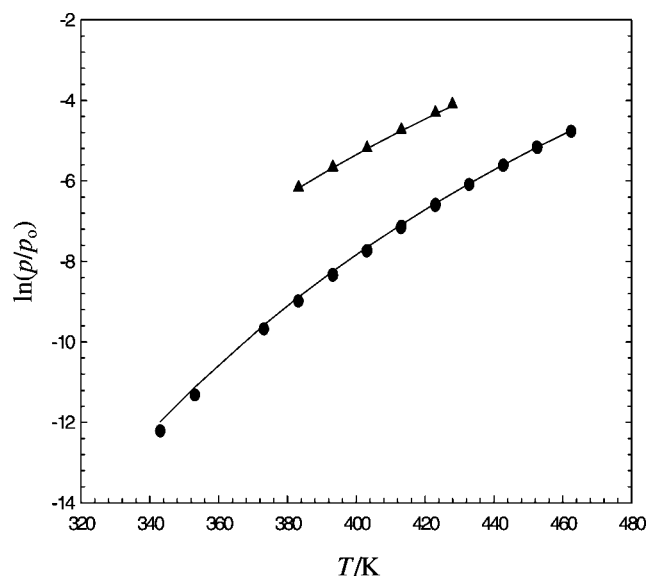

Figure 1. Comparison of literature vapor pressures expressed as $\ln(p/p_o)$ where $p_o = 101.325$ kPa (symbols) and those obtained in this work (lines) for fluorene (triangles) and triphenylmethane (circles) over the temperature range reported for the Antoine constants (Table 3D).

Table 5. Summary of the Temperature Dependence of Retention Time, Enthalpies of Transfer, and Vaporization Enthalpies of the PAHs Studied

	slope		$\Delta_{sln}^{g}H_{m}(493\ K)$	$\Delta_{l}^{g}H_{m}(298.15\ K)/$ kJ·mol^{-1}	
run 2	K	intercept	kJ·mol^{-1}	lit.	calcd
decane	−4755.1	11.43	39.53	51.42	52.1
naphthalene	−4986.6	10.82	41.46	55.4	54.8
diphenylmethane	−6063.2	12.24	50.41	67.9	67.47
biphenylene	−5972.9	11.89	49.66		66.4 ± 2.7
acenaphthene	−6025.3	11.88	50.09	66.2	67.0
fluorene	−6366.9	12.25	52.93	72.1	71.0
hexadecane	−7286.8	14.39	60.58	81.35	81.8

$$\Delta_{l}^{g}H_{m}(298.15\ K)/kJ \cdot mol^{-1} = (1.414 \pm 0.052)\Delta_{sln}^{g}H_{m}(493\ K) - (3.79 \pm 0.9), (r^2 = 0.9947) \tag{6}$$

	slope		$\Delta_{sln}^{g}H_{m}(493\ K)$	$\Delta_{l}^{g}H_{m}(298.15\ K)/$ kJ·mol^{-1}	
run 3	K	intercept	kJ·mol^{-1}	lit.	calcd
decane	−4205.6	10.13	34.96	51.42	51.5
naphthalene	−4530.7	9.74	37.67	55.4	55.2
biphenylene	−5553.4	10.9	46.17		66.6 ± 2.2
diphenylmethane	−5648.3	11.25	46.96	67.9	67.7
acenaphthene	−5610.2	10.9	46.64	66.1	67.3
fluorene	−5951.9	11.27	49.48	72.1	71.1
hexadecane	−6876.3	13.41	57.17	81.35	81.5

$$\Delta_{l}^{g}H_{m}(298.15\ K)/kJ \cdot mol^{-1} = (1.35 \pm 0.044)\Delta_{sln}^{g}H_{m}(430\ K) - (4.26 \pm 0.79), (r^2 = 0.9958) \tag{7}$$

	slope		$\Delta_{sln}^{g}H_{m}(493\ K)$	$\Delta_{l}^{g}H_{m}(298.15\ K)/$ kJ·mol^{-1}	
run 4	K	intercept	kJ·mol^{-1}	lit.	calcd
anthracene	−5591.4	9.902	46.48	79.9	81.8
eicosane	−6750.0	11.92	56.13	101.8	99.8
triphenylmethane	−6299.0	10.824	52.37	93.8	92.8
2,3-benzofluorene	−6600.9	10.722	54.88		97.4 ± 5.0
triphenylene	−7140.5	11.175	59.36		105.8 ± 5.3
2,3-benzanthracene	−7184.4	11.19	59.73		106.7 ± 5.5
octacosane	−9467.1	14.882	78.71	141.9	142.1
perylene	−8030.0	11.891	66.76	118.5	119.7

$$\Delta_{l}^{g}H_{m}(298.15\ K)/kJ \cdot mol^{-1} = (1.869 \pm 0.07)\Delta_{sln}^{g}H_{m}(568\ K) - (5.12 \pm 1.8), (r^2 = 0.9956) \tag{8}$$

	slope		$\Delta_{sln}^{g}H_{m}(493\ K)$	$\Delta_{l}^{g}H_{m}(298.15\ K)/$ kJ·mol^{-1}	
run 5	K	intercept	kJ·mol^{-1}	lit.	calcd
anthracene	−5397	9.572	44.87	79.9	81.3
eicosane	−6538.4	11.558	54.36	101.81	98.9
triphenylmethane	−6205.4	10.663	51.59	93.8	93.8
2,3-benzofluorene	−6517.8	10.578	54.19		98.6 ± 5.1
triphenylene	−7051.5	11.02	58.62		106.8 ± 5.5
2,3-benzanthracene	−7044.1	10.944	58.56		106.7 ± 5.4
octacosane	−9303.4	14.593	77.34	141.9	141.7
perylene	−7939.2	11.732	66	118.5	120.5

$$\Delta_{l}^{g}H_{m}(298.15\ K)/kJ \cdot mol^{-1} = (1.869 \pm 0.07)\Delta_{sln}^{g}H_{m}(568\ K) - (5.12 \pm 1.8), (r^2 = 0.9956) \tag{9}$$

	slope		$\Delta_{sln}^{g}H_{m}(493\ K)$	$\Delta_{l}^{g}H_{m}(298.15\ K)/$ kJ·mol^{-1}	
run 6	K	intercept	kJ·mol^{-1}	lit.	calcd
triphenylmethane	−6327.6	10.892	52.61	93.8	94.0
docosane	−7490.9	12.773	62.28	111.9	111.3
1,2-benzanthracene	−7133.8	11.197	59.31		106.0 ± 2.7
octacosane	−9516.7	14.985	79.12	141.9	141.5
3,4-benzofluoranthene	−7855.5	11.826	65.31		116.8 ± 2.9
perylene	−8054.6	11.949	66.96	118.5	119.8

$$\Delta_{l}^{g}H_{m}(298.15\ K)/kJ \cdot mol^{-1} = (1.792 \pm 0.042)\Delta_{sln}^{g}H_{m}(560\ K) - (0.23 \pm 0.87), (r^2 = 0.9983) \tag{10}$$

Table 5 Continued

run 7	slope		$\Delta_{sln}{}^gH_m$(493 K)	$\Delta_l{}^gH_m$(298.15 K)/ kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit.	calcd
eicosane	−6806.1	12.033	56.58	101.81	101.4
triphenylmethane	−6299.3	10.839	52.37	93.8	93.9
docosane	−7487	12.766	62.24	111.9	111.3
1,2-benzanthracene	−7129.5	11.188	59.27		106.8 ± 2.7
octacosane	−9542.5	15.032	79.33	141.9	141.5
3,4-benzofluoranthene	−7859.3	11.832	65.34		116.8 ± 3.0
perylene	−8066.3	11.968	67.06	118.5	119.8

$$\Delta_l^gH_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.762 \pm 0.044)\Delta_{sln}^gH_m(558\ \text{K}) - (1.63 \pm 0.91), (r^2 = 0.9982) \tag{11}$$

run 8	slope		$\Delta_{sln}{}^gH_m$(493 K)	$\Delta_l{}^gH_m$(298.15 K)/ kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit.	calcd
hexadecane	−6295.8	12.402	52.34	81.35	81.8
1-methylfluorene	−5964.8	11.096	49.59		77.2 ± 3.6
octadecane	−6992.8	13.119	58.14	91.44	91.5
2-methylanthracene	−6526.8	11.557	54.26		85.0 ± 3.9
eicosane	−7748.2	13.962	64.42	101.8	102.0
docosane	−8331.8	14.486	69.27	111.9	110.1
p-terphenyl-d$_{14}$	−7571.2	12.891	62.94		99.5 ± 4.4
tetracosane	−9270.3	15.704	77.07	121.9	123.1

$$\Delta_l^gH_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.668 \pm 0.067)\Delta_{sln}^gH_m(509\ \text{K}) - (5.507 \pm 1.29), (r^2 = 0.9951) \tag{12}$$

run 9	slope		$\Delta_{sln}{}^gH_m$(493 K)	$\Delta_l{}^gH_m$(298.15 K)/ kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit.	calcd
eicosane	−7370.8	13.727	61.27794185	101.81	101.9
docosane	−8026.2	14.417	66.73	111.9	111.7
tetracosane	−8706.3	15.159	72.38	121.9	121.9
triphenylene	−7629.2	12.733	63.43		105.8 ± 0.9
hexacosane	−9368.8	15.874	77.89	131.7	131.8
3,4-benzofluoranthene	−8269.1	13.231	68.75		115.4 ± 0.9
benzo[k]fluoranthene	−8357.5	13.383	69.48		116.7 ± 0.9

$$\Delta_l^gH_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.796 \pm 0.013)\Delta_{sln}^gH_m(540\ \text{K}) - (8.13 \pm 0.16), (r^2 = 0.9999) \tag{13}$$

run 10	slope		$\Delta_{sln}{}^gH_m$(493 K)	$\Delta_l{}^gH_m$(298.15 K)/ kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit.	calcd
eicosane	−7169.2	13.184	59.60	101.81	102.2
1-methylanthracene	−6072.4	10.985	50.48		86.9 ± 1.0
9-methylanthracene	−6160.6	11.043	51.22		88.1 ± 1.0
2-ethylanthracene	−6390.3	11.362	53.1		91.3 ± 1.1
docosane	−7865.2	13.947	65.4	111.9	112.0
pyrene	−6458.9	11.183	53.71		92.3 ± 1.1
tetracosane	−8573.3	14.741	71.28	121.9	121.9
chrysene	−7409.1	12.16	61.60	106.2	105.6
hexacosane	−9281.9	15.544	77.17	131.7	131.8
octacosane	−9992.8	16.357	83.08	141.9	141.8

$$\Delta_l^gH_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.686 \pm 0.019)\Delta_{sln}^gH_m(534\ \text{K}) - (1.77 \pm 0.38), (r^2 = 0.9995) \tag{14}$$

run 11	slope		$\Delta_{sln}{}^gH_m$(493 K)	$\Delta_l{}^gH_m$(298.15 K)/ kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit.	calcd
eicosane	−7150.3	13.155	59.44	101.81	102.2
1-methylanthracene	−6061.8	10.973	50.40		87.0 ± 1.0
9-methylanthracene	−6142.5	11.016	51.07		88.1 ± 1.0
2-ethylanthracene	−6373.6	11.338	52.99		91.4 ± 1.0
docosane	−7857.8	13.938	65.33	111.9	112.0
pyrene	−6457.3	11.187	53.68		92.5 ± 1.0
tetracosane	−8568.6	14.736	71.24	121.9	121.9

Table 5   Continued

run 11	slope		$\Delta_{sln}{}^gH_m$(493 K)	$\Delta_l{}^gH_m$(298.15 K)/ kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit.	calcd
chrysene	−7397.5	12.143	61.50	106.2	105.6
hexacosane	−9281.9	15.544	77.17	131.7	131.9
octacosane	−9992.8	16.357	83.08	141.9	141.8

$$\Delta_l^gH_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.675 \pm 0.0176)\Delta_{sln}^gH_m(534\ \text{K}) - (2.58 \pm 0.37), (r^2 = 0.9996) \qquad (15)$$

run 12	slope		$\Delta_{sln}{}^gH_m$(493 K)	$\Delta_l{}^gH_m$(298.15 K)/ kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit.	calcd
nonacosane	−10038	16.841	83.45	147.1	147.1
triacontane	−10389	17.241	86.37	152.3	152.3
hentriacontane	−10717	17.603	89.10	157.3	157.2
p-quaterphenyl	−9305.2	14.96	77.36		136.1 ± 1.6
dotriacontane	−11087	18.04	92.17	162.5	162.8
benzo[ghi]perylene	−8823.7	13.75	73.36		128.9 ± 1.5
tritriacontane	−11400	18.374	94.78	167.6	167.4

$$\Delta_l^gH_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.80 \pm 0.02)\Delta_{sln}^gH_m(538\ \text{K}) - (3.06 \pm 0.18), (r^2 = 0.9996) \qquad (16)$$

run 13	slope		$\Delta_{sln}{}^gH_m$(493 K)	$\Delta_l{}^gH_m$(298.15 K)/ kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit.	calcd
phenanthrene	−5661.3	10.515	47.07	78.3	78.6
2-methylanthracene	−6055.2	10.936	50.34		84.0 ± 1.4
1-methylphenanthrene	−6087.8	10.951	50.61		84.5 ± 1.4
docosane	−8019.2	14.191	66.67	111.9	111.3
2,3-benzofluorene	−6942.3	11.798	57.72		96.4 ± 1.5
tricosane	−8397.7	14.634	69.82	117	116.6
tetracosane	−8797.8	15.122	73.14	121.9	122.1
pentacosane	−9174.5	15.567	76.27	126.8	127.3

$$\Delta_l^gH_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.67 \pm 0.025)\Delta_{sln}^gH_m(509\ \text{K}) - (0.033 \pm 0.57), (r^2 = 0.9993) \qquad (17)$$

run 14	slope		$\Delta_{sln}{}^gH_m$(493 K)	$\Delta_l{}^gH_m$(298.15 K)/ kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit.	calcd
docosane	−7902	14.184	65.692	111.9	111.9
tetracosane	−8608.1	14.972	71.56	121.9	122.0
hexacosane	−9306.7	15.752	77.37	131.7	131.7
benzo[e]pyrene	−8349.6	13.203	69.42		118.2 ± 0.3
benzo[a]pyrene	−8364.1	13.2	69.54		118.4 ± 0.3

$$\Delta_l^gH_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.70 \pm 0.004)\Delta_{sln}^gH_m(540\ \text{K}) - (0.532 \pm 0.038), (r^2 = 0.9999) \qquad (18)$$

run 15	slope		$\Delta_{sln}{}^gH_m$(493 K)	$\Delta_l{}^gH_m$(298.15 K)/ kJ·mol^{-1}	
	K	intercept	kJ·mol^{-1}	lit.	calcd
tetradecane	−5914.2	13.349	49.17	71.7	71.6
biphenylene	−5491.6	11.964	45.66		66.3 ± 0.6
hexadecane	−6718.6	14.274	55.86	81.4	81.6
octadecane	−7512.2	15.221	62.45	91.4	91.5
2-phenylindene	−6938.2	13.617	57.68		84.3 ± 0.7
4H-cyclopenta(def)phenanthrene	−6862.6	13.245	57.05		83.4 ± 0.7
eicosane	−8334.3	16.227	69.29	101.8	101.7

$$\Delta_l^gH_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.50 \pm 0.012)\Delta_{sln}^gH_m(468\ \text{K}) - (2.1 \pm 0.18), (r^2 = 0.9999) \qquad (19)$$

Table 5 Continued

| run 16 | slope | | $\Delta_{sln}^{g}H_m(493\ K)$ | $\Delta_l^{g}H_m(298.15\ K)/$ kJ·mol^{-1} | |
	K	intercept	kJ·mol^{-1}	lit.	calcd
eicosane	−7833.7	15.16	65.13	101.8	101.8
9,10-dimethylanthracene	−7268.8	13.398	60.43		94.5 ± 0.2
docosane	−8623.1	16.103	71.69	111.9	111.9
tetracosane	−9396.2	17.024	78.12	121.9	121.9
1,2-benzanthracene	−8048.5	14.091	66.91		104.5 ± 0.2
2,3-benzanthracene	−8107.7	14.114	67.40		105.3 ± 0.2
hexacosane	−10155	17.925	84.42	131.7	131.7

$$\Delta_l^{g}H_m(298.15\ K)/kJ\cdot mol^{-1} = (1.55 \pm 0.003)\Delta_{sln}^{g}H_m(503\ K) - (0.83 \pm 0.04), (r^2 = 0.9999) \tag{20}$$

| run 17 | slope | | $\Delta_{sln}^{g}H_m(493\ K)$ | $\Delta_l^{g}H_m(298.15\ K)/$ kJ·mol^{-1} | |
	K	intercept	kJ·mol^{-1}	lit.	calcd
tetracosane	−8083.8	13.83	67.21	121.9	121.7
pentacosane	−8417.9	14.192	69.98	126.8	126.7
hexacosane	−8758.2	14.568	72.81	131.7	131.7
chrysene	−7058.1	11.504	58.68	106.2	106.4
octacosane	−9450.4	15.343	78.57	141.9	142.0
3,4-benzofluoranthene	−7820.6	12.237	65.02		117.8 ± 0.5
nonacosane	−9789.4	15.72	81.39	147.2	147.1
tricontane	−10145	16.128	84.34	152.3	152.4

$$\Delta_l^{g}H_m(298.15\ K)/kJ\cdot mol^{-1} = (1.793 \pm 0.008)\Delta_{sln}^{g}H_m(560\ K) - (1.20 \pm 0.17), (r^2 = 0.9999) \tag{21}$$

| run 18 | slope | | $\Delta_{sln}^{g}H_m(493\ K)$ | $\Delta_l^{g}H_m(298.15\ K)/$ kJ·mol^{-1} | |
	K	intercept	kJ·mol^{-1}	lit.	calcd
tetracosane	−8215.5	14.097	68.30	121.9	121.9
pentacosane	−8545.5	14.451	71.04	126.8	126.9
hexacosane	−8885.8	14.826	73.87	131.7	132.1
chrysene	−7160.3	11.72	59.53	106.2	105.8
octacosane	−9557.4	15.562	79.46	141.9	142.4
benzo[k]fluoranthene	−7936.5	12.461	65.98		117.7 ± 2.0
nonacosane	−9895.3	15.936	82.27	147.1	147.5
triacontane	−10140	16.147	84.30	152.3	151.2

$$\Delta_l^{g}H_m(298.15\ K)/kJ\cdot mol^{-1} = (1.834 \pm 0.028)\Delta_{sln}^{g}H_m(560\ K) - (3.32 \pm 0.61), (r^2 = 0.9988) \tag{22}$$

| run 19 | slope | | $\Delta_{sln}^{g}H_m(493\ K)$ | $\Delta_l^{g}H_m(298.15\ K)/$ kJ·mol^{-1} | |
	K	intercept	kJ·mol^{-1}	lit.	calcd
tetracosane	−8205.9	14.143	68.22	121.9	121.8
pentacosane	−8543.2	14.512	71.02	126.8	126.8
hexacosane	−8879.6	14.88	73.82	131.7	131.8
chrysene	−7159	11.776	59.52	106.2	106.2
octacosane	−9558.7	15.634	79.47	141.9	142.0
benzo[k]fluoranthene	−7943.1	12.535	66.04		117.9 ± 0.3
nonacosane	−9900.6	16.016	82.31	147.1	147.1
triacontane	−10245	16.405	85.17	152.3	152.2

$$\Delta_l^{g}H_m(298.15\ K)/kJ\cdot mol^{-1} = (1.794 \pm 0.004)\Delta_{sln}^{g}H_m(559\ K) - (0.608 \pm 0.097), (r^2 = 0.9988) \tag{23}$$

| run 20 | slope | | $\Delta_{sln}^{g}H_m(493\ K)$ | $\Delta_l^{g}H_m(298.15\ K)/$ kJ·mol^{-1} | |
	K	intercept	kJ·mol^{-1}	lit.	calcd
tetracosane	−7787.3	13.307	64.74	121.9	121.7
pentacosane	−8122.8	13.671	67.53	126.8	126.7
hexacosane	−8465.3	14.05	70.38	131.7	131.9
chrysene	−6767.8	10.993	56.26	106.2	106.3
octacosane	−9140.5	14.795	75.99	141.9	142.0
3,4-benzofluoranthene	−7494.1	11.66	62.30		117.2 ± 0.5
nonacosane	−9473.5	15.161	78.76	147.1	147.0
triacontane	−9823.7	15.559	81.67	152.3	152.3

$$\Delta_l^{g}H_m(298.15\ K)/kJ\cdot mol^{-1} = (1.81 \pm 0.007)\Delta_{sln}^{g}H_m(561\ K) - (4.49 \pm 0.16), (r^2 = 0.9999) \tag{24}$$

above, vapor pressures for fluorene[8] and triphenylmethane[9] have been reported at elevated temperatures, T = (383 to 428) K and T = (343 to 462) K, respectively (Table 3D). Figure 1

illustrates the fit between the vapor pressures derived by correlation (line) and the experimental values (symbols) in the literature. The average absolute deviation in ln(p/p_o) between
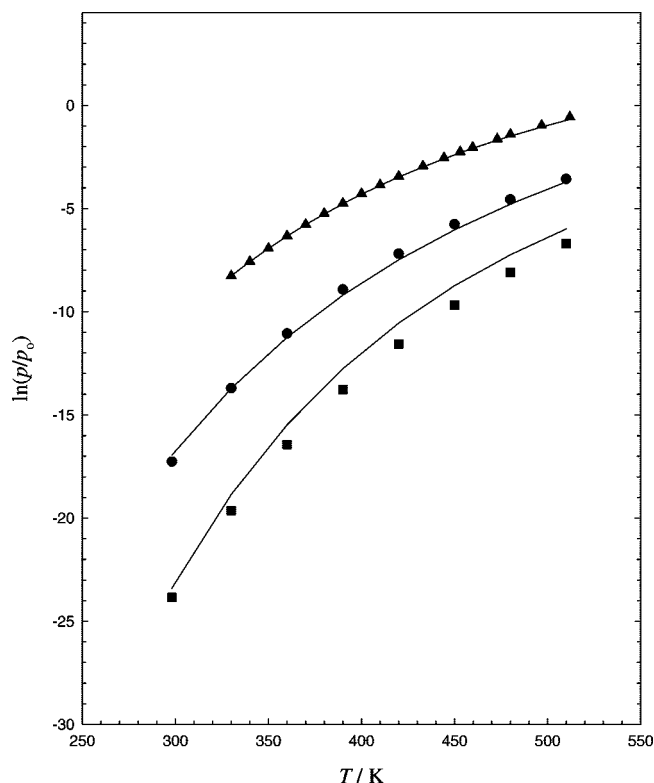
Figure 2. Comparison of literature vapor pressures expressed as $\ln(p/p_o)$ where $p_o = 101.325$ kPa as a function of temperature for diphenylmethane (triangles), pyrene (circles), and benz[*a*]pyrene (squares) with the values calculated from this work (lines). Data for diphenylmethane are experimental. Literature data for pyrene below $T = 433$ K and for benzo[*a*]pyrene below $T = 453$ K are extrapolations of the Cox equation, and the remainder are experimental.

those calculated by correlation and experimental results for fluorene and triphenylmethane was 0.024 and 0.069, respectively, over the temperature range indicated above. These results demonstrate that the suitability of using *n*-alkane vapor pressure data as standards for PAHs.

Vaporization Enthalpies of PAHs

Table 5 summarizes the results of a number of correlations using known vaporization enthalpies of various *n*-alkanes and PAHs to evaluate the vaporization enthalpies of a series of other PAHs that are unknown. The equation correlating vaporization enthalpies of the known values with enthalpies of transfer are given below each correlation. The uncertainties associated with vaporization enthalpies reported for each correlation were calculated from the uncertainty associated with the slope and intercept associated with each correlation equation, eqs 6 to 24. The vaporization enthalpy results are summarized in Table 6. In cases where the vaporization enthalpy was measured by more than one correlation, the uncertainty associated with the mean is an average of each uncertainty.

Since the vaporization enthalpies of the PAHs studied are solids at room temperature, comparison of the values obtained in this study can not be directly compared to experimental values. However, it is possible to evaluate some of the results using thermodynamic cycles. Available experimental sublimation and fusion enthalpies were used in conjunction with eq 25 to evaluate the vaporization enthalpy of a number of these compounds.

$$\Delta_l^g H_m(298.15 \text{ K}) = \Delta_{cr}^g H_m(298.15 \text{ K}) - \Delta_{cr}^l H_m(298.15 \text{ K}) \tag{25}$$

Table 7 summarizes the results calculated according to eq 25 and the values measured by correlation–gas chromatography for those cases where sufficient experimental sublimation and fusion data are available. In cases where experimental sublimation enthalpy data were not available at $T = 298.15$ K, eq 26 was used to adjust sublimation enthalpies from the temperature of measurement to $T = 298.15$ K. Equation 27 was used to adjust fusion enthalpies from the melting temperature to $T = 298.15$ K.[13,17] These temperature adjustments require heat capacities of the condensed phases, $C_p(\text{cr})$, $C_p(\text{l})$. Heat capacities, estimated by group additivity, are also included in Table 7.[18]

$$\Delta_{cr}^g H_m(298.15 \text{ K}) = \Delta_{cr}^g H_m(T_m/\text{K}) + [[0.75 + 0.15 C_p(\text{cr})]/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}][(T/\text{K} - 298.15)/1000 \tag{26}$$

$$\Delta_{cr}^l H_m(298.15 \text{ K}) = \Delta_{cr}^l H_m(T_{fus}) + [[0.15 C_p(\text{cr}) - 0.26 C_p(\text{l})/\text{J} - 9.83)]/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}][(T_{fus}/\text{K} - 298.15]/1000 \tag{27}$$

An examination of Table 7 in cases where it has been possible to construct thermochemical cycles shows that the vaporization enthalpies measured in this work fall within the experimental uncertainties associated with the values calculated by eq 25.

Table 6 also includes vaporization enthalpy values estimated by a simple two-parameter equation, eq 28[31]

$$\Delta_l^g H_m(298.15 \text{ K}) = [(4.69 \pm 0.08(n_C - n_Q) + (1.3 \pm 0.2)n_Q + (3.0 \pm 0.2)]/\text{kJ} \cdot \text{mol}^{-1} \tag{28}$$

where n_C refers to the total number of carbons and n_Q refers to the number of quaternary sp[3] hybridized carbon atoms. Comparison of the last two columns of Table 6 clearly shows that eq 28 underestimates the vaporization enthalpies of the polyaromatic hydrocarbons, particularly those that are planar or near planar. The tendency of eq 28 to underestimate aromatic hydrocarbons, particularly the larger ones, has previously been observed.[32]

Vapor Pressures of The PAHs Studied

Using the temperature dependence of retention times provided in Table 5 along with $\ln(p/p_o)$ values calculated for the standards using eqs 3, 4, and 5 and the parameters in Tables 3A to 3D, $\ln(p/p_o)$ values for the PAHs listed in Table 5 were correlated with $\ln(t_o/t_a)$ values using the protocol described above over the temperature range $T = (298.15 \text{ to } 510 \text{ K})$ at $T = 30$ K intervals. In cases where the temperature dependence of retention time of a particular substance was evaluated in more than one correlation, the $\ln(t_o/t_a)$ values from each correlation were averaged and the average value was correlated against $\ln(p/p_o)$ of the standards. The resulting $\ln(p/p_o)$ values obtained by correlation were then plotted against $1/T$ and the resulting curve fit to eq 3. The parameters resulting from the fit are summarized in Table 8.

Experimental subcooled vapor pressure data near ambient temperatures for most of the PAHs studied are not available. Data are available for diphenylmethane which is a low melting solid. While the vaporization enthalpy of diphenylmethane was used as a standard, the vapor pressures of this substance were not, and therefore the equations describing the retention dependence on temperature in runs 2 and 3 of Table 5 were used to calculate $\ln(p/p_o)$ values for this substance as a function

Table 6. Summary of the Vaporization Enthalpies Measured by Correlation Gas Chromatography

		$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1}			average	estimated[b]
$C_{12}H_8$	biphenylene	66.4 ± 2.7	66.6 ± 2.2	66.3 ± 0.6	66.4 ± 1.7	59.3 ± 1.0
$C_{13}H_{10}$	fluorene	72.4 ± 1.7			72.4 ± 1.7	64.0 ± 1.1
$C_{14}H_{12}$	1-methylfluorene	77.2 ± 3.6			77.2 ± 3.6	68.7 ± 1.1
$C_{15}H_{12}$	2-phenylindene	84.3 ± 0.7			84.3 ± 0.7	73.4 ± 1.2
$C_{15}H_{12}$	1-methylanthracene	86.9 ± 1.0	87.0 ± 1.0		87.0 ± 1.0	73.4 ± 1.2
$C_{15}H_{12}$	2-methylanthracene	85.0 ± 3.9	84.0 ± 1.4		84.5 ± 2.7	73.4 ± 1.2
$C_{15}H_{12}$	9-methylanthracene	88.1 ± 1.0	88.1 ± 1.0		88.1 ± 1.0	73.4 ± 1.2
$C_{15}H_{12}$	1-methylphenanthrene	84.5 ± 1.4			84.5 ± 1.4	73.4 ± 1.2
$C_{15}H_{10}$	4H-cyclopenta(*def*)phenanthrene	83.4 ± 0.7			83.4 ± 0.7	73.4 ± 1.2
$C_{16}H_{10}$	pyrene	92.3 ± 1.1	92.5 ± 1.0		92.4 ± 1.1	78.0 ± 1.3
$C_{16}H_{14}$	9,10-dimethylanthracene	94.5 ± 0.2			94.5 ± 0.2	78.0 ± 1.3
$C_{16}H_{14}$	2-ethylanthracene	91.3 ± 1.1	91.4 ± 1.0		91.4 ± 1.1	78.0 ± 1.3
$C_{17}H_{12}$	2,3-benzofluorene	97.4 ± 5.0	98.6 ± 5.1	96.4 ± 1.5	97.5 ± 3.9	82.7 ± 1.4
$C_{18}H_{12}$	1,2-benzanthracene	106.0 ± 2.7	106.8 ± 2.7	104.5 ± 0.2	105.8 ± 1.9	87.4 ± 1.5
$C_{18}H_{12}$	2,3-benzanthracene	106.7 ± 5.5	106.7 ± 5.4	105.3 ± 0.2	106.2 ± 3.7	87.4 ± 1.5
$C_{18}H_{12}$	triphenylene	105.8 ± 5.3	106.8 ± 5.5	105.8 ± 0.9	106.1 ± 3.9	87.4 ± 1.5
$C_{18}D_{14}$	*p*-terphenyl-d$_{14}$	99.5 ± 4.4			99.5 ± 4.4	87.4 ± 1.5
$C_{19}H_{16}$	triphenylmethane	93.2 ± 2.2			93.2 ± 2.2	92.1 ± 1.5
$C_{20}H_{12}$	benzo[*a*]pyrene	118.4 ± 0.3	117.1 ± 1.6[a]		117.8 ± 1.0	96.8 ± 1.6
$C_{20}H_{12}$	benzo[*e*]pyrene	118.2 ± 0.3			118.2 ± 0.3	96.8 ± 1.6
$C_{20}H_{12}$	benzo[*k*]fluoranthene	116.7 ± 0.9	117.7 ± 2.0	117.9 ± 0.3	117.4 ± 1.1	96.8 ± 1.6
$C_{20}H_{12}$	3,4-benzofluoranthene	116.8 ± 2.9	116.8 ± 3.0	115.4 ± 0.9		
		117.8 ± 0.5	117.2 ± 0.5		116.8 ± 1.6	96.8 ± 1.6
$C_{22}H_{12}$	benzo[*ghi*]perylene	128.9 ± 1.5			128.9 ± 1.5	106.2 ± 1.8
$C_{22}H_{14}$	1,2:3,4-dibenzanthracene	132.3 ± 1.8[a]			132.3 ± 1.8	106.2 ± 1.8
$C_{22}H_{14}$	1,2:5,6-dibenzanthracene	131.1 ± 1.4[a]			131.1 ± 1.4	106.2 ± 1.8
$C_{24}H_{18}$	*p*-quaterphenyl	136.1 ± 1.6			136.1 ± 1.6	115.6 ± 1.9
$C_{24}H_{18}$	1,3,5-triphenylbenzene	133.4 ± 2.0[a]			133.4 ± 2.0	115.6 ± 1.9

[a] Ref 5. [b] Estimated using eq 28.

Table 7. Comparison of Measured Vaporization Enthalpies with Those Calculated by Equation 25

	C_p(l)	C_p(cr)	$\Delta_{cr}^l H_m$(298 K)	$\Delta_{cr}^g H_m$(298 K)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}	
	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	eq 25	this work
biphenylene	235.6	174	18.7 ± 1.4[a]	83.8 ± 0.6[b]	65.1 ± 2.2	66.4 ± 1.7
pyrene	311.2	227.2	10.2 ± 2.3[c]	100.3 ± 3.6[d]	90.1 ± 4.7	92.4 ± 1.0
triphenylene	353.4	261	13.9 ± 3.6[e]	119.5 ± 2.4[f]	105.6 ± 4.3	106.1 ± 3.9
p-terphenyl-d$_{14}$	366.4	279	23.6 ± 3.9[g]	125.6 ± 1.6[h]	102.0 ± 4.2	99.5 ± 4.4
benzo[*a*]pyrene	385.4	279.2	6.7 ± 3.5[i]	120.5 ± 2.7[j]	116.7 ± 3.9	117.8 ± 1.0
benzo[*e*]pyrene	385.4	279.2	5.9 ± 3.5[i]	123.0 ± 1.8[k]	117.1 ± 3.9	118.2 ± 0.3
benzo[*k*]fluoranthene	384.7	278.6	14.5 ± 4.3[l]	133.8 ± 4.5[l]	119.3 ± 6.1	117.4 ± 1.1

[a] $\Delta_{cr}^l H_m$(385.4 K) = (22.6 ± 0.7) kJ·mol^{-1} (385.4 K). This work, see Supporting Information. [b] Ref 19. [c] $\Delta_{cr}^l H_m$(423.8 K) = (17.36 ± 0.04) kJ·mol^{-1}; ref 20. [d] Ref 21. [e] $\Delta_{cr}^l H_m$(471 K) = (24.74 ± 0.01) kJ·mol^{-1}; ref 21. [f] $\Delta_{cr}^g H_m$(395 K) = (115.6 ± 2.0); adjusted to T = 298.15 K using eq 26; ref 22. [g] $\Delta_{cr}^l H_m$(482.4 K) = 35.3 ± 0.4 kJ·mol^{-1} for the unlabeled compound; ref 23. [h] Datum for the unlabeled compound; ref 24. [i] $\Delta_{cr}^l H_m$(454 K) = (16.6 ± 0.8) kJ·mol^{-1}; ref 25. [j] The average of $\Delta_{cr}^g H_m$(395 K) = (118.3 ± 1.2) kJ·mol^{-1} adjusted to T = 298.15 K (122.6 kJ·mol^{-1}), ref 25, $\Delta_{cr}^g H_m$(298.15 K) = (118.1 ± 2.0) kJ·mol^{-1}, ref 29, and $\Delta_{cr}^g H_m$(408 K) (113.3 ± 3.1) adjusted to T = 298.15 K (118.0 ± 3.5 kJ·mol^{-1}), ref 30. [k] $\Delta_{cr}^g H_m$(395 K) = (119.1 ± 1.2) kJ·mol^{-1}; ref 26. [l] $\Delta_{cr}^l H_m$(489 K) = (27.5 ± 0.1) kJ·mol^{-1}; ref 27.

of temperature using the other known compounds as standards. Vapor pressure data for pyrene and benzo[*a*]pyrene are also available in the form of the Cox equation. Since the Cox equation extrapolates quite well over a limited temperature range, we have also used partially extrapolated vapor pressures for comparison as well as vapor pressures for which this equation is directly applicable. These comparisons are shown in Figure 2. Literature values are represented by the symbols, and the values obtained in this work are represented by the lines. Comparisons of the results for diphenylmethane are excellent over the entire temperature range. The average absolute difference in ln(p/p_o) between this work and the literature[28] is 0.04. Comparison of values for pyrene are also quite good with an average absolute error in ln(p/p_o) of 0.21. Benzo[*a*]pyrene has the largest error with an average absolute deviation in ln(p/p_o) of 0.84. Ruuzicka et al. report vapor pressures for benzo[*a*]pyrene over a 10 K range and combined their results with other literature values. At 451.9 K, they report a vapor pressure of

7.1 Pa for benzo[*a*]pyrene. The vapor pressure calculated by correlation−gas chromatography at this temperature is 18.1 Pa, roughly a factor of 2 larger. Results obtained at 461.8 K are also off by a similar factor. The discrepancy observed between this work and the experimental results for benzo[*a*]pyrene is considerably larger than for any of the other results obtained in this study.

Subcooled vapor pressures for a number of PAHs have been reported in the literature. Most of these have been measured by gas chromatography using approaches that differ from the approach used in this work. Table 9 compares values in the literature at T = 298.15 K with those obtained in this work. Our results appear to be in best agreement with the subcooled liquid vapor pressures cited in column 4 calculated from the vapor pressure of the solid according to the equation given in footnote a of Table 9. The results in column 3 were also obtained by gas chromatography using a different protocol. Vapor pressures of the remaining PAHs not listed in this table can be

Table 8. Summary of the Parameters of the Third-Order Polynomial, Equation 3, Calculated by Correlation for the PAHs of this Study

	$10^{-8}A$	$10^{-6}B$	C	
	T^3	T^2	T	D
biphenylene	147336207.1	−1912159.03	−119.691	5.477
diphenylmethane	115104919.3	−1585090.3	−1317.607	7.085
fluorene	281912267.6	−3039483.96	2358.69	3.348
1-methylfluorene	186870736.8	−2448715.91	737.475	4.527
4H-cyclopenta(*def*)phenanthrene	281948344	−3381686.99	3081.917	1.903
2-phenylindene	249783869.2	−3103982.53	2204.907	3.087
1-methylanthracene	253190269.5	−3124542	1885.73	3.537
2-methylanthracene	196916080.8	−2517940.73	70.957	5.244
9-methylanthracene	256952510.4	−3172745.66	1933.223	3.456
1-methylphenanthrene	181137987.8	−2275711.89	−913.277	6.312
pyrene	272098419.3	−3361297.08	2143.069	3.095
9,10-dimethylanthracene	284338787.7	−3522193.91	2591.339	2.668
2-ethylanthracene	257375467.1	−3214538.04	1815.719	3.679
2,3-benzofluorene	244120457.7	−3097765.94	780.109	4.616
1,2-benzanthracene	282250430.8	−3627106.05	1948.441	3.323
2,3-benzanthracene	290595955.4	−3674856.98	1937.572	3.354
triphenylene	268335765.5	−3471269.68	1311.11	4.051
p-terphenyl-d$_{14}$	250438718.5	−3269234.63	1407.876	4.207
triphenylmethane	76236039.7	−1716464.79	−2378.221	7.648
benzo[*a*]pyrene[a]	362132279	−4462435	3363.69	1.852
benzo[*e*]pyrene	361778000.9	−4467130.9	3358.284	1.935
benzo[*k*]fluoranthene	340115133.8	−4248262.11	2729.014	2.689
3,4-benzofluoroanthene	326007471.4	−4123674.37	2417.768	2.985
benz[*e*]acephenanthrylene	344544546.3	−4296000.47	2953.31	2.393
benzo[*ghi*]perylene	404342365.1	−4955693.15	3885.116	1.278
1,2:3,4 dibenzanthracene[b]	422327238.1	−5189596.52	4340.621	1.277
1,2:5,6 dibenzanthracene[b]	423491900.7	−5187595.06	4420.352	1.118
p-quaterphenyl	375623111.3	−4787612.49	2943.198	3.038
1,3,5-triphenylbenzene[b]	353704496.4	−4572620.47	2525.485	3.679

[a] Calculated as an average from the temperature dependence of retention time using the standards in run 14 and the standards reported in ref 5. [b] Calculated from the data reported in ref 5.

Table 9. Comparison of Some Subcooled Liquid Vapor Pressures of PAHs at $T = 298.15$ K

		p_{liquid}/Pa			
		ref 1	ref 1[a]	ref 3	this work
$C_{14}H_{12}$	fluorene	0.194	0.526	0.43	0.46
$C_{13}H_{10}$	diphenylmethane			2.2[b]	2.02
$C_{15}H_{12}$	1-methylfluorene	0.071	0.136		0.14
$C_{15}H_{12}$	2-methylanthracene	0.017	0.0207	0.017	0.020
$C_{15}H_{10}$	1-methylphenanthrene	0.016	0.0186		0.018
$C_{16}H_{14}$	pyrene			$3.8 \cdot 10^{-3}$	$3.22 \cdot 10^{-3}$
$C_{17}H_{12}$	2,3-benzofluorene	$1.9 \cdot 10^{-3}$	$1.07 \cdot 10^{-3}$		$1.03 \cdot 10^{-3}$
$C_{18}H_{12}$	1,2-benzanthracene			$1.86 \cdot 10^{-4}$	$1.55 \cdot 10^{-4}$
$C_{18}H_{12}$	triphenylene	$6.2 \cdot 10^{-4}$	$2.39 \cdot 10^{-4}$		$1.3 \cdot 10^{-4}$
$C_{18}H_{14}$	*p*-terphenyl-d$_{14}$	$1.14 \cdot 10^{-3}$	$5.4 \cdot 10^{-4}$		$1.03 \cdot 10^{-3c}$
$C_{20}H_{12}$	benzo[*a*]pyrene			$9.3 \cdot 10^{-6}$	$6.95 \cdot 10^{-6}$
$C_{20}H_{12}$	benzo[*e*]pyrene			$9.8 \cdot 10^{-6}$	$6.94 \cdot 10^{-6}$
$C_{20}H_{12}$	benzo[*k*]fluoranthene	$5.34 \cdot 10^{-5}$	$8.96 \cdot 10^{-6}$	$1.2 \cdot 10^{-5}$	$9.26 \cdot 10^{-6}$
$C_{20}H_{12}$	3,4-benzofluoroanthene			$1.29 \cdot 10^{-5}$	$1.05 \cdot 10^{-5}$
$C_{22}H_{12}$	benzo[*ghi*]perylene	$5.52 \cdot 10^{-6}$	$4.28 \cdot 10^{-7}$		$4.31 \cdot 10^{-7}$
$C_{22}H_{14}$	1,2:3,4 dibenzanthracene[b]	$3.7 \cdot 10^{-6}$	$2.51 \cdot 10^{-7}$		$2.81 \cdot 10^{-7}$
$C_{22}H_{14}$	1,2:5,6 dibenzanthracene[b]	$4.69 \cdot 10^{-6}$	$3.44 \cdot 10^{-7}$		$3.35 \cdot 10^{-7}$

[a] Vapor pressures calculated from the following relationship: $p_L = p_S/\exp[(\Delta_{fus}S/R)(1 - T_{fus}/T)]$, where p_L, p_S, $\Delta_{fus}S$, R, T_{fus}, and T represent the vapor pressure of the liquid and solid, the entropy of fusion, the gas constant, the melting temperature, and $T = 298.15$ K, respectively. [b] Uncorrected. [c] The vapor pressure evaluated in this work, terphenyl-d_{14}, is expected to be slightly larger than for the unlabeled material.[13]

calculated over the temperature range $T = 298.15$ to $T = 510$ K using eq 3 and the parameters listed in Table 8.

Summary

Vapor pressures and vaporization enthalpies of a series of PAHs have been evaluated by correlation−gas chromatography. The vaporization enthalpy results appear in good agreement with literature values. The largest discrepancy in vapor pressure is observed for benzo[*a*]pyrene for which the vapor pressure is off by approximately a factor of 2.

Supporting Information Available:

Tables including the experimental retention times described in the text and literature references of the standards used. This material is available free of charge via the Internet at http://pubs.acs.org.

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