Enthalpies of Vaporization and Vapor Pressures of Some Deuterated Hydrocarbons. Liquid−Vapor Pressure Isotope Effects

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Liquid−vapor pressures as a function of temperature and enthalpies of vaporization of a series of both liquid and solid hydrocarbons and their perdeuterated analogues have been determined by correlation−gas chromatography. The applicability of this technique is first demonstrated by reproducing the vapor pressure isotope effect of cyclohexane-d_{12} and benzene-d_6. Other hydrocarbons studied include the perdeuterated forms of hexane, toluene, heptane, the *p*- and *o*-xylenes, naphthalene, biphenyl, acenaphthene, phenanthrene, anthracene, hexamethylbenzene, *p*-terphenyl, perylene, and chrysene. Vapor pressures and vaporization enthalpies of unlabeled hexamethylbenzene and perylene are also reported. Inverse vapor pressure isotope effects of the liquid phase are observed for all the substances examined. Vaporization enthalpy differences between unlabeled and labeled hydrocarbons are small and generally slightly positive. Vapor pressure−temperature relationships are reported in the form of a third-order polynomial that appears to reproduce experimental liquid−vapor pressures from $T = 298.15$ K to the boiling temperature.

Introduction

Deuterated compounds are frequently used as internal standards in a variety of assays, particularly in conjunction with gas chromatography−mass spectrometric analyses.[1–5] Depending on the amount and nature of the isotopic substitution, current use of high-resolution capillary columns can cause fractionation and, in some cases, separation of the target compound from the isotopically substituted internal standard. This article reports the vapor pressures and vaporization enthalpies of several commercially available perdeuterated hydrocarbons that can be quantitatively separated by gas chromatography. These physical properties have been measured by correlation−gas chromatography.

Vapor pressure isotope effects have been measured for a variety of compounds. With deuterated molecules, both normal ($p_H/p_D > 1$) and inverse vapor pressure isotope effects ($p_H/p_D < 1$) have been reported.[6] Relatively few vapor pressure and vaporization enthalpy measurements have been reported for larger perdeuterated hydrocarbons, and with the exception of compounds with exchangeable hydrogens (such as alcohols, amines, and acids), cyclohexane-d_{12} and benzene-d_6 are the only hydrocarbons for which vapor pressure data for the liquid state are readily available.[7–11] The vapor pressures of cyclohexane-d_{12} and benzene-d_6 have been repeatedly measured, and the most recent results generally are in very good agreement.[7–10] For most hydrocarbons studied, inverse vapor pressure isotope effects have generally been observed, $p_D > p_H$.[12]

Vapor pressure and sublimation enthalpy measurements for naphthalene-d_8 and phenanthrene-d_{10} as solids have also been reported.[13] Measurements on these compounds have only been reported once, and comparisons of the results reported for the unlabeled hydrocarbons are not in terribly good agreement with literature values.[14]

Correlation gas chromatography is not a direct method for measuring vaporization enthalpy or vapor pressure. What is measured is the temperature dependence of adjusted retention time, t_a, for a series of analytes. The adjusted retention time is the time an analyte spends on the column, and this time is inversely proportional to the compound's vapor pressure on the stationary phase of the column. The following linear relationship is observed

$$\ln(t_o/t_a) = A - B/T \tag{1}$$

What is measured directly from the slope of plots of $\ln(t_o/t_a)$ versus $1/T$ is the enthalpy of transfer ($\Delta_{sln}{}^gH_m(T)$) from the stationary phase of the column to the gas phase, where $B = \Delta_{sln}{}^gH_m(T)/R$ and R is the gas constant. The term, t_o, is the reference time, 1 min. The enthalpy of transfer is related to the vaporization enthalpy ($\Delta_l{}^gH_m(T)$) through the following thermodynamic cycle

$$\Delta_{sln}{}^gH_m(T) = \Delta_l{}^gH_m(T) + \Delta_{sln}H_m(T) \tag{2}$$

The term $\Delta_{sln}H_m(T)$ represents the interaction of the compound with the stationary phase of the column. Equation 2 applies to both solids and liquids because the solute is present on the stationary phase in dilute concentrations. Numerically, $\Delta_{sln}H_m(T)$ is the smaller of the two terms on the right-hand side of the equation. By a judicious choice of structurally related standards with known vaporization enthalpies, plots of $\Delta_l{}^gH_m(T)$ versus $\Delta_{sln}{}^gH_m(T)$ are linear, and vaporization enthalpies of the unknown species can be obtained from the resulting correlation equation of the standards.[15,16] Similarly, plots of $\ln(t_o/t_a)$ vs $\ln(p/p_o)$ are also found to correlate in a linear fashion implying that the A factors also correlate (eq 3 with eq 4).[15,16] Since vaporization enthalpies and vapor pressures of only a few deuterated hydrocarbons are available, a direct correlation between eq 5 and 6 is precluded. The question arises: how much of an error does the correlation of eq 4 with eq 3 in combination with A_d and $\Delta_{sln}{}^gH_m(T)_d$ to evaluate A'_d and $\Delta_l{}^gH_m(T)_d$ introduce?

$$\ln(t_o/t_a)_h = A_h - \Delta_{sln}{}^gH_m(T)_h/RT \tag{3}$$

$$\ln(p/p_o)_h = A'_h - \Delta_l{}^gH_m(T)_h/RT \tag{4}$$

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$$\ln(t_o/t_a)_d = A_d - \Delta_{sln}{}^{g}H_m(T)_d/RT \quad (5)$$

$$\ln(p/p_o)_d = A'_d - \Delta_l{}^{g}H_m(T)_d/RT \quad (6)$$

To address this question, the vaporization enthalpy and vapor pressure of cyclohexane and benzene were evaluated first using the literature vaporization enthalpies and vapor pressures of the unlabeled hydrocarbons and the temperature dependence of the adjusted retention times of both deuterated and undeuterated substances.[7–10] Since the retention times of labeled and unlabeled cyclohexane and benzene overlapped at some temperatures, two separate sets of correlations were performed.

Experimental Section

The perdeuterated compounds were purchased from Aldrich Chemical Co. The isotopic purity as cited by the manufacturer in atom % was: benzene-d_6, 99.6; cyclohexane-d_{12}, 99.6; hexane-d_{14}, 99; toluene-d_8, 99.6; heptane-d_{16}, 99; *o*-xylene-d_{10}, 99+; *p*-xylene-d_{10}, 99; octane-d_{18}, 98; naphthalene-d_8, 99; decane-d_{22}, 99; biphenyl-d_{10}, 99; anthracene-d_{10}, 98; phenanthrene-d_{10}, 98. A mixture of deuterated compounds, acenaphthene-d_{10}, chrysene-d_{12}, naphthalene-d_8, perylene-d_{12}, and phenanthrene-d_{10}, was also purchased from Restek Corp., catalogue # 31885. Correlation gas chromatography experiments were performed on three different HP 5890 Gas Chromatographs equipped with split/splitless injection ports and flame ionization detectors at a split ratio of approximately 100/1. Retention times were rounded to three significant figures following the decimal point using HP software interfaced to a computer. Labeled and unlabeled compounds were identified by their retention times and by GC−MS studies. The instruments were run isothermally on several different columns that included a 30 m SPB 5 column, a 60 m OV-5 column (runs 1 to 4), and a 15 m RTX-1 capillary column (runs 5 and 6). To obtain temperatures below ambient, the columns were immersed in a refrigerated bath (VWR Scientific Products). A typical chromatogram is shown in Figure 1. 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 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 reference from the retention time of each analyte, t_r, 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 maintained by the gas chromatograph was constant to ± 0.1 K. Plots of $\ln(t_o/t_a)$, vs $1/T$, where t_o = 1 min, were all 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 as Supporting Information. The uncertainties reported in column 4 of Tables 1 and 2 and 8 to 10 are the uncertainties calculated from the uncertainty in the slope. 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. Since differences in vaporization enthalpies between the labeled and unlabeled hydrocarbons are relative measurements, we believe that the uncertainty associated with the reproducibility of these differences is a better measure of the uncertainty in enthalpy associated with the isotope effect. This uncertainty is listed in the sixth column of Table 3 and the next to last column of Table 11 and represents two standard deviations of the mean.

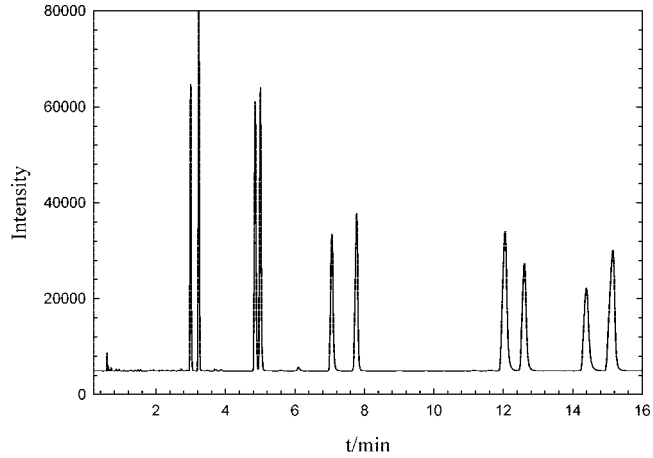

Figure 1. Typical gas chromatogram of a series of labeled/unlabeled hydrocarbons run on an RTX-1 column at T = 300 K. In order of elution, heptane-d_{16}/heptane, toluene-d_8/toluene, octane-d_{18}/octane, *p*-xylene-d_{10}/*p*-xylene, *o*-xylene-d_{10}/*o*-xylene. The small peak with the shortest retention time is methane.

At a few temperatures in runs 5 to 8, the column was not capable of resolving all the labeled and unlabeled peaks, even though the peaks corresponding to the deuterated compounds were observed as shoulders. In these few instances, the line shape, S(t), was fit as a sum of two Gaussian curves, eq 7[17]

$$S(t) = C\{(1-x)/[(2\pi)^{0.5}\sigma] * e - (t-t_d)^2/2[\sigma^2] + x/[(2\pi)^2] * e[-(t-t_h)^2/2\sigma^2]\} \quad (7)$$

where C is an attenuation factor; x is the mole fraction of the unlabeled hydrocarbon; σ is a measure of the line width; and t_d and t_h represent the retention times of the deuterated and undeuterated hydrocarbons as a function of the experimental retention time, t/min. Retention times evaluated from line shape analysis are indicated in bold italics in the Supporting Information.

Benzene-h$_6$/d$_6$ and Cyclohexane-h$_{12}$/d$_{12}$. Tables 1 and 2, A and B, summarize duplicate results of plotting $\ln(t_o/t_a)$ versus $1/T$ for both benzene and cyclohexane and using hexane, heptane, and toluene as additional standards. Retention times measured for these experiments are provided in the Supporting Information. The correlation observed for cyclohexane, eq 8 and 9, according to the correlation coefficient appears more linear than for benzene, eq 10 and 11. This in part is due to the larger spread in values of $\Delta_{sln}{}^{g}H_m(T)$. The vaporization enthalpies obtained from the first four runs are summarized in Table 3. The literature vaporization enthalpies reported in column 7 are recommended values.[18,19] The vaporization enthalpy of benzene is the value recommended by Majer and Svoboda.[19] The uncertainty reported in column 6 represents two standard deviations of the mean. The reproducibility in the vaporization enthalpies of the standards, however, is very good. Although the vaporization enthalpies calculated by the correlation differ from the recommended values by a few tenths of a kilojoule, the reproducibility of the results in runs

Table 1. Enthalpies of Transfer of Hexane, Cyclohexane, Heptane, Toluene, and their Perdeuterated Analogues

A. run 1[a]	slope / K	intercept	$\Delta_{sln}{}^{g}H_m$(293 K) / kJ·mol^{-1}	$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} (lit.)	(calcd)
hexane-d_{14}	−3439.9	10.286	28.60 ± 0.73		31.46 ± 1.5
hexane	−3472.3	10.308	28.87 ± 0.73	31.52[c]	31.73 ± 1.6
cyclohexane-d_{12}	−3576.4	10.111	29.73 ± 0.76		32.62 ± 1.6
cyclohexane	−3601.7	10.127	29.94 ± 0.77	33.12[d]	32.83 ± 1.6
heptane-d_{16}	−4018.6	11.215	33.41 ± 0.78		36.35 ± 1.8
heptane	−4058.5	11.252	33.74 ± 0.80	36.57[c]	36.69 ± 1.8
toluene-d_8	−4209.2	11.184	34.99 ± 0.84		37.97 ± 1.9
toluene	−4215.1	11.169	35.04 ± 0.86	38.06[d]	38.02 ± 1.9

B. run 2[b]	slope / K	intercept	$\Delta_{sln}{}^{g}H_m$(293 K) / kJ·mol^{-1}	$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} (lit.)	(calcd)
hexane-d_{14}	−3277.6	9.776	27.25 ± 0.17		31.43 ± 1.6
hexane	−3312.3	9.805	27.54 ± 0.17	31.52[c]	31.74 ± 1.6
cyclohexane-d_{12}	−3401.3	9.557	28.28 ± 0.18		32.54 ± 1.6
cyclohexane	−3432.5	9.592	28.54 ± 0.18	33.12[d]	32.82 ± 1.7
heptane-d_{16}	−3827.2	10.605	31.82 ± 0.20		36.37 ± 1,8
heptane	−3862.6	10.627	32.11 ± 0.22	36.57[c]	36.69 ± 1.9
toluene-d_8	−3999.1	10.51	33.25 ± 0.21		37.92 ± 1.9
toluene	−4010.6	10.512	33.34 ± 0.23	38.06[d]	38.02 ± 1.9

[a] $$\Delta_l{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.017 \pm 0.053)\Delta_{sln}{}^{g}H_m(293\ \mathrm{K}) + (2.38 \pm 0.27)\ (r^2 = 0.9946) \quad (8)$$

[b] $$\Delta_l{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.081 \pm 0.057)\Delta_{sln}{}^{g}H_m(293\ \mathrm{K}) + (1.97 \pm 0.28)\ (r^2 = 0.9944) \quad (9)$$

[c] Ref 18. [d] Ref 19.

Table 2. Enthalpies of Transfer and Vaporization of Hexane, Benzene, Heptane, and Their Perdeuterated Analogues

A. run 3[a]	slope / K	intercept	$\Delta_{sln}{}^{g}H_m$(274 K) / kJ·mol^{-1}	$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} (lit.)	(calcd)
hexane-d_{14}	−3307.3	9.9266	27.50 ± 0.21		31.73 ± 7.0
hexane	−3340.7	9.9517	27.77 ± 0.21	31.52[c]	32.01 ± 7.0
benzene-d_6	−3484.4	9.8571	28.97 ± 0.22		33.25 ± 7.4
benzene	−3484.5	9.8363	28.97 ± 0.22	33.92[d]	33.25 ± 7.4
heptane-d_{18}	−3855.0	10.748	32.05 ± 0.24		36.43 ± 8.2
heptane	−3891.3	10.773	32.35 ± 0.24	36.57[c]	36.74 ± 8.2

B. run 4[b]	slope / K	intercept	$\Delta_{sln}{}^{g}H_m$(281 K) / kJ·mol^{-1}	$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} (lit.)	(calcd)
hexane-d_{14}	−3270.8	9.7785	27.19 ± 0.20		31.74 ± 7.0
hexane	−3302.8	9.7985	27.46 ± 0.20	31.52[c]	32.02 ± 7.0
benzene-d_6	−3446	9.7015	28.65 ± 0.20		33.25 ± 7.3
benzene	−3446.4	9.682	28.65 ± 0.20	33.92[d]	33.25 ± 7.3
heptane-d_{18}	−3820.3	10.605	31.76 ± 0.20		36.46 ± 8.1
heptane	−3854	10.62	32.04 ± 0.20	36.57[c]	36.74 ± 8.2

[a] $$\Delta_l{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.0333 \pm 0.253)\Delta_{sln}{}^{g}H_m(274\ \mathrm{K}) + (3.316 \pm 0.88)\ (r^2 = 0.943) \quad (10)$$

[b] $$\Delta_l{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.032 \pm 0.254)\Delta_{sln}{}^{g}H_m(281\ \mathrm{K}) + (3.684 \pm 0.853)\ (r^2 = 0.9429) \quad (11)$$

[c] Ref 18. [d] Recommended value;[19] the average vaporization enthalpy calculated from the vapor pressure data in the isotope studies[7–10] is (34.24 ± 0.25) kJ·mol^{-1}.

1 and 2 and runs 3 and 4 is considerably better. If the vaporization enthalpies at T = 298.15 K for benzene and toluene are calculated using the vapor pressures reported in the vapor pressure isotope studies from T = 283.15 K to T = 313.15 K (from plots of ln p vs $1/T$), mean vaporization enthalpies for labeled and unlabeled cyclohexane[7–9] and labeled and unlabeled benzene[7–10] of {(33.05 ± 0.4), (33.32 ± 0.065), (34.28 ± 0.24), and (34.24 ± 0.25)} kJ·mol^{-1} are calculated. The uncertainties represent two standard deviations of the mean. A difference in vaporization enthalpy between labeled and unlabeled cyclohexane of (0.274 ± 0.039) kJ·mol^{-1} can be calculated from the literature studies;[7–9] a difference of (0.038 ± 0.018) kJ·mol^{-1} is calculated for benzene.[7–10] These differences are values averaged from the differences observed in each individual study. These values can be compared to results obtained from correlation−gas chromatography. Differences of [(0.245 ± 0.05) and 0.0] kJ·mol^{-1} are obtained for cyclohexane and benzene, respectively (Table 3). These results suggest that although the enthalpy differences observed between the deuterated and protio analogues are small, the relative results obtained by correlation gas chromatography seem reproducible and qualitatively correct within experimental error.

To determine how well the slopes and intercepts obtained from gas chromatographic retention times can reproduce experimental vapor pressures, the values reported in Tables

Table 3. Summary of Vaporization Enthalpies of Runs 1 to 4

	run 1	run 2	run 3	run 4	$\Delta_l^g H_m$(298 K) / kJ·mol^{-1} average	$\Delta_l^g H_m$(298 K) / kJ·mol^{-1}	
	<293>	<293>	<274>	<281>	runs 1 to 4	(lit.)	ref
hexane-d_{14}	31.46	31.43	31.73	31.74	31.59 ± 0.17		
hexane	31.73	31.74	32.01	32.02	31.88 ± 0.16	31.52	18
cyclohexane-d_{12}	32.62	32.54			32.58 ± 0.08		
cyclohexane	32.83	32.82			32.83 ± 0.01	33.12	19
benzene-d_6			33.25	33.25	33.25		
benzene			33.25	33.25	33.25	33.92	19
heptane-d_{16}	36.35	36.37	36.43	36.46	36.40 ± 0.05		
heptane	36.69	36.69	36.74	36.74	36.72 ± 0.03	36.56	18
toluene-d_8	37.97	37.92			37.95 ± 0.05		
toluene	38.02	38.02			38.02	38.06	19

Table 4. Parameters of the Third-Order Polynomial, Equation 12

	A / T^3	B / T^2	C / T	D	T/K range	ref
cyclohexane	−13846729	−100748.09	−2861.97	9.202	287 to 353	9
cyclohexane	174941198	−1874406.7	2666.94	3.482	283 to 383	8
cyclohexane	−15555292	−86835.6	−2902.23	9.245	283 to 353	7
cyclohexane	48464404	−686869.14	−1033.87	7.311	280 to 360	lit. avg.[a]
cyclohexane-d_{12}	192490340	−2030272.6	3161.2	3.001	283 to 383	8
cyclohexane-d_{12}	−71200496	444269.89	−4548.93	10.981	287 to 353	9
cyclohexane-d_{12}	−49408652	230407.71	−3861.34	10.256	283 to 360	7[b]
cyclohexane-d_{12}	23911171	−451401	−1751.13	8.080	280 to 360	lit. avg.[a]
cyclohexane-d_{12}	49053636	−691209	−994.044	7.279	280 to 360	this work[c]
benzene	602122486	−6070230	16234.5	−10.978	280 to 353	8
benzene	−15049221	−101875.5	−2913.7	9.409	278 to 353	9
benzene	9069522.7	−325121	−2223.33	8.694	280 to 360	10[d]
benzene	−15530876	−101704.1	−2895.14	9.363	283 to 360	7[b]
benzene	144290103	−1641390.8	2023.83	4.151	280 to 360	lit. avg.[e]
benzene-d_6	613896321	−6189194.0	16637.21	−11.407	280 to 353	8
benzene-d_6	−12007241	−133201.5	−2802.64	9.301	280 to 256	9
benzene-d_6	−17010792	−99252.2	−2866.43	9.320	283 to 353	7[b]
benzene-d_6	6691080.7	−312615.45	−2234.2	8.703	280 to 360	10[d]
benzene-d_6	147141891	−1676318.9	2160.26	4.004	280 to 360	lit. avg.[a]
benzene-d_6	144325337	−1641878.1	2026.48	4.170	280 to 360	this work[f]
toluene-d_8	9461361.5	−366210.4	−2450.1	8.735	280 to 360	this work[c]
hexane-d_{14}	−17917619	−45199.7	−2909.62	9.429	280 to 360	this work[f]
heptane-d_{16}	−5444070	−218518.5	−2758.6	9.220	280 to 360	this work[g]
anthracene	747019108.9	−4582798	2099.196	5.491	496 to 778	36, 37

[a] Average vapor pressures calculated from refs 7 to 9 and fit to eq 12. [b] Calculated from the Antoine constants reported in the paper; [c] Calculated by averaging vapor pressures from runs 1 and 2. [d] Calculated from eq 14 and fit to eq 12. [e] Average vapor pressures calculated from refs 7 to 10 and fit to eq 12. [f] Calculated by averaging vapor pressures from runs 3 and 4. [g] Calculated by averaging vapor pressures from runs 1 to 4.

Table 5A. Parameters of the Cox Equation

	A_o	$A_1 \cdot 10^3$ / T^{-1}	$A_2 \cdot 10^6$ / T^{-2}	T_b / K
hexane[18]	2.79797	−2.0221	2.2876	341.863
heptane[18]	2.8647	−2.1132	2.251	371.552
octane[18]	2.9015	−0.00205	2.01076	398.793
decane[18]	2.9669	−0.00193	1.64463	447.269
biphenyl[31]	2.93082	−0.001447	1.0038	528.422
phenanthrene[39]	3.423726	−1.030247	0.677377	372.36[a]
acenaphthene[39]	3.246001	−0.873359	0.53659254	366.535[a]

[a] This value represents an arbitrary chosen reference temperature corresponding to the vapor pressure, p_o, in eq 13 of 28.70 Pa for phenanthrene and 198.0 Pa for acenaphthene;[39] otherwise, p_o = 101.325 kPa.

1 and 2 were used to evaluate the vapor pressures of the deuterated compounds using the vapor pressures reported for their protio counterparts. Experimental vapor pressures reported previously for cyclohexane, cyclohexane-d_{12}, benzene, and benzene-d_6 [7−10] by different workers were compared and found to be in good agreement with each other. The temperature−vapor pressure dependence of these materials is reported in different formats in the literature. For convenience, reported vapor pressures or those calculated from various equations used by the authors were fit to the third-order polynomial, eq 12

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

where p_o = 101.325 kPa. The constants for this equation are reported in Table 4. Vapor pressures from the literature or those calculated using the author's equations were subsequently averaged, and the average value was used in the correlations. The A to D constants of the polynomial (eq 12) generated from averaged p/p_o values for cyclohexane, cyclohexane-d_{12}, benzene, and benzene-d_6 are also reported in Table 4, noted as lit. avg. in the last column of the table. This equation was used for all comparisons. Vapor pressures for the n-alkanes were obtained from the Cox Equation, eq 13, using the parameters recommended by Ruzicka and Majer.[18] These values are reported in

Table 5A. Literature values for benzene and benzene-d_6 were also calculated by the ABT equation, eq 14.[10]

$$\ln(p/p_o) = \{1 - (T_b/\mathrm{K})/(T/\mathrm{K})\} \exp(A_o + A_1(T/\mathrm{K}) + A_2(T/\mathrm{K})^2) \quad (13)$$

$$\ln(p/\mathrm{Pa}) = A(1)/\{(T/\mathrm{K}) + A(2)\} + A(3) + A(4)(T/\mathrm{K}) + a(5)(T/\mathrm{K})^2 \quad (14)$$

The vapor pressures of toluene were calculated from the Wagner equation, eq 15a reported by Chirico et al.[20]

$$\ln(p/p_c) = (1/T_r)[A_W(1 - T_r) + B_W(1 - T_r)^{1.5} + C_W((1 - T_r)^a + D_W(1 - T_r)^b] \quad (15)$$

$$a = 2.5, b = 5 \quad (15a)$$

$$a = 2, b = 4 \quad (15b)$$

where $T_r = T/T_c$. The parameters of the Wagner equation for toluene are reported in Table 5C.

The vapor pressures of deuterated cyclohexane and benzene were calculated from their respective retention times according to the following protocol as summarized in Table 6 for cyclohexane (run 1) at $T = 298.15$ K. Values of $\ln(t_o/t_a)$ were calculated from the slope and intercept for all the compounds in the run and correlated with literature $\ln(p/p_o)_H$ values for the protio compounds. From the correlation equation, eq 16 provided at the bottom of Table 6, values of $\ln(p/p_o)$ were calculated for the compounds in the run, column 6. Since the p/p_o values calculated for the protio compounds from correlation eq 16, column 8, differed slightly from the literature values, column 7, these values were normalized by multiplying each pressure in column 8 by the factor necessary to convert this value to the experimental literature value for the protio compound. For example, the factor necessary to adjust the calculated p/p_o value of cyclohexane from 10.96 to 12.96 is 1.182 (i.e., 12.96/10.96). This factor was also used to adjust the observed vapor pressure of cyclohexane-d_{12}. Similar factors were computed to adjust

Table 5B. Parameters of the Ambrose, Broderick, and Townsend Equation (ABT)[10]

	$A(1)$ / K	$A(2)$ / K	$A(3)$	$A(4)$ / K^{-1}	$A(5)\cdot 10^5$ / K^{-2}	range / K
benzene	−4417.727	−15.883	28.97528	−0.016661	1.2274	324 to 560
benzene-d_6	−4324.653	−18.717	28.78636	−0.01655	1.23289	324 to 560

Table 5C. Parameters of the Wagner Equation [a]

	A_W	B_W	C_W	D_W	T_c / K	p_c / kPa
toluene[20]	−7.40224	1.82331	−2.18976	−3.3765	592.5	4162
o-xylene[21]	−7.457432	1.519744	−1.030912	−3.997287	630.3	3730
p-xylene[22]	−7.59306	1.77964	−1.24526	−3.93248	616.2	3510
naphthalene[24]	−7.79639	2.25115	−2.7033	−3.2266	748.4	4105

[a] Equation 15a was used to calculate vapor pressures of toluene and naphthalene; equation 15b was used for *o*- and *p*-xylene.

Table 6. Vapor Pressure Calculations for Run 1[a]

$T = 298.15$ K	slope / K	intercept	$\ln(t_o/t_a)$	$\ln(p/p_o)$ (lit.)	$\ln(p/p_o)$ (calcd)	p/p_o (lit.)	p/p_o (calcd)	p/p_o (adj.)
hexane-d_{14}	−3439.9	10.286	−1.25		−1.47		23.27	22.15
hexane	−3472.3	10.308	−1.34	−1.61	−1.56	20.18[b]	21.21	20.18
cyclohexane-d_{12}	−3576.4	10.111	−1.88		−2.15		11.8	13.98
cyclohexane	−3601.7	10.127	−1.95	−2.05	−2.22	12.98	10.96	12.98
heptane-d_{16}	−4018.6	11.215	−2.26		−2.56		7.86	6.77
heptane	−4058.5	11.252	−2.36	−2.81	−2.66	6.10[b]	7.08	6.10
toluene-d_8	−4209.2	11.184	−2.93		−3.28		3.83	3.95
toluene	−4215.1	11.169	−2.97	−3.28	−3.31	3.80[c]	3.69	3.80

[a] $\ln(p/p_o) = (1.073 \pm 0.14)\ln(t_o/t_a) - (0.128 \pm 0.165)$; $T = 298.15$ K, $r^2 = 0.9678$ (16)

[b] Ref 18. [c] Ref 20.

Table 7. Comparison of Vapor Pressures of Cyclohexane/Cyclohexane-d_{12} and Benzene/Benzene-d_6 Measured Directly and by Correlation Gas Chromatography

	cyclohexane				benzene			
T	p/p_o -$d_{12(\mathrm{lit.})}$	p/p_o -$d_{12(\mathrm{this\ work})}$	p/p_o -$h_{12(\mathrm{lit.})}$	100 δ^a	p/p_o -$d_{6(\mathrm{lit.})}$	p/p_o -$d_{6(\mathrm{this\ work})}$	p/p_o -$h_{6(\mathrm{lit.})}$	100 δ^a
280	0.0583	0.0577	0.0532	12.0	0.0518	0.0518	0.0506	0
290	0.0959	0.0947	0.0877	15.0	0.0866	0.0865	0.1247	−0.3
298.15	0.1396	0.138	0.1281	14.0	0.1279	0.1277	0.0845	0.5
310	0.2316	0.229	0.2134	14.0	0.2162	0.2158	0.2107	7.3
320	0.3429	0.3393	0.3172	14.0	0.3246	0.3241	0.3165	6.2
330	0.4938	0.4888	0.4582	14.0	0.4731	0.4724	0.4614	6
340	0.6932	0.6864	0.6451	14.0	0.6706	0.6698	0.6542	4.9
350	0.9513	0.9418	0.8874	15.0	0.9266	0.9259	0.9045	3.2
360	1.2789	1.2654	1.195	16.0	1.251	1.2507	1.2218	1.0

[a] $\delta = [(p/p_o)_{(\mathrm{d,lit.})} - (p/p_o)_{(\mathrm{d,this\ work})}]/[(p/p_o)_d - (p/p_o)_{(h)}]_{\mathrm{lit.}}$; $p_o = 101.325$ kPa.

Table 8. Summary of Enthalpies of Transfer and Vaporization of Runs 5 and 6

A. run 5[a]	slope / K	intercept	$\Delta_{sln}{}^{g}H_m$(366 K) / kJ·mol^{-1}	$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} (lit.)	(calcd)
heptane-d_{16}	−3361.3	10.489	27.946 ± 0.26		35.81 ± 0.9
heptane	−3420.8	10.58	28.441 ± 0.23	36.57[c]	36.50 ± 0.9
toluene-d_8	−3448.3	10.226	28.669 ± 0.15		37.76 ± 0.9
toluene	−3558.9	10.503	29.589 ± 0.64	38.06[d]	38.10 ± 0.9
octane-d_{18}	−3847.7	11.137	31.990 ± 0.16		41.44 ± 1.0
octane	−3882.2	11.151	32.277 ± 0.19	41.56[c]	41.84 ± 1.0
p-xylene-d_{10}	−3934.5	10.865	32.711 ± 0.33		42.45 ± 1.0
p-xylene	−3945.5	10.857	32.803 ± 0.32	42.42[d]	42.58 ± 1.0
o-xylene-d_{10}	−3982.4	10.847	33.110 ± 0.32		43.00 ± 1.0
o-xylene	−3987.1	10.811	33.149 ± 0.41	43.45[d]	43.06 ± 1.0
decane-d_{22}	−4738.1	12.230	39.393 ± 0.35		51.76 ± 1.1
decane	−4762.2	12.192	39.593 ± 0.42	51.42[c]	52.04 ± 1.1
naphthlene-d_{10}	−4981.5	11.745	41.416 ± 0.39		54.58 ± 1.2
naphthlene	−4982.8	11.730	41.427 ± 0.38	55.40[e]	54.59 ± 1.2
biphenyl-d_{10}	−5901.8	13.098	49.068 ± 0.36		65.23 ± 1.4
biphenyl	−5888.7	13.038	48.959 ± 0.38	64.90[f]	65.08 ± 1.4
hexamethylbenzene-d_{18}	−6166.2	13.399	51.266 ± 0.33		68.30 ± 1.4
hexamethylbenzene	−6195.8	13.390	51.512 ± 0.37		68.64 ± 1.4

B. run 6[b]	slope / K	intercept	$\Delta_{sln}{}^{g}H_m$(366 K) / kJ·mol^{-1}	$\Delta_l{}^{g}H_m$(298 K)/kJ·mol^{-1} (lit.)	(calcd)
heptane-d_{16}	−3347.2	10.450	27.827 ± 0.39		35.79 ± 0.9
heptane	−3393.7	10.507	28.214 ± 0.36	36.57[c]	36.31 ± 0.9
toluene-d_8	−3473.7	10.296	28.879 ± 0.38		37.39 ± 0.9
toluene	−3563.8	10.519	29.628 ± 0.36	38.06[d]	38.38 ± 0.9
octane-d_{18}	−3831.6	11.095	31.854 ± 0.40		41.26 ± 1.0
octane	−3866.9	11.113	32.148 ± 0.40	41.56[c]	41.66 ± 1.0
p-xylene-d_{10}	−3933.2	10.87	32.699 ± 0.44		42.41 ± 1.0
p-xylene	−3945.2	10.865	32.799 ± 0.44	42.42[d]	42.55 ± 1.0
o-xylene-d_{10}	−3985.3	10.863	33.132 ± 0.43		43.00 ± 1.0
o-xylene	−3992.8	10.839	33.195 ± 0.48	43.45[d]	43.08 ± 1.0
decane-d_{22}	−4761.7	12.304	39.587 ± 0.45		51.77 ± 1.1
decane	−4794.2	12.293	39.857 ± 0.49	51.42[c]	52.14 ± 1.1
naphthlene-d_{10}	−5022.4	11.868	41.754 ± 0.38		54.72 ± 1.2
naphthlene	−5019.5	11.842	41.730 ± 0.39	55.40[e]	54.69 ± 1.2
biphenyl-d_{10}	−5941.4	13.216	49.394 ± 0.30		65.10 ± 1.4
biphenyl	−5930.6	13.164	49.305 ± 0.33	64.90[f]	64.98 ± 1.4
hexamethylbenzene-d_{18}	−6203.1	13.510	51.570 ± 0.28		68.06 ± 1.4
hexamethylbenzene	−6238.5	13.518	51.864 ± 0.28		68.46 ± 1.4

[a] $$\Delta_l{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.393 \pm 0.026)\Delta_{sln}{}^{g}H_m(366\ \mathrm{K}) - (3.132 \pm 0.48)\ (r^2 = 0.9980) \quad (17)$$

[b] $$\Delta_l{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.36 \pm 0.026)\Delta_{sln}{}^{g}H_m(366\ \mathrm{K}) - (2.05 \pm 0.48)\ (r^2 = 0.9979) \quad (18)$$

[c] Ref 18. [d] Ref 19. [e] Ref 23. [f] Ref 31.

the vapor pressures of the other deuterated compounds present in this run, column 9 (hexane-d_{14}, 0.951; heptane-d_{16}, 0.862; toluene-d_8, 1.03). The adjusted vapor pressures for both runs were then averaged, and this process was repeated every 10 K from $T = 280$ to $T = 360$ K. For hexane-d_{14} and heptane-d_{16}, since these compounds were used in all four runs, the adjusted vapor pressures of all four runs were averaged. The values of $\ln(p/p_o)$ for all compounds were then fit to eq 12. These parameters are also reported in Table 4 as "this work". A similar procedure was followed for benzene as well. A qualitative view of the quality of the fit is illustrated in Figure 2 for cyclohexane and Figure 3 for benzene. A more quantitative evaluation of the vapor pressures obtained by correlation for both cyclohexane and benzene as a function of temperature is given in Table 7. Columns 2 and 3 and 6 and 7 of Table 7 compare the literature vapor pressure to values calculated from retention time data for both cyclohexane and benzene, respectively. The literature values cited are also average values calculated using eq 12 as noted above. In cyclohexane, the isotope effect, column 4, appears slightly attenuated by this protocol. The comparisons for benzene, column 8, are better. If the comparisons are averaged over the temperature range considered, an error of approximately 10 % is suggested. It appears that the approximations noted above are reasonably accurate in providing both vapor pressures and vaporization enthalpies of the corresponding deuterated hydrocarbons. The vapor pressures of a series of other deuterated hydrocarbon were subsequently measured.

Vaporization Enthalpies of Some Labeled Aromatic Hydrocarbons. The vaporization enthalpies of toluene-d_8, octane-d_{18}, *o*- and *p*-xylene-d_{10}, decane-d_{22}, naphthalene-d_8, biphenyl-d_{10}, hexamethylbenzene, and hexamethylbenzene-d_{18} were evaluated next in duplicate runs. Since toluene-d_8 and heptane-d_{16} were also evaluated in runs 1 to 4, using different standards, these compounds were also evaluated independently in these runs as well to test for consistency. Retention times measured for these materials are also reported in the Supporting Information. The slopes, intercepts and vaporization enthalpies for each run are summarized in Table 8. Vaporization enthalpies for both the labeled and unlabeled hydrocarbons were calculated using the vaporization enthalpies of the unlabeled compounds as standards. This resulted in correlation eq 17 and eq 18, found for runs 5 and 6 in Table 8.

Similarly, vaporization enthalpies of labeled phenanthrene, anthracene, acenaphthene, *p*-terphenyl, chrysene and perylene

Table 9. Enthalpies of Transfer and Vaporization of Runs 7 and 8

A. run 7[a]	slope / K	intercept	$\Delta_{sln}{}^{g}H_m$(432 K) / kJ·mol^{-1}	$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} (lit.)	(calcd)
naphthalene	−4715.8	11.074	39.21 ± 0.28	55.40[c]	55.36 ± 0.3
biphenyl-d_{10}	−5510.3	12.118	45.81 ± 0.21		64.77 ± 0.03
biphenyl	−5528.6	12.143	45.96 ± 0.24	64.90[d]	64.99 ± 0.3
hexamethylbenzene-d_{18}	−5819	12.528	48.38 ± 0.23		68.43 ± 0.3
hexamethylbenzene	−5856.2	12.548	48.69 ± 0.22		68.87 ± 0.3
phenanthrene-d_{10}	−6642.8	13.096	55.23 ± 0.22		78.20 ± 0.4
phenanthrene	−6646.5	13.087	55.26 ± 0.21	78.30[e]	78.24 ± 0.4
anthracene-d_{10}	−6670.9	13.116	55.46 ± 0.22		78.53 ± 0.4
anthracene	−6679.3	13.121	55.53 ± 0.21	78.60[f]	78.63 ± 0.4

B. run 8[b]	slope / K	intercept	$\Delta_{sln}{}^{g}H_m$(424 K) / kJ·mol^{-1}	$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} (lit.)	(calcd)
naphthalene	−4706.3	11.054	39.13 ± 0.16	55.40[c]	55.09 ± 0.2
biphenyl-d_{10}	−5504.8	12.108	45.77 ± 0.15		64.46 ± 0.3
biphenyl	−5528.5	12.145	45.96 ± 0.15	64.90[d]	64.73 ± 0.3
hexamethylbenzene-d_{18}	−5816.5	12.525	48.36 ± 0.15		68.11 ± 0.3
hexamethylbenzene	−5860.2	12.56	48.72 ± 0.15		68.63 ± 0.3
phenanthrene-d_{10}	−6653.2	13.122	55.32 ± 0.18		77.93 ± 0.3
phenanthrene	−6659.1	13.118	55.36 ± 0.17	78.30[e]	78.00 ± 0.3
anthracene-d_{10}	−6681.8	13.143	55.55 ± 0.17		78.27 ± 0.3
anthracene	−6688.6	13.145	55.61 ± 0.16	78.60[f]	78.35 ± 0.3

[a] $$\Delta_l{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.426 \pm 0.006)\Delta_{sln}{}^{g}H_m(432\ \mathrm{K}) - (0.55 \pm 0.084)\ (r^2 = 0.9999) \quad (19)$$

[b] $$\Delta_l{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.411 \pm 0.006)\Delta_{sln}{}^{g}H_m(424\ \mathrm{K}) - (0.13 \pm 0.08)\ (r^2 = 0.9999) \quad (20)$$

[c] Ref 23. [d] Ref 31. [e] Ref 32. [f] Ref 40.

Table 10. Enthalpies of Transfer and Vaporization of Runs 9 and 10

A. run 9[a]	slope / K	intercept	$\Delta_{sln}{}^{g}H_m$(470 K) / kJ·mol^{-1}	$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} (lit.)	(calcd)
naphthalene	−4278.7	10.143	35.57 ± 0.88	55.40[c]	53.45 ± 3.1
acenaphthene-d_{10}	−5288.3	11.189	43.97 ± 0.49		67.18 ± 3.5
acenaphthene	−5369.8	11.334	44.64 ± 0.37	66.20[d]	68.28 ± 3.5
phenanthrene-d_{10}	−6178.1	12.068	51.36 ± 0.52		79.27 ± 3.8
phenanthrene	−6217.9	12.139	51.69 ± 0.25	78.30[e]	79.82 ± 3.9
p-terphenyl-d_{10}	−7812.9	14.272	64.95 ± 0.27		101.5 ± 4.6
p-terphenyl	−7823.8	14.278	65.04 ± 0.27	102.00[f]	101.65 ± 4.6
chrysene-d_{12}	−8136.1	14.162	67.64 ± 0.27		105.9 ± 4.7
chrysene	−8147.2	14.167	67.73 ± 0.25	108.40[g]	106.05 ± 4.7
perylene-d_{12}	−9117.2	15.103	75.80 ± 0.35		119.24 ± 5.2
perylene	−9140.1	15.135	75.99 ± 0.28	118.50[h]	119.55 ± 5.2

B. run 10[b]	slope / K	intercept	$\Delta_{sln}{}^{g}H_m$(471 K) / kJ·mol^{-1}	$\Delta_l{}^{g}H_m$(298.15 K)/kJ·mol^{-1} (lit.)	(calcd)
naphthalene	−4253.2	10.058	35.36 ± 0.91	55.40[c]	54.07 ± 2.6
acenaphthene-d_{10}	−5185.4	10.929	43.11 ± 0.82		67.23 ± 2.9
acenaphthene	−5217.5	10.978	43.38 ± 0.85	66.20[d]	67.68 ± 2.9
phenanthrene-d_{10}	−6024.5	11.692	50.09 ± 1.01		79.07 ± 3.2
phenanthrene	−6069.7	11.775	50.46 ± 0.90	78.30[e]	79.71 ± 3.2
p-terphenyl-d_{10}	−7623	13.812	63.38 ± 1.13		101.63 ± 3.8
p-terphenyl	−7630.6	13.811	63.44 ± 1.11	102.00[f]	101.74 ± 3.8
chrysene-d_{12}	−7945.3	13.698	66.05 ± 1.15		106.18 ± 3.9
chrysene	−7954.1	13.698	66.13 ± 1.15	108.40[g]	106.3 ± 3.9
perylene-d_{12}	−8908.9	14.597	74.07 ± 1.30		119.78 ± 4.3
perylene	−8888.5	14.538	73.90 ± 1.23	118.50[h]	119.49 ± 4.3

[a] $$\Delta_l{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.636 \pm 0.060)\Delta_{sln}{}^{g}H_m(470\ \mathrm{K}) - (4.433 \pm 2.07)\ (r^2 = 0.9946) \quad (21)$$

[b] $$\Delta_l{}^{g}H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.698 \pm 0.053)\Delta_{sln}{}^{g}H_m(471\ \mathrm{K}) - (5.954 \pm 1.75)\ (r^2 = 0.9961) \quad (22)$$

[c] Ref 23. [d] Ref 42. [e] Ref 32. [f] Ref 45. [g] Ref 47. [h] Ref 53.

were evaluated in two series of duplicate runs. The results for these materials are reported in Tables 9 and 10. The vaporization enthalpy of perylene has been reported previously using the technique of correlation−gas chromatography.[53] Since that time, the vaporization enthalpies of the *n*-alkanes used as standards have been re-evaluated, and the value of perylene has been adjusted to reflect the new values of these standards.[15,16] A new value of 118.7 kJ·mol^{-1} has been calculated. The Supporting Information also reports two additional gas chromatographic experiments used in evaluating the value of perylene. The mean vaporization enthalpy for perylene derived from all the measurements is (118.5 ± 0.5) kJ·mol^{-1}. The results of runs 5 to 10

Table 11. Summary of Vaporization Enthalpies of Run 5 to Run 10

	$\Delta_l^g H_m$(298 K) / kJ·mol^{-1}						$\Delta_l^g H_m$(298 K) / kJ·mol^{-1}		$\Delta_h^d \Delta_l^g H_m$[a] / kJ·mol^{-1}	
	run 5	run 6	run 7	run 8	run 9	run 10	average	(lit.)		ref
heptane-d_{16}	35.81	35.79					35.80			
heptane	36.50	36.31					36.41	36.57	0.61 ± 0.24	18
toluene-d_8	37.76	37.39					37.58			
toluene	38.10	38.38					38.24	38.06	0.67 ± 0.91	19
octane-d_{18}	41.44	41.26					41.35			
octane	41.84	41.66					41.75	41.56	0.40	18
p-xylene-d_{10}	42.45	42.41					42.43			
p-xylene	42.58	42.55					42.57	42.36	0.13 ± 0.01	19
o-xylene-d_{10}	43.00	43.00					43.0			
o-xylene	43.06	43.08					43.07	43.48	0.07 ± 0.02	19
decane-d_{22}	51.76	51.77					51.77			
decane	52.04	52.14					52.09	51.42	0.32 ± 0.13	18
naphthalene-d_8	54.58	54.72					54.65			
naphthalene	54.59	54.69	55.36	55.09	53.45	54.07	54.64[b]	55.40	−0.01 ± 0.06	23
biphenyl-d_{10}	65.23	65.10	64.77	64.46			64.89			
biphenyl	65.08	64.98	64.99	64.73			64.95	64.90	0.06 ± 0.22	31
hexamethylbenzene-d_{18}	68.30	68.06	68.43	68.11			68.23			
hexamethylbenzene	68.64	68.46	68.87	68.63			68. 56		0.42 ± 0.08	
phenanthrene-d_{10}			78.20	77.93	79.27	79.07	78.62			
phenanthrene			78.24	78.00	79.82	79.71	78.65	78.70	0.32 ± 0.04	32
anthracene-d_{10}			78.53	78.27			78.4			
anthracene			78.63	78.35			78.49	79.00	0.09 ± 0.3	40
acenaphthene-d_{10}					67.18	67.23	67.21			
acenaphthene					68.28	67.68	67.98	66.2	0.77 ± 0.92	42
p-terphenyl-d_{10}					101.5	101.63	101.57			
p-terphenyl					101.65	101.74	101.7	102.0	0.13 ± 0.06	45
chrysene-d_{12}					105.9	106.18	106.04			
chrysene					106.05	106.3	106.18	108.4	0.13 ± 0.04	47
perylene-d_{12}					119.24	119.78	119.51			
perylene					119.55	119.49	119.52	118.5	0.01 ± 0.85	53

[a] Average $\Delta_l^g H_m(298\ K)_h - \Delta_l^g H_m(298\ K)_d$ observed for each run; the uncertainty represents two standard deviations associated with the scatter observed for the mean. [b] Average of runs 5 and 6.

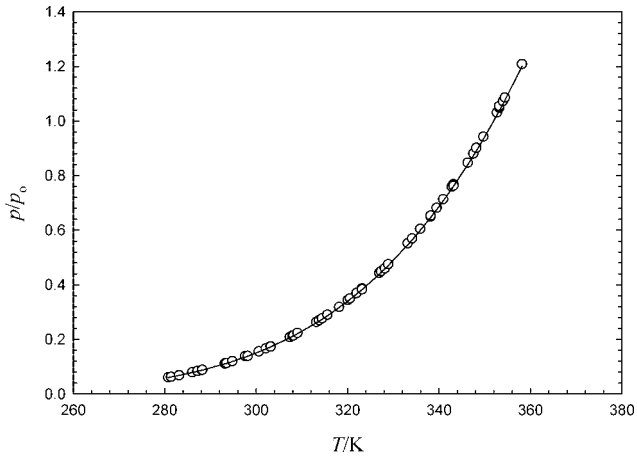

Figure 2. Experimental vapor pressures of cyclohexane-d_{12}: ○, literature values; line, this study; p_o = 101.325 kPa.

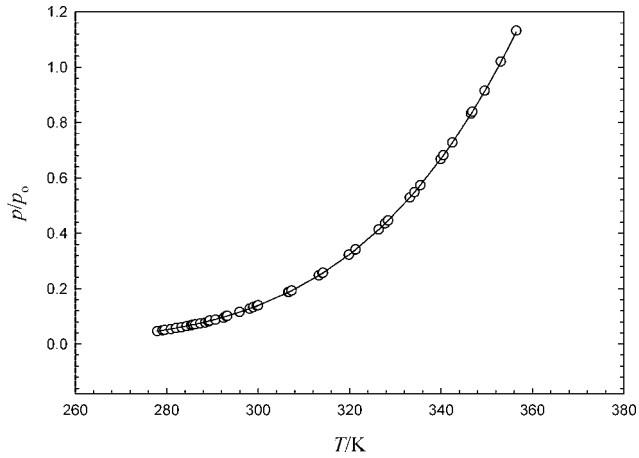

Figure 3. Experimental vapor pressures of benzene-d_6: ○, literature values; line, this study; p_o = 101.325 kPa.

are summarized in Table 11. This table illustrates the reproducibility of the vaporization enthalpy results obtained from duplicate runs as well as results obtained by using different standards. The values of the standards used and their origin are also included in the table. Small enthalpy differences between the unlabeled and labeled hydrocarbons are observed for most compounds investigated. The magnitude of the difference observed appears to be dependent on the amount of isotopic substitution, but the location of the substitution may also play a role. Since many of the hydrocarbons examined in runs 5 to 10 are solids at T = 298.15 K, the vaporization enthalpies and vapor pressure equations reported below for these material are for the hypothetical subcooled liquid.

Vapor Pressure Isotope Effects of Some Aromatic Hydrocarbons. While the vaporization enthalpy differences measured for the unlabeled and labeled hydrocarbons are relatively small (column 10 in Table 11), their vapor pressures are sufficiently different to affect baseline separation under most of the temperatures investigated. Therefore, in addition to measuring the enthalpy differences between the two forms, we have also examined their vapor pressures. Experimental vapor pressures are available for all the unlabeled hydrocarbons in Table 8 except for hexamethylbenzene. These were used as standards. The vapor pressures used as standards for the compounds in Table 9 were naphthalene, biphenyl, and phenanthrene. The equations used to calculate the vapor pressures of

Table 12. Calculation of the Vapor Pressures of a Series of Aromatic Hydrocarbons by Correlation[a]

$T = 298.15$ K	$\ln(t_o/t_a)$ run 8	$\ln(t_o/t_a)$ run 7	$(t_o/t_a)\cdot 10^5$ (avg)	$\ln(t_o/t_a)$ (avg)	$\ln(p/p_o)$ (exptl)	$\ln(p/p_o)$ (calcd)	$\ln(p/p_o)$ (exptl)	$\ln(p/p_o)$ adjusted
naphthalene	−4.731	−4.743	876.56	−4.737	−7.978	−7.985	−7.978	−7.978
diphenyl-d_{10}	−6.355	−6.364	173.04	−6.359		−10.217		−10.227
diphenyl	−6.398	−6.400	166.35	−6.399	−10.281	−10.271	−10.281	−10.281
hexamethylbenzene-d_{18}	−6.984	−6.989	92.444	−6.986		−11.079		−11.079
hexamethylbenzene	−7.095	−7.094	82.966	−7.094		−11.228		−11.228
phenanthrene-d_{10}	−9.193	−9.184	10.221	−9.188		−14.108		−14.104
phenanthrene	−9.217	−9.205	9.9926	−9.211	−14.135	−14.139	−14.135	−14.135
anthracene-d_{10}	−9.268	−9.258	9.4863	−9.263		−14.210		−14.210
anthracene	−9.289	−9.281	9.2799	−9.285		−14.241		−14.241

[a] $$\ln(p/p_o)_{calcd} = 1.3755 \ln(t_o/t_a)_{avg} - 1.469 \quad (r^2 = 0.9999) \qquad (23)$$

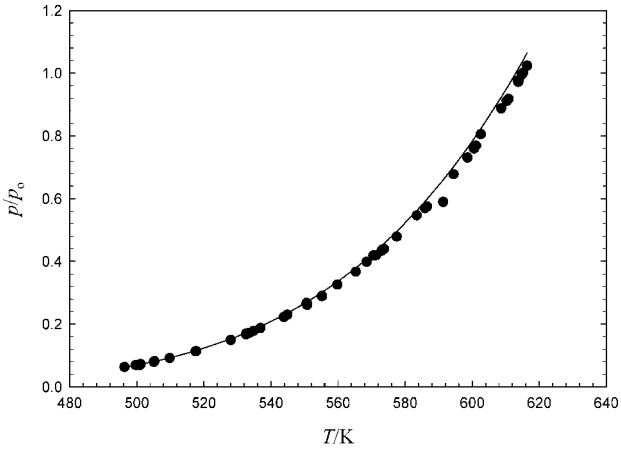

Figure 4. Comparison of experimental vapor pressures of anthracene over the temperature range T = (496 to 616) K to the extrapolated values calculated from the retention time equations of the vapor pressures of the standards of Table 9. The circles are experimental values, and the line represents the values calculated using the parameters of eq 12 reported in Table 13 for anthracene: p_o = 101.325 kPa.

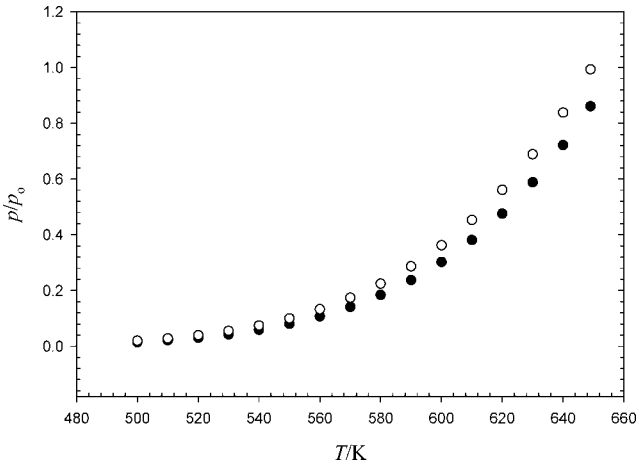

Figure 5. Comparison of vapor pressures calculated from retention time data ○ for p-terphenyl to experimental values calculated from the Antoine equation. ●, log p/kPa = $A - B/(T/\text{K} + C)$ where A = 6.16107, B = 2125.84, and C = −145.29;[46] p_o = 101.325 kPa.

all the unlabeled standards from T = 298.15 K to T = 500 K are reported in Table 5A to C. Vapor pressures have also been reported for liquid anthracene.[36,37] The temperature range for which vapor pressures are available for liquid anthracene is quite high (T = 496 K to T = 778 K), due to the compound's high melting point. Since the use of this data at T = 298.15 K would require a significant extrapolation, these vapor pressures were not used as standards but rather as a test case to examine how well vapor pressures calculated for anthracene by correlation, when extrapolated, were able to reproduce the experimental values at these elevated temperatures. The literature vapor pressure values for anthracene were combined[36,37] and fit to a third-order polynomial. The resulting constants for this polynomial, eq 12, are reported at the bottom of Table 4. The standards used for the vapor pressure calculations of the compounds in Table 10 were naphthalene, acenaphthene, phenanthrene, and perylene. Vapor pressures for liquid perylene by correlation gas chromatography were not previously reported.[54] Vapor pressures were evaluated in an independent series of correlations using a variety of n-alkanes as vapor pressure standards over the temperature range T = 298.15 K to T = 500 K. The n-alkanes, octacosane, triacontane, dotriacontane, and tritriacontane were used to evaluate both the vapor pressure and vaporization enthalpy of perylene using the protocol outlined above. The retention times and corresponding information used for the evaluation of both vaporization enthalpy and vapor pressure of perylene are provided in the Supporting Information. Constants for the Antoine equation are also available for p-terphenyl from T = 499 K to T = 700 K.[46] Since this temperature range is also quite high, the Antoine constants have been similarly used as a test of the vapor pressure results obtained from the correlations.

The calculations of vapor pressure for these hydrocarbons followed a similar protocol as described above for toluene and benzene. The temperature dependence of retention time for the hydrocarbons measured in runs 5 to 10 was used to calculate $\ln(t_o/t_a)$ values. A typical set of results at T = 298.15 K is illustrated in Table 12 for runs 7 and 8 (Table 9). The corresponding t_o/t_a values calculated for each run were averaged, and the natural logarithm of this average value was plotted against the corresponding experimental $\ln(p/p_o)$ of the standards. In this case, $\ln(p/p_o)$ values for naphthalene, diphenyl, and phenanthrene at T = 298.15 K were used. This resulted in eq 23 which was used in turn to calculate $\ln(p/p_o)$ values for all the compounds in the run at T = 298.15 K. Since the resulting $\ln(p/p_o)$ values calculated for the standards using eq 23 differed slightly from the experimental values, a normalization factor was used to adjust the calculated $\ln(p/p_o)$ value of each standard to the experimental value. This normalization factor was also used to adjust the corresponding isotopically substituted compound as well. Since experimental values for hexamethylbenzene and anthracene were either unavailable or not used, the $\ln(p/p_o)$ values calculated from eq 23 for these compounds were retained and used in subsequent calculations. This process was repeated for each compound over the temperature range T = 298.15 K to T = 500 K at 20 K intervals. The resulting $\ln(p/p_o)$ values were then fit to eq 12, resulting in the parameters

Table 13. Summary of the Parameters of the Third-Order Polynomial, Equation 12, Estimated and Experimental Boiling Temperatures and Vapor Pressure Isotope Effects at $T = 298.15$ K

	A / T^3	B / T^2	C / T	D	T_b/K (calcd)	T_b/K (exptl)[a]	p_h/p_d	runs
cyclohexane-d_{12}	49053636	−691209	−994.044	7.279	352	353.9	0.928[b]	1,2
benzene-d_6	144325337	−1641878	2026.48	4.170	352.5	353.3	0.661[c]	3,4
toluene-d_8	−42775261	88847	−3696.58	9.806	383.1	383.8	0.926	5,6
toluene-d_8	9461361.5	–366210.4	–2450.1	8.735	382.7	383.8	0.962	1,2
hexane-d_{14}	−17917619	−45199	−2909.62	9.429	339.3	341.9	0.909	3,4
heptane-d_{16}	−5444070	−218518	−2758.6	9.220	368	371.4	0.892	1,2
heptane-d_{16}	−185771709	1304565	−6937.93	12.924	369	371.4	0.878	5,6
octane-d_{18}	−180452237	1164391	−6799.10	12.648	396.1	398.8	0.882	5,6
p-xylene-d_{10}	−71657137	282831	−4622.31	10.628	410.1	411.5	0.945	5,6
o-xylene-d_{10}	−89591864	419760	−5088.30	11.06	415.7	417.6	0.937	5,6
decane-d_{22}	−181912624	1023235	−7013.39	12.705	443.2	447.2	0.860	5,6
naphthlene-d_8	3500944	−460358	−3654.57	9.35	489.9	491.1	0.976	5,6
biphenyl-d_{10}	27551616	−780763	−3552.93	9.401	525.4	528.4	0.979	5,6
biphenyl-d_{10}	85104849	−1263131	−2180.46	8.085	527.9	528.4	0.947	7,8
hexamethylbenzene-d_{18}	−104226552	309415	−6846.75	12.463	532.3	537.2	0.872	5,6
hexamethylbenzene-d_{18}	51918116	−953267	−3511.78	9.464	539.1	537.2	0.862	7,8
hexamethylbenzene	85376172	−1283535	−2488.25	8.474	539.6	537.2		5,6
hexamethylbenzene	54039809	−975464	−3489.15	9.409	542.5	537.2		7,8
phenanthrene-d_{10}	85840683	−1308934	−3371.68	8.690	608.8	613	0.970	7,8
phenanthrene-d_{10}	88849200.8	−1329272	−3273.04	8.541	610.3	613	0.910	9,10
anthracene-d_{10}	95208069	−1408116	−3082.40	8.376	612.3	613	0.970	7,8
anthracene	95758558	−1413713	−3073.66	8.359	613	613		7,8
perylene-d_{12}	333536294	−4253372	2519.6	3.012	784.2	na[d]	0.979	9,10
perylene	335699657	−4269274	2557.59	2.961	786.4	na[d]		SI[e]
acenaphthene-d_{10}	83420063	−1151267	−2848.85	8.486	550.0	552.2	0.88	9,10
p-terphenyl-d_{14}	174485880	−2511329	−1309.48	7.356	648.3	649.2	0.96	9,10
p-terphenyl	175908596	−2525730	−1277.36	7.319	649.4	649.2		9,10
chrysene-d_{12}	247447559	−3233954	462.43	5.084	709.3	721.2	0.957	9,10
chrysene	248993159	−3249677	497.8	5.04	710.8	721.2		9,10

[a] Boiling temperature of the unlabeled hydrocarbon.[46] [b] Literature value: 0.918. [c] Literature value: 0.661. [d] Not available. [e] Derived from data given in the Supporting Information using the protocol described in this work.

Table 14. Comparison of Subcooled Vapor Pressures of Some PAHs at $T = 298.15$ K

	p/Pa this work	p/Pa lit.[56]
anthracene	$6.64 \cdot 10^{-2}$	$7.24 \cdot 10^{-2}$
perylene	$4.57 \cdot 10^{-6}$	$4.88 \cdot 10^{-6}$
p-terphenyl	$7.35 \cdot 10^{-4}$	$5.40 \cdot 10^{-4}$
chrysene	$1.39 \cdot 10^{-4}$	$1.70 \cdot 10^{-4}$

reported in Table 13. A similar procedure was used to calculate the vapor pressures of the compounds in Tables 8 and 10. The protocol followed for evaluation of the vapor pressures from $T = 298.15$ K to $T = 500$ K was the same as was followed for the data in Table 9. Vapor pressures for all the unlabeled hydrocarbons except hexamethylbenzene are available and were used as standards for the compounds in Table 8. Vapor pressures for naphthalene, acenapthene, and phenanthrene are available, and vapor pressures for perylene were evaluated in this work as noted above. These compounds were used as standards for the compounds in Table 10. Coefficients for calculation of the vapor pressures of acenaphthene-d_{10}, *p*-terphenyl-d_{14}, perylene-d_{12}, terphenyl, terphenyl-d_{14}, chrysene-d_{12}, and chrysene obtained from the correlations are given in Table 13. These coefficients were also generated from vapor pressure data covering the temperature range $T = 298.15$ K to $T = 500$ K evaluated at 20 K intervals. Similar normalization factors were used to adjust the calculated $\ln(p/p_o)$ value of each standard and its deuterated analogue obtained from the correlation to the experimental value. Experimental vapor pressure values for the remaining compounds were not adjusted.

Results

As a check on the consistency and accuracy of the vapor pressure values obtained by this treatment, as noted above, the vapor pressures calculated by extrapolation for anthracene and *p*-terphenyl by correlation were compared to those measured experimentally. The comparisons are shown in Figures 4 and 5. Combined experimental values of p/p_o for anthracene are plotted against temperature in Figure 4.[36,37] The line represents extrapolated values calculated from the correlation equations of Table 9 using eq 12 and the parameters reported for anthracene in Table 13. The boiling temperature calculated for anthracene using eq 12 by extrapolation is $T_b = 613$ K. Experimental values of $T_b = 613$ K[46] and 614.4 K[55] have been reported. Figure 5 illustrates how the vapor pressures for *p*-terphenyl calculated from the correlation equations of Table 10 and extrapolated from (500 to 640) K using eq 12 compare to the values calculated from the Antoine constants. In this case, the vapor pressure values obtained from eq 12 appear to be slightly greater than those obtained from the Antoine constants. It should be noted, however, that extrapolation of the vapor pressures using eq 12 predicts a boiling temperature for *p*-terphenyl of $T_b = 649$ K; the Antoine constants predict a boiling temperature of $T_b = 657$ K. The experimental value reported is $T_b = 649.15$ K.[46]

Boiling temperatures for most of the deuterated hydrocarbons have not been reported but would be expected to be very similar to the unlabeled materials. As a check on the consistency of the vapor pressures generated from the different standards in runs 1 to 10, the boiling temperatures predicted by eq 12 have been compared to experimental values in columns 6 and 7 of Table 13. All of the values are close to the experimental values for the unlabeled material, as would be expected. Agreement of the estimated value of T_b for hexamethylbenzene, for which vapor pressure data were not available, is also quite good. Furthermore, the consistency in the predicted boiling temper-

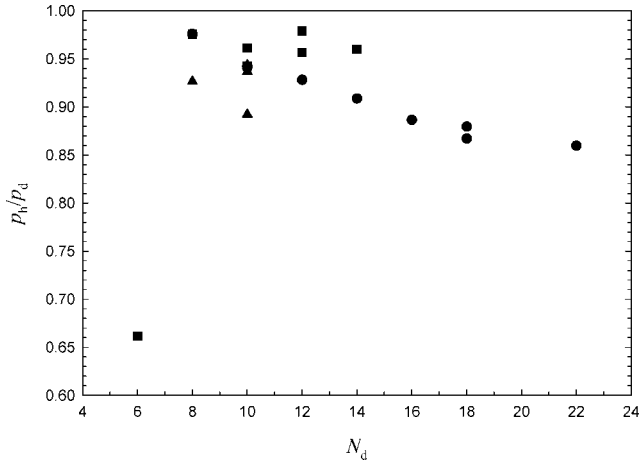

Figure 6. Vapor pressure isotope effects, p_h/p_d, as a function of the number of deuterium atoms, N_d. The squares represent compounds with deuterium substitution only at sp^2 carbon atoms; the circles are deuterium substitution only at sp^3 centers; and the triangles are deuterium substitution at both sp^2 and sp^3 carbon atoms.

atures generated from experiments conducted with different standards under different experimental conditions is particularly reassuring.

The vapor pressure isotope effects calculated for each of the materials investigated is provided in the second to the last column in Table 13 at $T = 298.15$ K. Figure 6 also summarizes these effects as a function of the number of deuterium substitutions. Values are averaged for those compounds in Table 13 with more than one value. As with vaporization enthalpies, both the structure and the amount of deuterium substitution seem to play a role in the magnitude of the effect. The outlier in the graph is the isotope effect observed for benzene-d_6. Since the vaporization enthalpies of benzene and benzene-d_6 are nearly identical, this effect appears to be due primarily to A' factor differences in eqs 4 and 6. As noted above, the isotope effect measured is in good agreement with previous measurements.

Since many polycyclic aromatic hydrocarbons (PAHs) are semivolatile and are found sorbed to aerosol particles, vapor pressures of the subcooled liquid are also of interest in evaluating their fate in the environment.[56] Table 14 compares the vapor pressures of the PAHs evaluated in this study to those previously reported in the literature. The vapor pressures from this work were calculated using eq 12 and the parameters reported in Table 13. Agreement between the two sets of data is quite good given the indirect manner by which these numbers have been obtained.

Conclusions

Liquid−vapor pressures and vaporization enthalpies of a series of perdeuterated hydrocarbons have been measured. The results clearly indicate that the resolution of current capillary columns is sufficient to discriminate between deuterated and nondeuterated compounds. Caution should be exercised in the quantitative evaluation of a target substrate if the deuterated target is being used as an internal standard.

Supporting Information Available:

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

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(23) The vaporization enthalpy of naphthalene is the mean of several determinations. Values of: ((48.7 ± 0.3) kJ·mol^{-1}, (384 to 539) K)[24], ((50.2 ± 0.8) kJ·mol^{-1}, (355 to 388) K),[25] ((50.6 ± 0.3) kJ·mol^{-1}, (353 to 452) K),[26] ((48.8 ± 0.6) kJ·mol^{-1}, (399 to 492) K),[27] ((47.2 ± 0.2) kJ·mol^{-1}, (360 to 497) K).[28] Adjusting to $T = 298.15$ K using the first equation in ref 29 using an estimated $C_{p,m}$(l) value of 205 J·mol^{-1}·K^{-1}[30] resulted in values of [(54.8 ± 0.4), (55.0 ± 1.2), (55.1 ± 1.1), (56.4 ± 2.0), (55.5 ± 1.8)] kJ·mol^{-1}, respectively, for an average value of (55.4 ± 1.4) kJ·mol^{-1}.

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(29) $\Delta_l^g H_m(298.15\ K)/kJ\cdot mol^{-1} = \Delta_l^g H_m(T_m/K) + [10.58 + 0.26(C_{p,m}(l))/J\cdot mol^{-1}\cdot K^{-1}]\{T_m/K-298.15\}/1000$. $\Delta_{cr}^g H_m(298.15\ K)/kJ\cdot mol^{-1} = \Delta_{cr}^g H_m(T_m/K) + [\ 0.75 + 0.15(C_{p,m}(cr))/J\cdot mol^{-1}\cdot K^{-1}]\{T_m/K-298.15\}/1000$. Chickos, J. S.; Hesse, D. G.; Liebman, J. F. Heat Capacity Corrections to a Standard State: A Comparison of New and Some Literature Methods for Organic Liquids and Solids. *Struct. Chem.* **1993**, *4*, 271–278.

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(42) The vaporization enthalpy of acenaphthene is the average of three determinations, (61.09, 366.5 K),[39] ((66.5 ± 6.0), 298.15 K),[43] ((60.3 ± 0.3), 367 K),[44] adjusted to $T = 298.15$ K using an estimated heat capacity, $C_{p,m}(l)$, of 243.8 $J\cdot mol^{-1}\cdot K^{-1}$ and adjusted using the first equation in ref 29. This resulted in values of (66.15, 66.5, and 66.0) $kJ\cdot mol^{-1}$ at $T = 298.15$ K and a mean value of 66.2 $kJ\cdot mol^{-1}$.

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(53) The vaporization enthalpy of perylene reported here differs from the value reported previously in that it has been re-adjusted using updated vaporization enthalpies of the *n*-alkanes[16] used as standards in the evaluation and using the data reported in ref 54. A value of 118.7 $kJ\cdot mol^{-1}$ was calculated.[54] In addition, two additional correlations for perylene are reported in the Supporting Information [(118.3 and 118.5) $kJ\cdot mol^{-1}$] resulting in an average vaporization enthalpy of 118.5 $kJ\cdot mol^{-1}$.

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