Vapor Pressures and Enthalpies of Sublimation of Ten Polycyclic Aromatic Hydrocarbons Determined via the Knudsen Effusion Method

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The vapor pressures of ten polycyclic aromatic hydrocarbons, ranging in molecular weight from (152 to 252) $g \cdot mol^{-1}$, were measured using the Knudsen effusion technique in the temperature range of (297 to 432) K. These compounds included those for which there were few or conflicting data in the literature: acenaphthylene, acenaphthene, fluoranthene, benzo[*a*]phenanthrene, 9,10-benzophenanthrene, benzo[*a*]pyrene, and perylene. Anthracene, fluorene, and pyrene were also examined to establish the reliability of the presently implemented method. Enthalpies of sublimation of these compounds were determined via application of the Clausius−Clapeyron equation.

Introduction

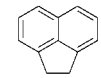
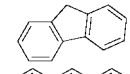
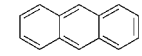
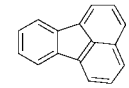
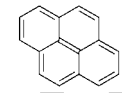
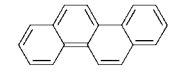
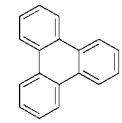
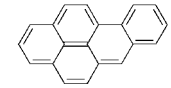
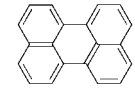
Vapor pressures of high molecular weight polycyclic organics provide essential information for predicting the combustion behavior of fossil fuels, as well as their fate and transport in the environment. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants of pyrogenic or petrogenic origin. Sixteen PAHs are classified by the U.S. Environmental Protection Agency as priority pollutants, given their carcinogenic nature. Several of the compounds selected for the present study are on this list. The current experimental work was motivated by a lack of, and inconsistencies in, vapor pressure and thermodynamic data currently available on PAHs.

It is often difficult to obtain vapor pressure data on high molecular weight, semivolatile organic compounds. High temperatures are required to obtain directly measurable vapor pressures, yet these high temperatures can result in the thermal degradation of the compounds of interest. Several compendia of vapor pressures and vaporization or sublimation enthalpies were recently published, including those by Chickos and Acree,[1] Delle Site,[2] Shiu and Ma,[3] and Yaws,[4] which detail many correlations, as well as uncertainty, in currently available vapor pressure data. As Delle Site remarks, "the uncertainty in the vapor pressure measurements increases as vapor pressure decreases," a common problem identified among vapor pressure data of PAHs, organic compounds with relatively low vapor pressures.[2] As noted by White,[5] very few PAHs have vapor pressure data available, so their work uses extrapolations to predict boiling points and enthalpies of vaporization. These extrapolations are necessary due to the dearth of available data on PAH; however, the accuracy of the predictions varies widely in the data set, which supports the need for the present experimental measurements.

Over the past decades, several research groups[6–14] have adapted the Knudsen effusion technique to indirectly measure vapor pressures of high molecular weight organic compounds, such as PAHs, via the molecular effusion of a vapor through an orifice under a high vacuum, at low to moderate temperatures. While each group employs its own variant of the Knudsen effusion method, the data obtained through these methods appear reasonably consistent for commonly used reference compounds, such as anthracene and naphthalene.

Due to the low temperatures, and hence the solid state of the polycyclic aromatic hydrocarbons measured in the present experiments, the reported vapor pressures are actually sublimation vapor pressures. The Clausius−Clapeyron equation is

Table 1. Polycyclic Aromatic Hydrocarbons Examined Using the Knudsen Effusion Technique

Compound	Formula	CAS Reg. No.	Molecular Weight	Min. Purity/%	Molecular Structure
Acenaphthylene[a]	$C_{12}H_8$	208-96-8	152.19	95+	
Acenaphthene[a]	$C_{12}H_{10}$	83-32-9	154.21	99	
Fluorene[a]	$C_{13}H_{10}$	86-73-7	166.22	97	
Anthracene[b]	$C_{14}H_{10}$	120-12-7	178.23	99	
Fluoranthene[a]	$C_{16}H_{10}$	206-44-0	202.26	98	
Pyrene[b]	$C_{16}H_{10}$	129-00-0	202.26	99	
Benzo[a]phenanthrene[a]	$C_{18}H_{12}$	218-01-9	228.29	97+	
9,10-benzophenanthrene[a]	$C_{18}H_{12}$	217-59-4	228.29	96+	
Benzo[a]pyrene[c]	$C_{20}H_{12}$	50-32-8	252.31	99	
Perylene[b]	$C_{20}H_{12}$	198-55-0	252.31	99+	

supplier: a: TCI America; b: Aldrich Chemical Co.; c: Pfaltz Chemical Co.

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typically used to correlate vapor pressures; in its integrated form it is often written with reference to the sublimation entropy, $\Delta_{sub}S$, as

$$\ln P^{o} = -\frac{\Delta_{sub}H}{RT} + \frac{\Delta_{sub}S}{R} \quad (1)$$

where P^{o} is the saturation vapor pressure; T is the absolute temperature; and R is the universal gas constant. This integrated form of the Clausius−Clapeyron equation, reflecting the Gibbs free energy difference between a solid and its vapor, is subject to the assumption that $\Delta_{sub}H$ is constant over the temperature range investigated and represents data in the pressure region of (10^{-4} to 10^{-1}) Pa quite well.

Experimental Section

Method. The Knudsen effusion technique indirectly determines vapor pressures from measurements of molecular effusion rates through a small orifice in a sample cell. The theory describing the Knudsen effusion process is well developed and widely known.[13,15,16] It is based on the kinetic theory of gases, from which Knudsen derived an expression for the slow isothermal effusion out of a small orifice in a cell, given a fixed internal pressure (in this case, the vapor pressure, P°)

$$P^{o} = \frac{m}{W_0 A_0}\sqrt{\frac{2\pi RT}{M}} \quad (2)$$

where m is the mass loss rate from the cell; A_0 is the orifice area; M is the molecular weight of the compound; and W_0 is the Clausing probability factor, a measure from zero to unity, of the probability that a molecule entering the orifice from inside the cell escapes through the orifice to the exterior of the cell. It may be calculated using a relation between the orifice effusion length, l, and orifice radius, r[13]

$$W_0 = \frac{1}{1 + \frac{3l}{8r}} \quad (3)$$

Tabulated values of the Clausing probability factor as a function of orifice size are available in the literature.[17] The cell may also be calibrated using reference compounds, such as fluorene and anthracene. Both approaches were employed here, and values of the Clausing factor were typically between 0.95 and 0.97. The Knudsen effusion equation is generally applicable as long as the area of the orifice is small enough and the pressure is low enough that equilibrium within the cell is truly maintained.[17]

The vapor pressures of ten PAHs were measured using the isothermal Knudsen effusion technique in a device previously described, but subject to a few modifications to the pumping, data recording, and temperature measurement systems.[12,16] The mass loss rate was continuously recorded using a Cahn 2000 microbalance accurate to ± 0.5 μg, and these data were logged, along with temperatures, onto a computer. The backpressure in the thermogravimetric (TGA) system was maintained at 10^{-5} Pa by a BOC Edwards turbomolecular pump. The cell was suspended on one arm of the microbalance and sat inside a black copper capsule within the glass vacuum enclosure. The presence of the blackened conductive capsule surrounding the sample cell was critical; without it, the heat transfer in the vacuum enclosure is too poor to reliably maintain the cell and measurement thermocouple at the same temperature. Temperatures were read by an Omega type K thermocouple positioned directly above the cell opening, calibrated to ± 0.1 K using an NIST-traceable thermometer. Again, positioning the thermocouple in the same black cavity radiation heat transfer environment as the sample cell is crucial to obtaining reliable results. To fabricate the sample cells, we pressed 001 gauge stainless steel shim stock into a (0.01 ± 0.005) cm^3 internal volume container using a cylindrical stainless steel mold. The effusion holes were made using a miniature drill press, resulting in holes with areas measuring approximately (0.003 ± 0.0005) cm^2. The cell was cleaned by heating it in a propane flame at 1000 °C to ensure removal of surface impurities and to blacken the surface of the cell to increase heat transfer via radiation. After filling with the sample, the cell was hermetically sealed using a hand press to ensure the only leak was through the effusion hole.

The continuous monitoring of mass loss and temperature enabled measurements at multiple temperatures for each effusion cell. This yields improved accuracy over methods where the vapor pressure is measured as a total mass loss over time, subject to start-up constraints of vacuum pumping, volatilization of compound impurities, and heating of the cells. This also implies that we need not start at a specific mass; rather, we covered the bottom of the effusion cell with a thin layer of sample, usually between (15 and 20) mg depending on the density, and measured the real-time mass loss.

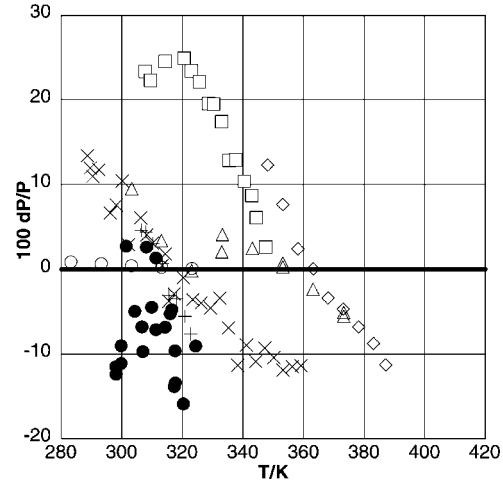

Figure 1. Deviation plot of vapor pressure of fluorene determined via the Knudsen effusion method compared to the average of literature values: •, this study; ○, ref 20; Δ, ref 26; □, ref 27; ◊, ref 28; ×, ref 38; +, ref 39.

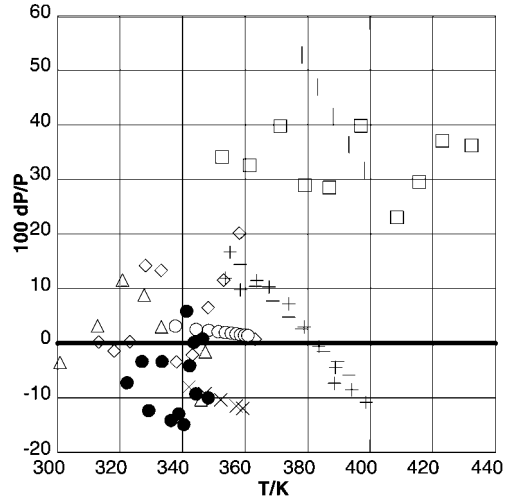

Figure 2. Deviation plot of vapor pressure of anthracene determined via the Knudsen effusion method compared to the average of literature values: •, this study; □, ref 7; Δ, ref 12; ○, ref 23; ◊, ref 29; +, ref 34; ×, ref 35; —, ref 36; |, ref 37.

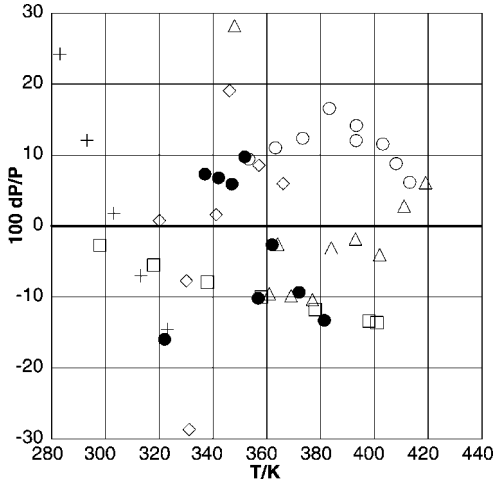

Figure 3. Deviation plot of vapor pressure of pyrene determined via the Knudsen effusion method compared to the average of literature values: •, this study; Δ, ref 7; ◇, ref 12; □, ref 20; +, ref 21; ○, ref 26.

Materials. The ten polycyclic aromatic hydrocarbons examined ranged in molecular weight from (152 to 252) g·mol^{-1}. They were purchased from several chemical suppliers, at a minimum purity of 95 %, as detailed in Table 1. The compounds were placed into the effusion cells as received, and at least 5 % (by mass) of each compound was sublimed before commencing data collection to ensure removal of any volatile impurities. This fractional sublimation was shown (in a previous publication) to be sufficient to remove all volatile impurities by the use of a mass spectrometer to measure the spectra of the effusing vapors. A spectrum taken following 1 % mass loss shows a multitude of volatile impurities, whereas after 6 % mass loss, the compound of interest accounts for over 99 % of the spectrum, with the remaining compounds being hydrogen, nitrogen, and oxygen, indicating the impurities are volatile in nature and do not affect our vapor pressure measurements.[18] For each compound examined, vapor pressure results were verified by a minimum of two independent sets of measurements in two different cells to ensure reproducibility. Additionally, each cell was subjected to different temperature profiles (i.e., one of increasing temperature, the second cell starting in the middle of the range, decreasing temperature, then increasing) to ensure reproducibility of data points.

Results and Discussion

The reliability of the experimental technique was established by comparing the measured vapor pressures of fluorene, anthracene, and pyrene to available literature values in a temperature range of (298 to 381) K. Figures 1, 2, and 3 illustrate the vapor pressures of these compounds and the corresponding literature data as deviations from a literature average. The agreement is generally quite good. Data from the present measurements are all shown as solid circles, whereas literature data are always open points. Present measurements provided an enthalpy of sublimation for anthracene of (98.5 ± 3.3) kJ·mol^{-1}, which may be compared to literature values ranging from (89.1 to 102.6) kJ·mol^{-1}. Sabbah et al.[19] remark that most sublimation enthalpy values of anthracene published over the past 50 years range from (85 to 105) kJ·mol^{-1} with a mean around 103.4 kJ·mol^{-1} at 298 K. The literature shows considerably greater uncertainty for pyrene, with published enthalpies of sublimation ranging from (91.1 to 103.1) kJ·mol^{-1}; however, our value of (97.8 ± 3.3) kJ·mol^{-1} fits well within this range. Sabbah et al. recommend a range of sublimation enthalpies of pyrene of (97.7 to 102.2) kJ·mol^{-1} at 298 K.[19] The present enthalpy of sublimation for fluorene of (87.1 ± 1.9) kJ·mol^{-1} is in reasonable agreement with the literature values, which range from (82.1 to 87) kJ·mol^{-1}.

Table 2 presents the raw data obtained in the present experiments, from applying Knudsen theory to the measurements. These data were used to calculate the enthalpies and entropies of sublimation of each compound, as displayed in Table 3. Table 3 also details the statistical significance of these results. A 95 % confidence interval was calculated for each set of experimental results using the linear regression program in STATA version 9SE for Macintosh.

Few data are available in the literature for acenaphthylene, as displayed in Figure 4, and the two published studies that we could locate show a large discrepancy in vapor pressures. The data from this study agree fairly well with those published by Sonnefeld et al.[20] although the present results are consistently lower; data from Stephenson and Malanowski's handbook[21] differ from our study and Sonnefeld's by several orders of magnitude. The enthalpies of sublimation as determined herein

Table 2. Summary of Vapor Pressures Obtained via the Knudsen Effusion Method

T/K	*P*/Pa	*T*/K	*P*/Pa	*T*/K	*P*/Pa	*T*/K	*P*/Pa
Acenaphthylene				Pyrene			
297.4	0.488	311.9	1.82	322.0	0.00895	356.8	0.339
297.6	0.531	314.8	3.45	337.1	0.0531	362.1	0.599
304.6	1.05	318.5	3.45	342.1	0.0943	372.0	1.30
304.7	1.08	318.6	3.47	347.1	0.147	381.4	2.81
306.7	1.14	319.7	4.14	352.3	0.227		
Acenaphthene				Benzo[*a*]phenanthrene			
297.6	0.290	302.8	0.508	372.4	0.0174	400.0	0.202
299.7	0.362	306.1	0.693	380.7	0.0372	400.4	0.212
300.5	0.413	310.7	1.12	385.2	0.0537	402.8	0.263
301.6	0.440	315.6	1.80	389.2	0.0761	403.0	0.254
				389.4	0.0750	404.8	0.277
				393.6	0.103	404.9	0.292
				394.2	0.136	405.1	0.306
				396.1	0.148	406.8	0.336
				398.1	0.168	408.6	0.379
				398.2	0.158		
Fluorene				9,10-Benzophenanthrene			
298.0	0.0661	311.2	0.301	368.4	0.0170	386.7	0.116
298.1	0.0652	314.3	0.414	377.4	0.0448	390.7	0.178
299.8	0.0840	316.0	0.460	377.7	0.0451	394.9	0.264
301.4	0.0988	316.5	0.531	378.0	0.0464	395.0	0.258
304.3	0.141	317.3	0.581		0.0672	399.1	0.375
306.6	0.178	317.6	0.613				
306.9	0.195	320.3	0.760				
308.1	0.218	324.4	1.27				
309.8	0.261						
Anthracene				Benzo[*a*]pyrene			
322.2	0.0160	341.2	0.119	392.3	0.0731	411.8	0.418
327	0.0260	342.3	0.131	393.5	0.0796	415.1	0.494
329.1	0.0333	343.6	0.141	397.8	0.129	415.5	0.537
333.4	0.0491	344.2	0.164	400.8	0.167	419.0	0.697
336.3	0.0720	346.4	0.192	402.3	0.180	419.7	0.733
338.7	0.0943	348.2	0.260	405.2	0.217	421.2	0.785
340.4	0.110			406.6	0.273	423.8	0.980
				411.5	0.394	423.9	1.02
Perylene				Fluoranthene			
390.0	0.0137	406.6	0.0720	326.8	0.0396	342.5	0.206
390.5	0.0147	406.8	0.0703	326.9	0.0411	343.9	0.248
391.2	0.0149	410.5	0.100	331.0	0.0616	345.3	0.258
393.7	0.0215	411.3	0.102	331.8	0.0632	348.0	0.330
397.7	0.0315	412.7	0.132	336.7	0.117	348.5	0.341
398.3	0.0303	413.4	0.142	338.7	0.129	350.9	0.463
402.2	0.0458	414.4	0.148	338.8	0.131	354.1	0.580
402.8	0.0476	418.4	0.196	338.9	0.144	359.2	1.05
403.7	0.0519	428.6	0.443	340.2	0.154		
405.7	0.0667	432.4	0.606				

Table 3. Application of the Clausius−Clapeyron Equation to Vapor Pressure Data

compound	formula	temp range/K	$\Delta_{sub}S/R$	$\Delta_{sub}H/RT$
acenaphthylene	$C_{12}H_8$	297 to 320	29.34	8298 ± 989[a]
acenaphthene	$C_{12}H_{10}$	298 to 316	30.59	9470 ± 269
fluorene	$C_{13}H_{10}$	298 to 324	32.85	10596 ± 229
anthracene	$C_{14}H_{10}$	322 to 348	32.59	11848 ± 399
fluoranthene	$C_{16}H_{10}$	327 to 359	32.49	11658 ± 332
pyrene	$C_{16}H_{10}$	322 to 381	31.94	11762 ± 392
benzo[*a*]phenanthrene	$C_{18}H_{12}$	372 to 409	31.43	13224 ± 430
9,10-benzophenanthrene	$C_{18}H_{12}$	368 to 399	36.64	15006 ± 350
benzo[*a*]pyrene	$C_{20}H_{12}$	392 to 424	32.17	13633 ± 375
perylene	$C_{20}H_{12}$	390 to 432	34.66	15175 ± 98

[a] Uncertainty calculated at a 95 % confidence interval using linear regression in STATA v.9E.

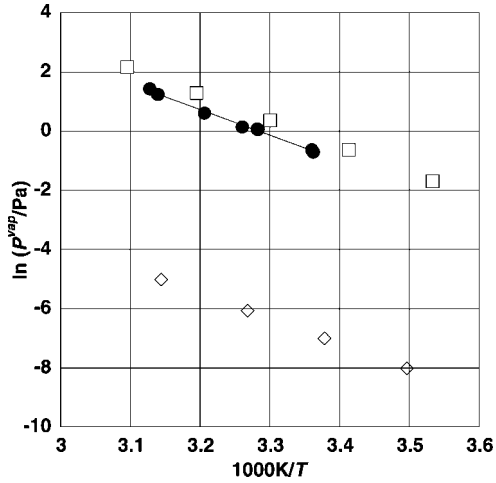

Figure 4. Vapor pressure of acenaphthylene determined via the Knudsen effusion method compared to available literature values: •, this study; □, ref 20; ◇, ref 21.

are compared to available literature values in Table 4. It is not known what original data set Stephenson and Malanowski used, though we suspect a conversion error due to the large difference in vapor pressure values but quite similar enthalpy of sublimation that they reported.

When comparing the data for acenaphthylene (Figure 4) to those obtained for acenaphthene (Figure 5), we obtained a slightly higher enthalpy of sublimation for the somewhat heavier acenaphthene (see Tables 3 and 4). The difference in these two compounds is that the acenaphthylene has one more unsaturated (double) bond than does acenaphthene. The actual difference in vapor pressures is seen to be a factor of 2, reflecting a contribution of the entropy of sublimation (which is higher for the relatively more saturated compound).

Literature data for fluoranthene show a distinct lack of consistency. Both Stephenson and Malanowski, as well as Boyd et al.,[22] cite enthalpies of sublimation of approximately 102 kJ·mol^{-1}. On the other hand, Sonnefeld et al. obtained a value of 84.5 kJ·mol^{-1} in largely the same temperature interval.[20] The data obtained in this study suggest an enthalpy of sublimation for fluoranthene of (96.9 ± 2.8) kJ·mol^{-1}, as measured in three independent trials involving 17 data points. Sonnefeld et al. studied a significantly lower temperature range than did we, so the direction of the difference is not what would be expected. These results are displayed in Figure 6. From this figure, our vapor pressure data appear to fit between these two earlier data sets, as implied by the enthalpies of sublimation. Sonnefeld et al. employed a dynamic coupled-column liquid chromatography technique, whereas Boyd et al. used an effusion cell for their work.

Table 4. Sublimation Enthalpies of Compounds Investigated Compared to Literature Data

temp. range K	$\Delta_{sub}H$ kJ·mol^{-1}	ref
	Fluorene	
298	87.6	25
298 to 324	87.1 ± 1.9	this study
303 to 373	87.0	26
308 to 336	84.5	27
348 to 387	82.1	28
	Anthracene	
283 to 323	91.7	20
298	99.4	25
318 to 363	100.0	12
322 to 348	98.5 ± 3.3	this study
337 to 360	100.4	23
338 to 361	102.6	29
352 to 432	101.0	7
358 to 392	94.8	30
365 (mean)	89.1	31
364 (mean)	89.5	31
	Pyrene	
283 to 323	91.1	20
298 to 401	97.1	21
320 to 366	103.1	12
322 to 381	97.8 ± 3.3	this study
348 to 419	92.7	7
352 (mean)	97.5	31
353 to 413	97.7	26
Acenaphthylene		
283 to 323	73.2	20
286 to 318	71.1	21
297 to 320	74.2 ± 8.2	this study
298	70.0	25
Acenaphthene		
290 to 311	82.1	21
291 to 307	81.6	32
293 to 342	78.0	27
298	84.6	1
299 to 320	78.7 ± 2.2	this study
338 to 366	83.3	28
339 to 366	83.4	21
	Fluoranthene	
283 to 323	84.5	20
298 to 303	102.4	21
327 to 359	96.9 ± 2.8	this study
328 to 353	102.1	22
	Benzo[*a*]phenanthrene	
358 to 463	117.9	21
372 to 409	109.9 ± 3.6	this study
390 to 417	118.9	23
	9,10-Benzophenanthrene	
363 to 468	107.6	21
368 to 399	124.8 ± 2.9	this study
380 to 404	115.6	23
	Benzo[*a*]pyrene	
358 to 431	118.3	11
392 to 424	113.3 ± 3.1	this study
	Perylene	
298	123.2	33
383 to 518	138.0	21
390 to 432	126.2 ± 0.82	this study
391 to 424	132.6	12

The vapor pressure data obtained here for benzo[*a*]phenanthrene in the temperature range of approximately (400 to 430) K agree well with data published by DeKruif, who also employed an effusion technique.[23] Below 400 K, the vapor pressures measured in these experiments are slightly lower than those reported by DeKruif, as seen in Figure 7. This appears to be the reason for the discrepancy between the enthalpy of

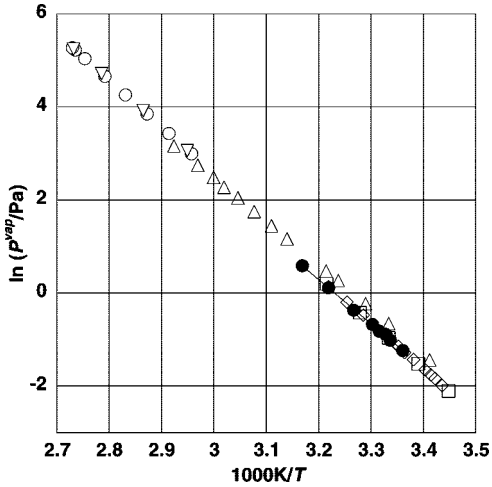

Figure 5. Vapor pressure of acenaphthene determined via the Knudsen effusion method compared to available literature values: •, this study; □, ref 21; , ref 21; Δ, ref 27; ○, ref 28; ◇, ref 32.

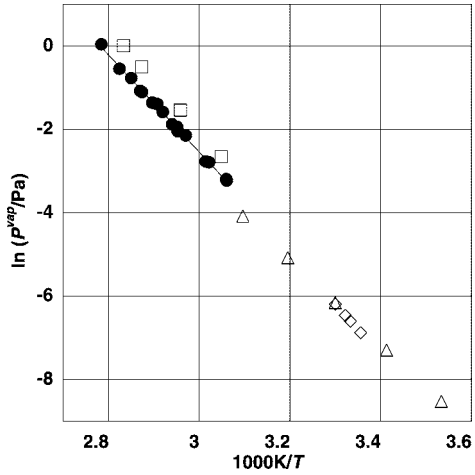

Figure 6. Vapor pressure of fluoranthene determined via the Knudsen effusion method compared to available literature values: •, this study; Δ, ref 20; ◇, ref 21; □, ref 22.

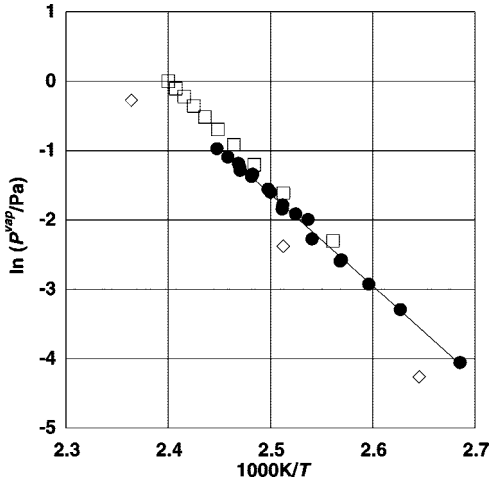

Figure 7. Vapor pressure of benzo[*a*]phenanthrene determined via the Knudsen effusion method compared to available literature values: •, this study; ◇, ref 21; □, ref 23.

sublimation for benzo[*a*]phenanthrene determined in this work, (109.9 ± 3.6) kJ·mol^{-1}, and DeKruif, (118.9 ± 2) kJ·mol^{-1}. The vapor pressure data from Stephenson and Malanowski are again consistently lower, though not nearly as dramatically as in the data for acenaphthylene.

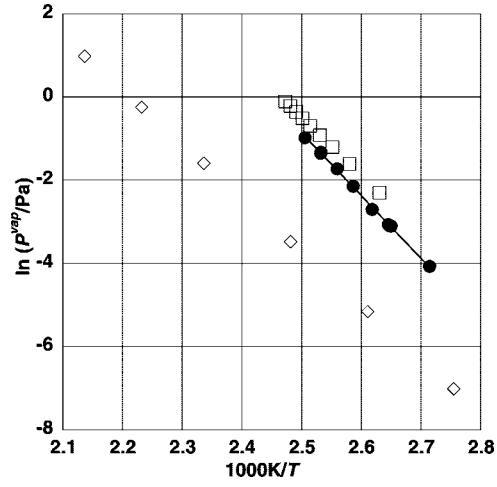

Figure 8. Vapor pressure of 9,10-benzophenanthrene determined via the Knudsen effusion method compared to available literature values: •, this study; ◇, ref 21; □, ref 23.

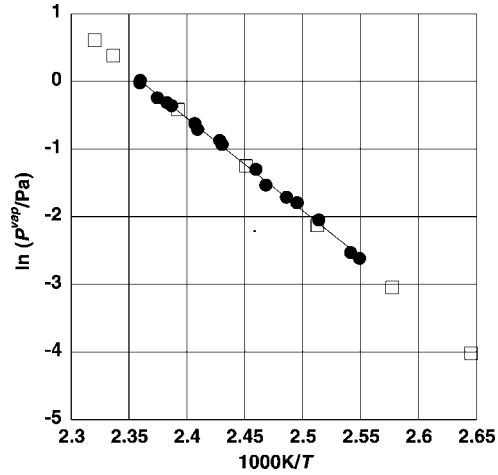

Figure 9. Vapor pressure of benzo[*a*]pyrene determined via the Knudsen effusion method compared to available literature values: •, this study; □, ref 11.

Figure 8 gives data for 9,10-benzophenanthrene, for which there are again significantly conflicting data reported in the literature. The vapor pressures measured in this study are a few percent lower than those reported by DeKruif, though unlike the data for benzo[*a*]phenanthrene, they tend to agree better as temperature decreases. The enthalpy of sublimation is (124.8 ± 2.9) kJ·mol^{-1} for this study, and (115.6 ± 2) kJ·mol^{-1} was reported by DeKruif.

Very few data are available in the literature for benzo[*a*]pyrene, a widely noted carcinogen.[24] However, the present results agree well with the vapor pressure results obtained earlier by Murray et al.[11] for the same compound (see Figure 9). Murray et al., working in a temperature range of (358 to 431) K, obtained a heat of sublimation of (118.3 ± 2.6) kJ·mol^{-1}, while the results of this study yield an enthalpy of sublimation of (113.3 ± 3.1) kJ·mol^{-1} in the narrower temperature range of (392 to 424) K. Hence, it is felt that the vapor pressure properties of this important PAH are well established at temperatures slightly above ambient (Figure 10).

Perylene, the largest polycyclic aromatic hydrocarbon investigated in the present study, is also the subject of some uncertainty within the literature. The present study led to a value for the heat of sublimation of (126.2 ± 0.82) kJ·mol^{-1}, falling slightly below the value obtained here earlier by Oja and

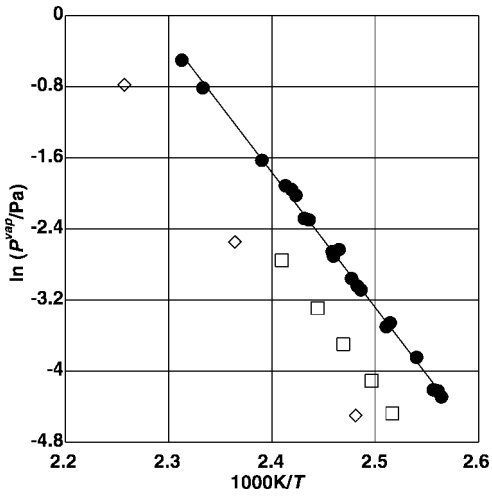

Figure 10. Vapor pressure of perylene determined via the Knudsen effusion method compared to available literature values: •, this study; □, ref 12; ◇, ref 21.

Suuberg[12] in the same general range of temperatures. The present vapor pressures were, however, a bit higher than those for that earlier work. Given the greater number of points in the present data set, the high purity of the sample, and the generally good agreement obtained between several different experiments, we feel that the present data set is more reliable. It should be noted that these data are from the highest range of temperatures studied in the present experiments. Temperature calibration of the thermocouple is performed in the relevant temperature range, so this should not be an issue. There was, moreover, no discrepancy with other data sets noted in the high temperature end of the pyrene results, which covers a similar range of temperatures as is of relevance for perylene.

We note that the enthalpies of sublimation of these ten compounds generally follow expected trends: successive addition of carbon and hydrogen atoms tends to increase the heat of sublimation. However, this trend is not absolute, as evidenced in Table 4. For example, fluoranthene and pyrene, both with identical molecular mass, and anthracene, with two fewer carbon atoms, all have statistically indistinguishable heats of sublimation in the same range of temperatures. However, statistically different enthalpies of sublimation are noted for both benzo[*a*]phenanthrene and 9,10-benzophenanthrene, at [(109.9 ± 3.6) and (124.8 ± 2.9)] kJ·mol^{-1}, respectively, both with a chemical formula of $C_{18}H_{12}$. A difference is also observed between perylene and benzo[*a*]pyrene, with enthalpies of sublimation of [(126.2 ± 0.82) and (113.31 ± 3.1)] kJ·mol^{-1}, respectively, even though each consists of 20 carbons and 12 hydrogen atoms. There is no particular surprise in these results, as reference to melting temperatures of the same compounds likewise confirms that subtle differences in structure manifest themselves as significant differences in thermodynamic properties. It is interesting to note that both 9,10-benzophenanthrene and perylene have central aromatic rings with a higher degree of molecular symmetry than their equal molecular mass counterparts, benzo[*a*]phenanthrene and benzo[*a*]pyrene, and both of the former compounds exhibit higher sublimation enthalpies and entropies. The trend does not carry over into the melting point.

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