Vapor Pressures and Enthalpies of Sublimation of Polycyclic Aromatic Hydrocarbons and Their Derivatives

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The vapor pressures of a series of polycyclic aromatic hydrocarbons (PAH) and heteroatom-containing PAH have been measured using the Knudsen effusion technique. Aromatic hydrocarbons examined included anthracene, phenanthrene, pyrene, 2,3-benzofluorene, naphthacene, perylene, pentacene, and coronene. Heteroatomic aromatic species examined included phenanthridine, perinaphthenone, 3-hydroxy-1-phenalen-1-one, benz[*g*]isoquinoline-5,10-dione, 1,2-benzodiphenylene sulfide, 1-hydroxypyrene, and 6,11-dihydroxy-5,12-naphthacenedione. The measurements were all made in the solid sublimation regime, and enthalpies of sublimation were calculated from the Clausius–Clapeyron equation.

Introduction

This paper presents the results of measurements of the vapor pressures of large polycyclic aromatic hydrocarbons (PAH), including those containing heteroatoms. The work was originally motivated by the lack of vapor pressure data on coal tars, which tend to have a highly aromatic nature and which also contain significant numbers of heteroatoms. Relatively few data are available on the vapor pressures of large polycyclics containing heteroatoms. Knowledge of vapor pressures of such compounds is important in predicting the pyrolysis behavior of coals, since most advanced models of coal pyrolysis utilize an evaporation step to describe the loss of tar from the particles (e.g., Suuberg, 1985; Solomon et al., 1988; Niksa and Kerstein, 1991; Fletcher et al., 1992). The present study is, however, only concerned with the behavior of pure compounds.

Many of the experimental data in the literature on large polycyclic aromatics have been measured in a pressure range from 0.01 to 103 Pa. Measurements of vapor pressures of high molecular weight materials require high temperatures to obtain conveniently measurable pressures, but high temperatures cannot be employed because of the concern about thermal decomposition during measurement. This, then, requires the use of moderate temperatures; our experience shows that even 525 K may be excessive for some typical pyrolysis tars. These restrictions require use of sensitive, indirect vapor pressure measurement techniques. In the present program of study, this led to the use of transpiration and effusion methods. Only the latter will be discussed here.

Because of the low temperatures employed in this work, the condensed aromatic phases are typically solids, and the measurements involve sublimation vapor pressures. In sublimation work, it is typical to find that the Clausius–Clapeyron equation, with a constant enthalpy of sublimation, $\Delta_{sub}H$, fits vapor pressure data reasonably well, i.e.

$$\mathrm{d}[\ln P°]/\mathrm{d}[1/T] = -\Delta_{sub}H/R \qquad (1)$$

Equation 1 may be integrated assuming $\Delta_{sub}H/R$ is a constant, where $P°$ is the saturation vapor pressure, T is

the absolute temperature, and R is the gas constant. This is found to generally be an excellent approximation throughout the work described below.

Experimental Section

The vapor pressures have been measured using a molecular effusion/thermogravimetry (TGA) technique. The particular implementation of the Knudsen effusion technique used here has been recently described in another publication, which also presented its modification for use in a nonisothermal mode (Oja and Suuberg, 1997). In the Knudsen method (e.g., Knudsen, 1909; Hollahan, 1962), a substance of interest effuses through a small pinhole, of known area, in an otherwise sealed container or cell. The measurement of vapor pressure involves determining the rate of mass loss from the effusion cell. Measurements here were made under isothermal conditions. The accuracy of the effusion cell temperature measurement is of paramount importance. Here, the temperature was measured with a precision of ±0.1 K, by a thermocouple in contact with an aluminum capsule that almost completely surrounds the effusion cell. The capsule is painted black and provides a radiation view factor for the cell that approaches unity. In this way, a relatively accurate measure of cell temperature may be obtained, since the main heat-transfer resistance exists between the capsule and surrounding aluminum block heater, as opposed to between cell and capsule (Oja and Suuberg, 1997).

In our implementation, the mass loss rate was continuously recorded using a Cahn 2000 recording electrobalance. The cell containing the pinhole leak was suspended on one arm of the balance, which has nominal sensitivity in the microgram level. The backpressure in the TGA system was maintained at 10^{-5} Pa, which has been noted to be sufficient so as to provide accuracy in the 10^{-4} Pa range of vapor pressures. The cell itself was maintained inside of the black capsule within the TGA and was in close proximity to a thermocouple within the capsule. Further details of the technique are provided elsewhere (Oja and Suuberg, 1997).

Materials Examined. Vapor pressures were measured for 15 aromatic species, with molecular weights in the range from 178 to 300 g/mol. Literature data were found on some of the heteroatom-containing aromatic hydrocarbons studied, but not all.

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Table 1. Compounds Examined

compound	formula	formula weight	melting point (K)	CAS reg no.[e]	purity (%)
anthracene[a]	$C_{14}H_{10}$	178.24	491	120-12-7	99+
phenanthrene[b]	$C_{14}H_{10}$	178.24	374	85-01-8	99
pyrene[c]	$C_{16}H_{10}$	202.3	429	129-00-0	99
2,3-benzofluorene[a]	$C_{17}H_{12}$	216.28	484−486	243-17-4	98
naphthacene[a]	$C_{18}H_{12}$	228.29	630	92-24-0	98
perylene[a]	$C_{20}H_{12}$	252.3	551	198-55-0	99+
pentacene[a]	$C_{22}H_{14}$	278.35	>573	135-48-8	98
coronene[d]	$C_{24}H_{12}$	300.36	711	191-07-1	97
phenanthridine[a]	$C_{13}H_9N$	179.22	381	229-87-8	99
perinaphthenone[a]	$C_{13}H_8O$	180.21	426−429	548-39-0	99
3-hydroxy-1*H*-phenalen-1-one[a]	$C_{13}H_8O_2$	196.21	537	5472-84-4	98
benz[*g*]isoquinoline-5,10 dione[a]	$C_{13}H_7O_2N$	209.21	451−453	46492-08-4	99
1,2-benzodi-phenylene sulfide[a]	$C_{16}H_{12}S$	234.32	461−463	239-35-0	99
1-hydroxypyrene[a]	$C_{16}H_{10}O$	218.26	452−455	5315-79-7	99
6,11-dihydroxy-5,12-naphthacenedione[a]	$C_{18}H_{10}O_4$	290.28	623	1785-52-0	98

[a] Supplier: Aldrich Chemical Co. [b] Kodak, Inc. [c] Sigma Chemical Company. [d] Pfaltz and Bauer, Inc. [e] Supplied by authors.
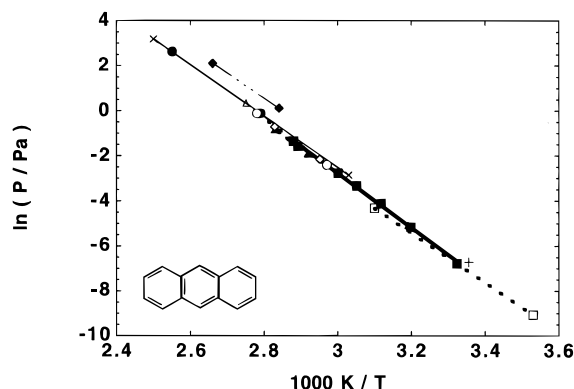

Figure 1. Vapor pressure data on anthracene, showing literature results and results obtained here using the isothermal Knudsen effusion method: solid circles, Macknick and Prausnitz (1979); ○, De Kruif (1980); △, Hansen and Eckert (1986); ▲, Kelley and Rice (1964); □, Sonnefeld et al. (1983); +, Nass et al. (1995); ◇, Bradley and Cleasby (1952); ◆, Inokuchi et al. (1952); ×, Bender et al. (1983); ■, this study. A similar summary has been presented by Oja and Suuberg (1997), supplemented here by additional literature data.

Figure 2. Vapor pressures for naphthacene, showing literature results and results obtained here using the isothermal Knudsen effusion method: ○, Inokuchi et al. (1952); △, Stephenson and Malanowski (1987); ×, De Kruif (1980); ■, this study. A similar summary has been presented by Oja and Suuberg (1997), supplemented here by additional literature data.

The compounds selected for study were all purchased in the highest available purities from a number of commercial suppliers, as noted below. All compounds were therefore used "as-received", except for one important feature of the preparations. At least 5 mass % of each compound was vaporized before measurements were begun. This ensured that if any very volatile impurities were present, they would be removed.

Melting points were measured for each compound using differential scanning calorimetry, and literature values were verified.

For each material studied, experimental vapor pressure results were obtained in two independent series of measurements. Thus a high degree of reproducibility was observed in the results presented here.

The compounds that were examined are listed in Table 1.

Results and Discussion

The results for anthracene and naphthacene have been published elsewhere, in a paper describing our implementation of the effusion technique (Oja and Suuberg, 1997). The results for anthracene are summarized in Figure 1 and Table 2. Figure 1 shows that excellent agreement has been obtained with other published values, and Figure 2 illustrates the same for naphthacene. Data from the litera-
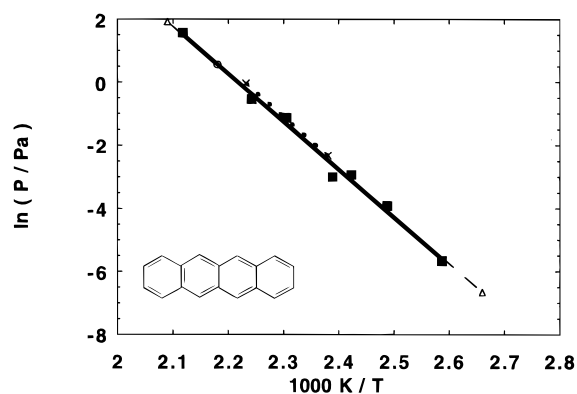
ture have been shown as lines connecting points at the reported maximum and minimum temperatures of the respective studies. The only exceptions were a few cases in which the temperature limits were not given (a single point is then shown) or in which a phase change was known to occur (only the data in the sublimation region are reported here).

An important feature that is clear from Figures 1 and 2 is that an assumption of constant enthalpy of sublimation is reasonable. Enthalpies of sublimation determined from our results provide an enthalpy of sublimation of (100.0 ± 2.8) kJ/mol for anthracene and (126.1 ± 1.3) kJ/mol for naphthacene. For all of the other measurements performed here, the results have also been successfully correlated using the integrated form of the Clausius−Clapeyron equation, with a constant enthalpy of vaporization

$$\ln(P/Pa) = A - B/(T/K) \qquad (2)$$

where A and B are constants, and it is recognized that $B = \Delta_{sub}H/R$. Table 2 summarizes the raw vapor pressure data, and Table 3 gives the values of A and B for all of the compounds studied together with the temperature range over which the data were obtained. Table 4 compares the enthalpies of sublimation obtained in this work with those reported earlier. The values of sublimation enthalpy are those calculated for the range of temperatures examined in each study. In a few cases, the authors have calculated the sublimation enthalpy at a particular temperature, and these values are indicated accordingly.

Table 2. Vapor Pressure Data Summary

T/K	P/Pa	T/K	P/Pa
		Anthracene	
300.85	0.00114	333.25	0.0620
312.85	0.00575	345.85	0.204
320.75	0.0162	347.25	0.258
327.75	0.0355		
		Phenanthrene	
303.49	0.0357	317.94	0.227
310.37	0.0909	321.25	0.323
313.92	0.140	332.93	0.998
		Pyrene	
320.10	0.00863	346.14	0.164
330.14	0.0243	357.14	0.428
331.13	0.0209	366.17	0.945
341.18	0.0852		
		2,3-Benzofluorene	
344.07	0.00454	370.70	0.0936
356.29	0.0188	397.55	1.23
		Naphthacene	
386.55	0.00344	433.84	0.322
401.93	0.0199	446.03	0.584
412.71	0.0535	472.14	4.81
418.59	0.0496		
		Perylene	
397.33	0.0114	409.11	0.0373
400.52	0.0164	415.02	0.0638
404.97	0.0249		
		Pentacene	
444.48	0.00161	473.44	0.0171
457.95	0.00413	476.25	0.0257
459.14	0.00421	485.75	0.0515
464.13	0.00760		
		Coronene	
421.05	0.00191	483.05	0.222
436.75	0.00686	483.15	0.309
451.25	0.0236	504.26	0.927
470.05	0.0895		
		Phenanthridine	
308.96	0.0143	328.73	0.177
316.29	0.0544	332.21	0.258
322.96	0.0936	336.63	0.402
		Perinaphthenone	
325.81	0.0242	340.39	0.118
326.94	0.0298	343.67	0.168
332.88	0.0538	347.83	0.239
336.78	0.0808		
		3-Hydroxy-1*H*-phenalen-1-one	
401.61	0.00725	418.41	0.0489
405.19	0.0104	426.26	0.101
411.35	0.0213	432.15	0.170
416.15	0.0341		
		Benz[*g*]isoquinoline-5,10 dione	
334.21	0.00885	357.57	0.115
342.89	0.0258	368.71	0.344
350.85	0.0572	381.35	1.13
		1,2-Benzodiphenylene Sulfide	
335.71	0.00227	366.81	0.0745
346.70	0.00852	373.97	0.144
349.47	0.0119	380.36	0.259
358.60	0.0307	388.11	0.517
		1-Hydroxypyrene	
369.60	0.0149	384.97	0.0784
375.53	0.0294	390.43	0.148
380.55	0.0501	394.50	0.207
		6,11-Dihydroxy-5,12-naphthacenedione	
425.89	0.0147	440.53	0.0568
429.55	0.0207	443.85	0.0760
435.92	0.0380	446.03	0.0931
437.06	0.0424		

Figure 3 shows the vapor pressure results obtained for phenanthrene, a compound that has also been examined by a number of workers. The present results are again
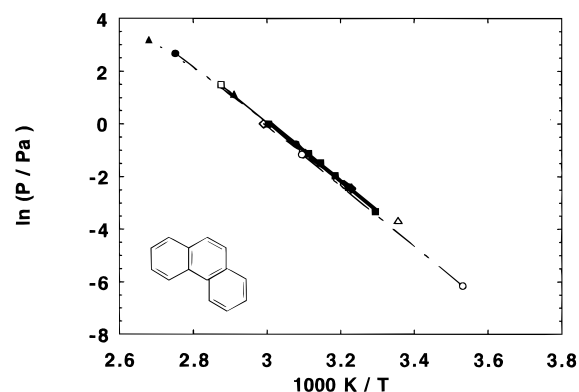

Figure 3. Vapor pressures for phenanthrene, showing literature results and results obtained here using the isothermal Knudsen effusion method: □, Sato et al. (1986); ◇, De Kruif (1980); ◆, Bradley and Cleasby (1952); ●, Macknick and Prausnitz (1979); ○, Sonnefeld et al. (1983); ▲, Bidleman (1984); △, Nass et al. (1995); ■, this study.
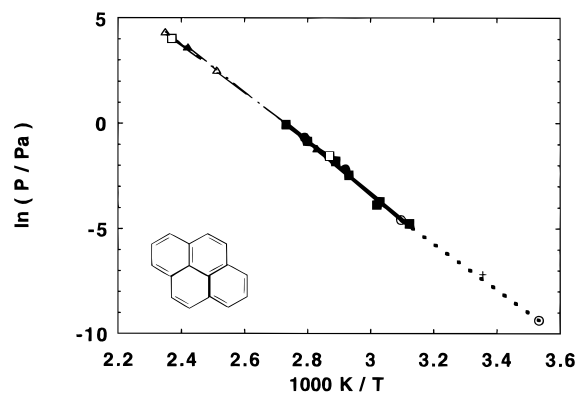

Figure 4. Vapor pressures for pyrene, showing literature results and results obtained here using the isothermal Knudsen effusion method: □, Malaspina et al. (1974); ●, Bradley and Cleasby (1952); ○, Sonnefeld et al. (1983); ▲, Sasse et al. (1988); △, Smith et al. (1980); ×, Nass et al. (1995); ■, this study.

seen to be in general agreement. The measured value of the enthalpy of sublimation is (95.0 ± 4.4) kJ/mol, as indicated in Table 4. The value obtained here agrees reasonably with several other values obtained in the same range of temperatures, but there is a significant variation in reported values. The uncertainty in the present value of enthalpy is too large to permit unequivocal support of one value over another.

Figure 4 shows the results for pyrene, another compound for which there are a number of literature correlations available. The agreement with other literature data on vapor pressure is seen to be generally reasonable. The calculated sublimation enthalpy is (103.1 ± 6.5) kJ/mol, which is a bit higher than other values reported in the literature (see Table 4).

Figure 5 provides data on 2,3-benzofluorene. The only other vapor pressure data that have been located on this compound suggest poor agreement, but the data are reported for a different temperature. The calculated enthalpy of sublimation is (119.3 ± 1.3) kJ/mol, which is again in significant disagreement with the only other reported value of 111.2 kJ/mol (see Table 4).

Figure 6 presents the data on perylene. Three other sets of data have been published for this compound. Agreement is not good in the temperature range of overlap. The data obtained on this compound were checked using another, less pure sample from a different supplier. There was only

Table 3. Summary of Results

| compound	formula	temp range/K	A	B
anthracene	$C_{14}H_{10}$	318–363	33.281	12 024 ($\pm$337)[a]
phenanthrene	$C_{14}H_{10}$	303–333	34.387	11 423 ($\pm$529)
pyrene	$C_{16}H_{10}$	308–398	33.856	12 400 ($\pm$776)
2,3 benzofluorene	$C_{17}H_{12}$	344–398	36.325	14 354 ($\pm$155)
naphthacene	$C_{18}H_{12}$	386–472	33.594	15 151 ($\pm$1077)
perylene	$C_{20}H_{12}$	391–424	35.702	15 955 ($\pm$431)
pentacene	$C_{22}H_{14}$	443–483	35.823	18 867 ($\pm$1631)
coronene	$C_{24}H_{12}$	421–504	31.72	16 006 ($\pm$609)
phenanthridine	$C_{13}H_9N$	309–437	34.92	12 045 ($\pm$1217)
perinaphthenone	$C_{13}H_8O$	326–348	32.201	11 690 ($\pm$296)
3-hydroxy-1*H*-phenalen-1-one	$C_{13}H_8O_2$	402–432	40.436	18 220 ($\pm$560)
benz[*g*]isoquinoline-5,10 dione	$C_{13}H_7O_2N$	334–381	34.218	13 005 ($\pm$188)
1,2 benzodi-phenylene sulfide	$C_{16}H_{12}S$	325–373	34.058	13 462 ($\pm$150)
1-hydroxypyrene	$C_{16}H_{10}O$	369–394	37.773	15 513 ($\pm$380)
6,11-dihydroxy-5,12-naphthacenedione	$C_{18}H_{10}O_4$	426–446	36.52	17 349 ($\pm$174)

[a] Uncertainty calculated at a 95% confidence level.
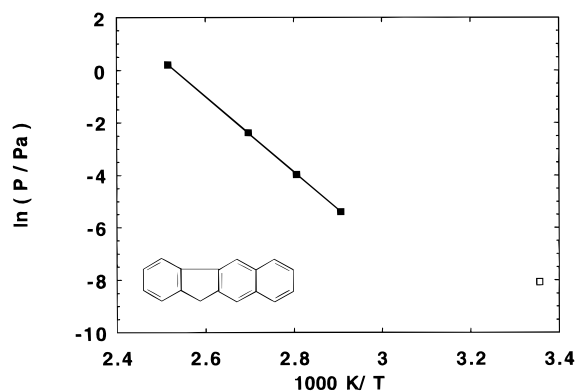
Figure 5. Vapor pressures for 2,3-benzofluorene obtained using the isothermal Knudsen effusion method: $\square$, Nass et al. (1995); $\blacksquare$, this study.
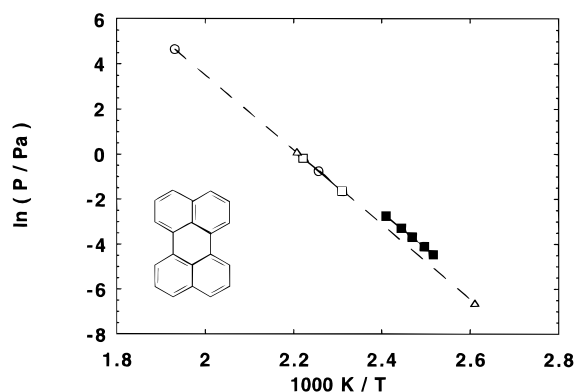

Figure 6. Vapor pressures for perylene, showing literature results and results obtained here using the isothermal Knudsen effusion method: $\square$, Stephenson and Malanowski (1987); $\bigcirc$, Gigli et al. (1973); $\triangle$, Hoyer and Peperle (1958); $\blacksquare$, this study.

a slight decrease in vapor pressure using this other sample, and the difference was not nearly large enough to explain the discrepancy. Thus there appears to be a need for further verification of the results obtained to date on this compound. The calculated enthalpy of vaporization is (132.6 $\pm$ 3.6) kJ/mol. The two previously published data sets shown in Figure 6 give values of sublimation enthalpy between 137.6 and 139.0 kJ/mol, both of which are outside the range of uncertainty in our values. It is apparent from Figure 6, however, that the major part of the discrepancy in vapor pressure results has to do with the value of A, rather than enthalpy. It should also be noted that the pressure and temperature ranges of the present measurements on this compound were not at all unusual, and

encountered with several other compounds, the results for which gave good agreement with the literature. Thus we have no ready explanation for the difference in our results from those in the literature. It should also be noted that other studies on perylene have given somewhat lower values of sublimation enthalpy, as may be noted from Table 4. Thus, there remains some considerable disagreement as to values for this compound.

Figure 7 shows the results for pentacene. In contrast to the previous case, the present vapor pressure results again agree reasonably with published literature values. The enthalpy of sublimation is quite high, (156.9 $\pm$ 13.6) kJ/mol. This value agrees quite reasonably with other reports of enthalpy of sublimation for this compound (see Table 4).

Figure 8 shows the results for coronene. These results are seen to be in good agreement with one set of published values, and at odds with two other sets. The measured value of enthalpy of sublimation is (133.1 $\pm$ 5.1) kJ/mol. This agrees well with one set of values reported in Table 4 but is at variance with several others, as might be expected from Figure 8.

Figure 9 presents the data obtained for phenanthridine. There is a significant discrepancy in the range of temperatures at which the present data overlap those of McEachern et al. (1975). In this case, the full set of data obtained by the latter group has been indicated on the figure as well. It appears that there is fair agreement when the present data are extrapolated to the lower temperature range of the McEachern et al. data. In this case, a single fit to all of the available data is shown on the figure. The value of the enthalpy of sublimation calculated from our data set alone is (100.1 $\pm$ 10.1) kJ/mol. Calculated from the combined data set, the value is 105.7 kJ/mol. Both values are quite far from the other reported value.

It is interesting to note that the enthalpy of sublimation for phenanthridine is only about 5% higher than that of the structurally very similar phenanthrene, the data for which are shown in Figure 9 as a line. The vapor pressure of the phenanthridine is seen to be lower than that of the phenanthrene by a factor of about 4 to 5, in the range of temperatures examined here.

The remaining figures all involve compounds for which no literature data were found. Figure 10 shows the results for perinaphthenone, for which the enthalpy of sublimation is (97.2 $\pm$ 2.5) kJ/mol. Figure 10 also gives the results for the structurally quite similar 3-hydroxy-1*H*-phenalen-1-one. This compound differs from perinaphthenone only in having an additional hydroxyl. The vapor pressure is

Table 4. Comparison of Sublimation Enthalpies Obtained in This Work with Published Values

temp range/K	$\Delta_{sub}H/$ kJ·mol^{-1}	reference
	Anthracene	
298	99.7	Nass et al. (1995)
283−323	91.7	Sonnefeld et al. (1983)
303−373	103.4	Hoyer and Peperle (1958)
313−363	102.6	Hansen and Eckert (1986)
318−363	100.0 (±2.8)	this study
337−360	100.3	De Kruif (1980)
339−353	101.9	Bradley and Cleasby (1952)
342−353	98.5	Kelley and Rice (1964)
358−392	94.8	Macknick and Prausnitz (1979)
354−399	94.6	Bender et al. (1983)
365	91.7	Inokuchi et al. (1952)
	Phenanthrene	
298	88.9	Nass et al. (1995)
273−333	95.9	Hoyer and Peperle (1958)
283−323	95.0	Sonnefeld et al. (1983)
303−333	95.0 (±4.4)	this study
315	90.8	Inokuchi et al. (1952)
315−335	90.5	De Kruif (1980)
323−348	96.5	Sato et al. (1986)
325−363	87.2	Macknick and Prausnitz (1979)
372	87.2	Osborn and Douslin (1975)
	Pyrene	
298	97.9	Nass et al. (1995)
298	100.2	Smith et al. (1980)
298	101.0	Malaspina et al. (1974)
283−323	91.2	Sonnefeld et al. (1983)
298−363	100.5	Hoyer and Peperle (1958)
308−398	103.1 (±6.5)	this study
345−358	93.9	Bradley and Cleasby (1952)
352	99.6	Inokuchi (1952)
348−419	92.7	Malaspina et al. (1974)
353−413	97.7	Sasse et al. (1988)
	2,3-Benzofluorene	
298	111.2	Nass et al. (1995)
344−398	119.3 (±1.3)	this study
	Naphthacene	
298	126.5	Nass et al. (1995)
386−472	126.1 (±9.0)	this study
385−475	124.7	Wakayama and Inokuchi (1967)
376−478	129.0	Stephenson & Malanowski (1987)
419−446	128.1	DeKruif (1980)
459	117.4	Inokuchi (1952)
	Perylene	
298	123.2	Nass et al. (1995)
391−424	132.6 (±3.6)	this study
415	129.6	Inokuchi (1952)
383−453	139.0	Hoyer and Peperle (1958)
443−518	137.6 (481 K)	Gigli et al. (1973)
	Pentacene	
443−483	156.9 (±13.6)	this study
495−530	154.5	DeKruif (1980)
444−565	158.2	Stephenson & Malanowski (1987)
	Coronene	
298	143.2	Nass et al. (1995)
407	151.9	Inokuchi (1952)
421−504	133.1 (±5.1)	this study
427−510	135.9	Murray et al. (1974)
425−515	128.4	Wakayama and Inokuchi (1967)
433−513	147.0	Hoyer and Peperle (1958)
	Phenanthridine	
288−323	94.6	McEachern et al. (1975)
309−437	100.1 (±10.1)	this study
	Perinaphthenone	
326−348	97.2 (±2.5)	this study
	3-Hydroxy-1*H*-phenalen-1-one	
402−432	151.5 (±4.7)	this study
	Benz[*g*]isoquinoline-5,10 dione	
334−381	108.1 (±1.6)	this study
	1,2 Benzodiphenylene Sulfide	
325−373	111.9 (±1.2)	this study
	1-Hydroxypyrene	
369−394	129.0 (±3.2)	this study
	6,11-Dihydroxy-5,12-naphthacenedione	
426−446	144.2 (±1.4)	this study
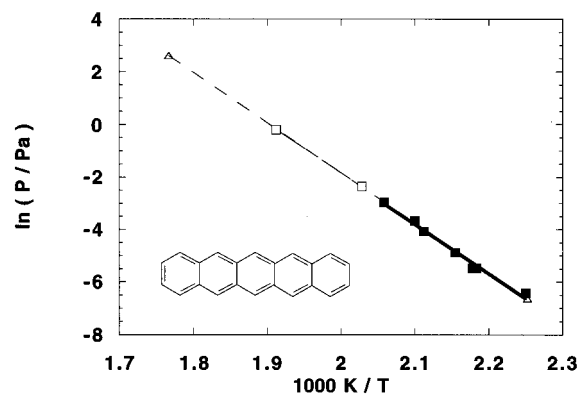
Figure 7. Vapor pressures for pentacene, showing literature results and results obtained here using the isothermal Knudsen effusion method: △, Stephenson and Malanowski (1987); □, De Kruif (1980); ■, this study.
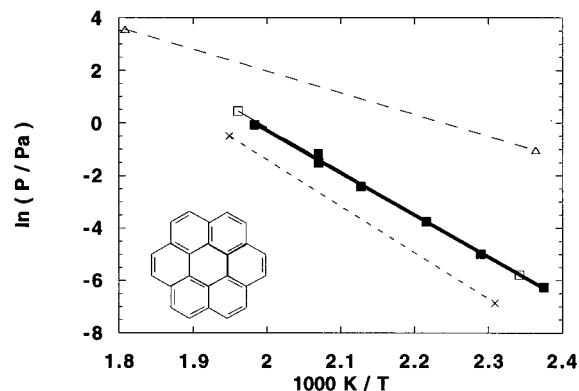
Figure 8. Vapor pressures for coronene, showing literature results and results obtained here using the isothermal Knudsen effusion method: △, Wakayama and Inokuchi (1967); □, Murray et al. (1974); ×, Hoyer and Peperle (1958); ■, this study.
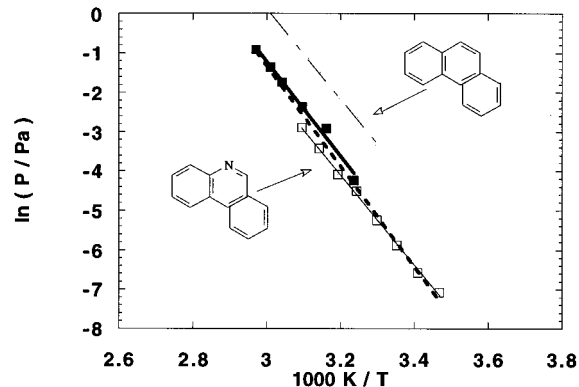
Figure 9. Vapor pressures for phenanthridine, showing literature results and results obtained here using the isothermal Knudsen effusion method. Comparison is also made with the results for phenanthrene (thin dashed line), reported in Figure 3. □, McEachern et al. (1975); ■, this study. The heavy dashed line shows the results of a regression combining the two sets of data.

tremendously decreased by the presence of a hydroxyl group. Note that it was impossible to obtain data on these compounds in an overlapping temperature range, owing to the large difference in vapor pressures. A large difference in vapor pressures is not unexpected, owing to the possibility of hydrogen bonding in one case. The enthalpy of sublimation for 3-hydroxy-1*H*-phenalen-1-one is (151.5 ± 4.7) kJ/mol. The difference in enthalpies of sublimation of these two compounds (54.3 kJ/mol) is of a magnitude that suggests that a hydrogen-bonding contribution, in-
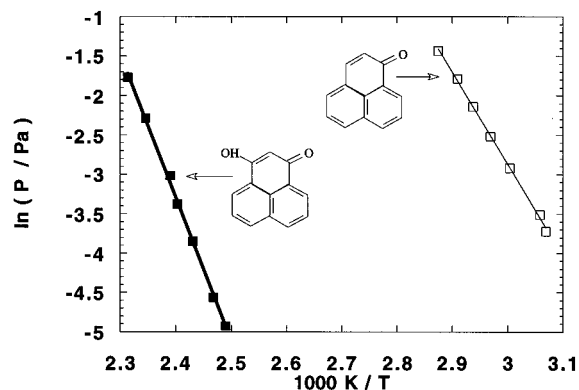
Figure 10. Vapor pressures for perinaphthenone (□) and 3-hydroxy-1*H*-phenalen-1-one (■) obtained using the isothermal Knudsen effusion method.
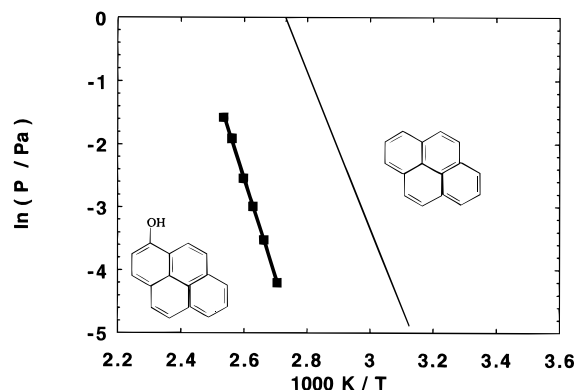

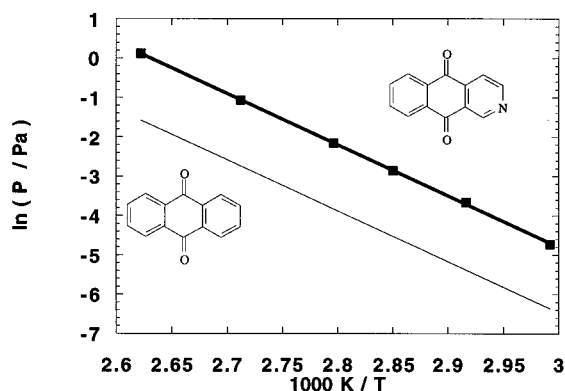**Figure 11.** Vapor pressures for benz[*g*]isoquinoline-5,10-dione obtained using the isothermal Knudsen effusion method (■). Data for anthraquinone, from Bardi et al. (1973), are shown for comparison (thin line).

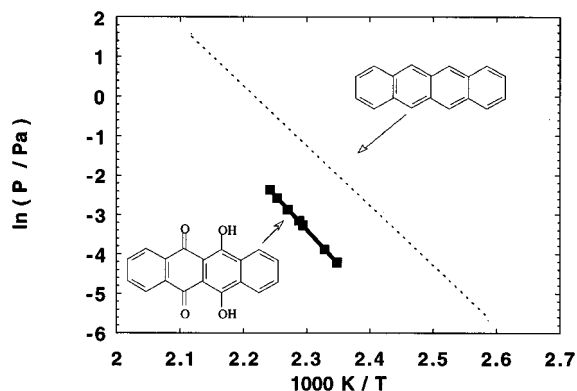**Figure 12.** Vapor pressures for 1,2-benzodiphenylenesulfide obtained using the isothermal Knudsen effusion method.

Figure 13. Vapor pressures for 1-hydroxypyrene obtained using the isothermal Knudsen effusion method (■). Data for pyrene, from Figure 4, are shown for comparison (thin line).

Figure 14. Vapor pressures for 6,11-dihydroxy-5,12-naphthacene-dione obtained using the isothermal Knudsen effusion method (■). Data for naphthacene, from Figure 2, are shown for comparison (dotted line).

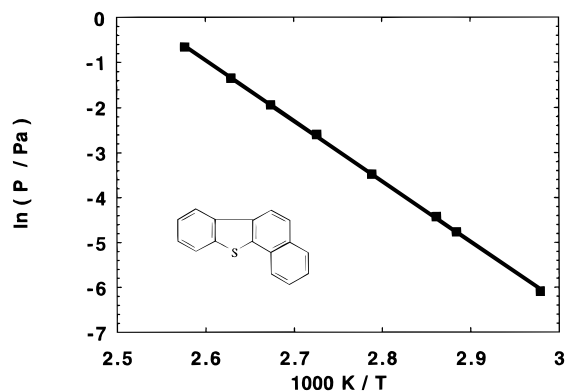volving the hydroxyl group, may be a major contributor.

Figure 11 shows the results for benz[*g*]isoquinoline-5,-10-dione. This compound is structurally quite similar to anthraquinone, data for which are shown for comparison (Bardi et al., 1973). The calculated enthalpy of sublimation for benz[*g*]isoquinoline-5,10-dione is (108.1 ± 1.6) kJ/mol. This is quite similar to the value for anthraquinone reported by Bardi et al., which at 357 K (in the middle of the temperature range of interest) is 110.6 kJ/mol. The vapor pressure of the anthraquinone is, however, seen to be lower by more than a factor of 5 than that of the nitrogen-containing analogue examined here.

Figure 12 shows the results for 1,2-benzodiphenylene sulfide. This compound gives an enthalpy of sublimation which is (111.9 ± 1.2) kJ/mol.

Figure 13 gives the results for 1-hydroxypyrene, which is similar in structure to pyrene. The figure shows the comparison of the vapor pressure behaviors of these two compounds. The enthalpy of sublimation for 1-hydroxy-pyrene is (129.0 ± 3.2) kJ/mol, which is significantly higher than the enthalpy of sublimation for pyrene (103.1 kJ/mol). The difference attributable to the addition of a hydroxyl group is in this case only 25.9 kJ/mol, which is substantially less than the contribution observed in the perinaphthenone case. Of course, the main hydrogen bonding possibilities in the present case are limited to hydroxyl–hydroxyl interactions only. In this respect, the value of the increment in enthalpy of sublimation appears quite reasonable. The vapor pressure of the hydroxyl-containing pyrene is almost 2 orders of magnitude decreased relative to pyrene itself.

Figure 14 presents the data for 6,11-dihydroxy-5,12-naphthacenedione and compares these data with those for naphthacene presented above. The enthalpy of sublimation for the substituted naphthacene is (144.2 ± 1.4) kJ/mol, which compares with the value of 95.0 for naphthacene itself. The observed vapor pressure for the substituted naphthacene is also approximately an order of magnitude lower than that for naphthacene itself.

Literature Cited

Bardi, G.; Gigli, R.; Malaspina, L.; Piacente, V. Vapor Pressure and Sublimation Enthalpy of Anthraquinone and of 1,5- and 1,6-Dihydroxyanthraquinone. *J. Chem. Eng. Data* **1973**, *18*, 126–130.

Bender, R.; Bieling, V.; Maurer, G. The Vapor Pressures of Solids: Anthracene, Hydroquinone, and Resorcinol. *J. Chem. Thermodyn.* **1983**, *15*, 585–594.

Bidleman, T. F. Estimation of Vapor Pressures for Nonpolar Organic Compounds by Capillary Gas Chromatography. *Anal. Chem.* **1984**, *56*, 2490−2496.

Bradley, R. S.; Cleasby, T. G. The Vapor Pressure and Lattice Energy of Some Aromatic Ring Compounds. *J. Chem. Soc.* **1953**, *2*, 1690−1692.

DeKruif, C. G. Enthalpies of Sublimation and Vapor Pressures of 11 Polycyclic Hydrocarbons *J. Chem. Thermodyn.* **1980**, *12*, 243−248.

Fletcher, T.; Kerstein, A.; Pugmire, R.; Solum, M.; Grant, D. Chemical Percolation Model for Devolatilization. 3. Direct Use of 13C NMR Data to Predict Effects of Coal Type. *Energy Fuels* **1992**, *6*, 414−431.

Gigli, R.; Malaspina, L.; Bardi, G. Vapor Pressure and Sublimation Enthalpy of Perylene. *Ann. Chim.* **1973**, *63*, 627−633.

Hansen, P. C.; Eckert, C. A. An Improved Transpiration Method for the Measurement of Very Low Vapor Pressures *J. Chem. Eng. Data* **1986**, *31*, 1−3.

Hollahan, J. Molecular Effusion: Its Newer Features and Applications. *J. Chem. Educ.* **1962**, *39*, 23−26.

Hoyer, H.; Peperle, W. Vapor Pressure Measurements on Organic Compounds and their Sublimation Heats. *Z. Elektrochem.* **1958**, *62*, 61−66.

Inokuchi, H.; Shiba, S.; Handa, T.; Akamatu, H. Heats of Sublimation of Condensed Polynuclear Aromatic Hydrocarbons. *Bull. Chem. Soc. Jpn.* **1952**, *25*, 299−302.

Kelley, J. D.; Rice, F. O. The Vapor Pressures of Some Polynuclear Aromatics. *J. Phys. Chem.* **1964**, *68*, 3794−3796.

Knudsen, M. *Ann. Phys.* **1909**, *28*, 999; *29*, 179.

Macknick, A. B.; Prausnitz, J. M. Vapor Pressures of High Molecular Weight Hydrocarbons. *J. Chem. Eng. Data* **1979**, *24*, 175−178.

Malaspina, L.; Bardi, G.; Gigli, R. Simultaneous Determination by Knudsen Effusion Microcalorimetric Technique of the Vapor Pressure and Enthalpy of Vaporization of Pyrene and 1,3,5-Triphenylbenzene, *J. Chem. Thermodyn.* **1974**, *6*, 1053−1064.

McEachern, D. M.; Iniguez, J. C.; Ornelas, H. C. Enthalpies of Combustion and Sublimation and Vapor Pressures of Three Benzoquinolines *J. Chem. Eng. Data* **1975**, *20*, 226−228.

Murray, J. J.; Pottie, R. F.; Pupp, C. The Vapor Pressures and Enthalpies of Sublimation of Five Polycyclic Aromatic Hydrocarbons. *Can. J. Chem.* **1974**, *52*, 557−563.

Nass, K.; Lenoir, D.; Kettrup, A. Calculation of the Thermodynamic Properties of Polycyclic Aromatic Hydrocarbons by an Incremental Procedure. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1735−1736.

Niksa, S.; Kerstein, A. R. FLASHCHAIN Theory for Rapid Coal Devolatilization Kinetics. 1. Formulation. *Energy Fuels* **1991**, *5*, 647−665.

Oja, V.; Suuberg, E. M. Development of a Non-Isothermal Knudsen Effusion Method and Application to PAH and Cellulose Tar Vapor Pressure Measurements. *Anal. Chem.* **1997**, *69*, 4619−4626.

Osborn, A. G.; Douslin, D. R. Vapor Pressures and Derived Enthalpies of Vaporization for Some Condensed-Ring Hydrocarbons. *J. Chem. Eng. Data* **1975**, *20*, 229−231.

Sasse, K.; Jose, J.; Merlin, J.-C. A Static Apparatus for Measurement of Low Vapor Pressures. Experimental Results on High Molecular Weight Hydrocarbons. *Fluid Phase Equilib.* **1988**, *42*, 287−304.

Sato, N.; Inomata, H.; Arai, K.; Saito, S. Measurement of Vapor Pressures for Coal-Related Aromatic Compounds by Gas Saturation Method. *J. Chem. Eng. Jpn.* **1986**, *19*, 145−147.

Smith, N. K.; Stewart, R. C., Jr.; Osborn, A. G.; Scott, D. W. Pyrene: Vapor Pressure, Enthalpy of Combustion, and Chemical Thermodynamic Properties. *J. Chem. Thermodyn.* **1980**, *12*, 919−926.

Solomon, P. R.; Hamblen, D. G.; Carangelo, R. M.; Serio, M. A.; Deshpande, G. V. General Model of Coal Devolatilization. *Energy Fuels,* **1988**, *2*, 405−422.

Sonnefeld, W. J.; Zoller, W. H.; May, W. E. Dynamic Coupled Column Liquid Chromatographic Determination of Ambient Temperature Vapor Pressures of Polynuclear Aromatic Hydrocarbons. *Anal. Chem.* **1983**, *55*, 275−280.

Stephenson, R. M.; Malanowski, S. *Handbook of the Thermodynamics of Organic Compounds*; Elsevier: Amsterdam, 1987.

Suuberg, E. M. Mass Transfer Effects in Pyrolysis of Coals: A Review of Experimental Evidence and Models. In *Chemistry of Coal Conversion*; Schlosberg, R., Ed.; Plenum: New York, 1985; pp 67−119.

Wakayama, N.; Inokuchi, H. Heats of Sublimation of Polycyclic Aromatic Hydrocarbons and their Molecular Packings. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2267−2271.