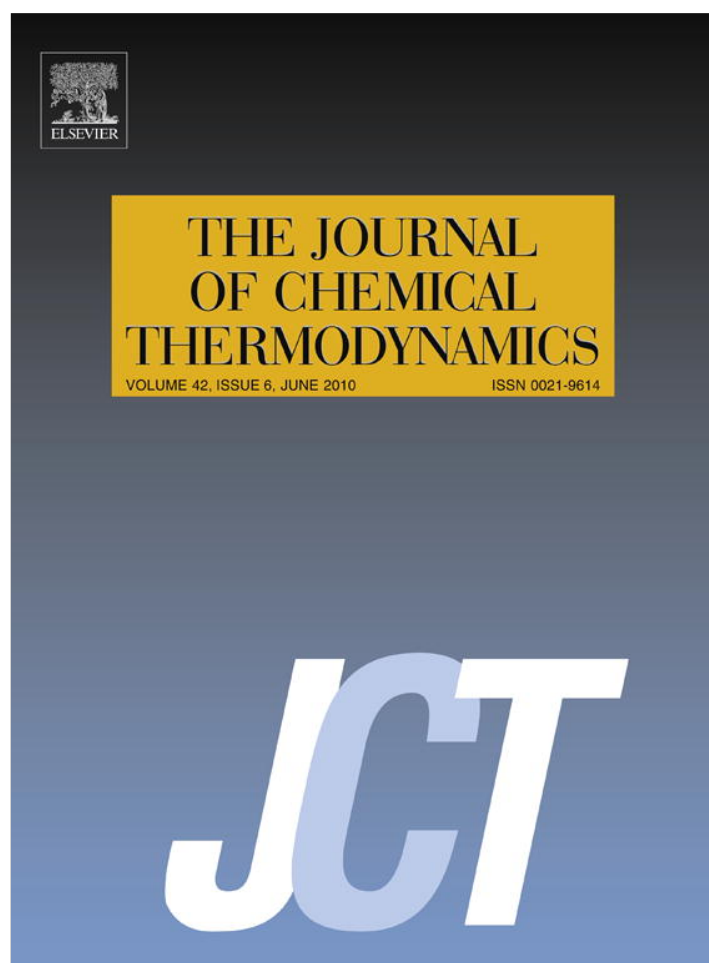


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# Vapor pressures and sublimation enthalpies of seven heteroatomic aromatic hydrocarbons measured using the Knudsen effusion technique

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## ABSTRACT

The vapor pressures of seven heteroatom-containing cyclic aromatic hydrocarbons, ranging in molecular weight from (168.19 to 208.21)  $\text{g} \cdot \text{mol}^{-1}$  were measured over the temperature range of (301 to 486) K using the isothermal Knudsen effusion technique. The compounds measured include: anthraquinone, 9-fluorenone, 9-fluorenone oxime, phenoxazine, phenoxathiin, and 9H-pyrido[3,4-b]indole. These solid-state sublimation measurements provided values that are compared to vapor pressures of parent aromatic compounds (anthracene and fluorene) and to others with substituent groups in order to examine the effects of alcohol, ketone, pyridine, and pyrrole functionality on this property. The enthalpies and entropies of sublimation for each compound were determined from the Clausius–Clapeyron equation. Though there is no consistent trend in terms of the effects of substitutions on changes in the enthalpy or entropy of sublimation, we note that the prevalence of enthalpic or entropic driving forces on vapor pressure depend on molecule-specific factors and not merely molecular weight of the substituents.

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## 1. Introduction

High molecular weight aromatic compounds, including polycyclic aromatic hydrocarbons (PAH) and their derivatives, polycyclic aromatic compounds (PAC), are common environmental pollutants, resulting from the incomplete combustion of coal, fossil fuels, and other anthropogenic sources. For example, fluorene, from which fluorenone is a known oxidation product, is commonly present in excess of 1% in coal tar mixtures. 9-Fluorenone, with its carbonyl group on a central carbon between aromatic rings, readily forms oximes, such as 9-fluorenone oxime [1]. The seven heteroatomic and heterocyclic aromatic compounds investigated herein are only some examples of compounds of potential interest, and for which few thermodynamic property measurements are available.

Vapor pressure data are important inputs into models that predict the fate and transport of such high molecular weight compounds. Yet few data exist on these classes of compounds, owing to the difficulty in obtaining such data. High molecular weight compounds tend to degrade at the high temperatures needed to measure their relatively low vapor pressures directly, such that indirect methods must be used. Here we employ the isothermal Knudsen effusion technique, which is commonly used for such measurements and which is well described in the literature [2–4].

The vapor pressures measured in the present experiments are sublimation vapor pressures, as these compounds all exist in the solid phase at near-ambient temperature and pressure. Under the common assumption of constant enthalpy of sublimation,  $\Delta H_{\text{sub}}$ , over the modest temperature ranges employed, the vapor pressure data may be represented by the integrated form of the Clausius–Clapeyron equation:

$$\ln P^{\text{vap}} = -\Delta H_{\text{sub}}/RT + \Delta S_{\text{sub}}/R, \quad (1)$$

where  $P^{\text{vap}}$  is the saturation vapor pressure of the compound,  $R$  the universal gas constant,  $T$  the absolute temperature, and  $\Delta S_{\text{sub}}$  the entropy of sublimation. This representation of the Clausius–Clapeyron equation considers the sublimed PAC to behave as an ideal gas, which under the current conditions of low pressure and moderate temperature is quite appropriate.

The vapor pressures of pure PAC span many orders of magnitude at ambient temperatures. Vapor pressures are sensitive to variables such as molecular weight, carbon to hydrogen ratio (bond saturation), as well as intramolecular bonding, and intermolecular bonding interactions.

## 2. Experimental

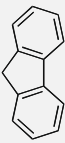
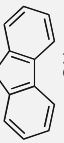
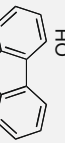
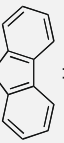
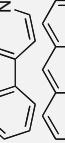
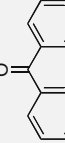
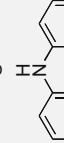
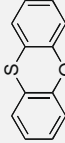

### 2.1. The Knudsen effusion technique

The Knudsen effusion technique is employed by numerous researchers, and derives from Knudsen's 1909 Kinetic Theory of

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**TABLE 1**  
Summary of compounds studied and sublimation enthalpy data obtained compared to fluorene [4] and anthracene [4] (uncertainty calculated at a 95% confidence interval via linear regression in STATA v.9FE).

Compound	CAS Reg. No.	Molecular weight/ (g · mol <sup>-1</sup> )	Min. purity/mass fraction	Temp range/K	$\ln(p^{vap}) = a - b \cdot 10^3/(K/T)$	$\Delta H_{sub}/(kJ \cdot mol^{-1})$	$\Delta S_{sub}/(kJ \cdot K^{-1} \cdot mol^{-1})$	$p^{vap}$ at 298 K/Pa via Equation (1)	Molecular structure
Fluorene C <sub>13</sub> H <sub>10</sub>	86-73-7	166.22	>0.97	298–324	$32.85 \pm 0.79$ $10.60 \pm 0.28$	$88.1 \pm 2.3$	$0.273 \pm 0.0066$	$6.58E-02$	
9-Fluorenone C <sub>13</sub> H <sub>8</sub> O	486-25-9	180.20	>0.98	301–343	$30.98 \pm 1.3$ $10.64 \pm 0.45$	$88.5 \pm 3.7$	$0.258 \pm 0.011$	$8.87E-03$	
9-Fluorenone oxime C <sub>13</sub> H <sub>10</sub> NO	1689-64-1	182.22	>0.95	326–366	$32.06 \pm 0.82$ $11.72 \pm 0.30$	$97.4 \pm 2.5$	$0.267 \pm 0.007$	$6.97E-04$	
9-Fluorenone oxime C <sub>13</sub> H <sub>9</sub> NO	2157-52-0	195.22	>0.97	375–399	$28.82 \pm 0.45$ $9.57 \pm 0.15$	$79.6 \pm 1.2$	$0.240 \pm 0.004$	$3.71E-02$	
9H-pyridolo[3,4-b]indole C <sub>11</sub> H <sub>8</sub> N <sub>2</sub>	244-63-3	168.19	>0.98	353–389	$33.83 \pm 0.58$ $13.77 \pm 0.24$	$114.5 \pm 2.0$	$0.281 \pm 0.005$	$4.20E-06$	
Anthracene C <sub>14</sub> H <sub>10</sub>	120-12-7	178.23	>0.99	322–348	$32.59 \pm 1.1$ $11.85 \pm 0.40$	$98.5 \pm 3.3$	$0.271 \pm 0.009$	$7.65E-04$	
Anthraquinone C <sub>14</sub> H <sub>8</sub> O <sub>2</sub>	84-65-1	208.21	>0.98	346–400	$34.53 \pm 1.5$ $13.83 \pm 0.60$	$115.0 \pm 5.0$	$0.287 \pm 0.012$	$6.93E-06$	
Phenoxazine C <sub>12</sub> H <sub>8</sub> NO	135-67-1	183.21	>0.95	330–365	$34.36 \pm 0.77$ $12.50 \pm 0.28$	$103.9 \pm 2.3$	$0.286 \pm 0.006$	$5.07E-04$	
Phenoxathin C <sub>12</sub> H <sub>6</sub> OS	262-20-4	200.26	>0.98	304–325	$35.60 \pm 0.82$ $11.58 \pm 0.27$	$96.3 \pm 2.2$	$0.296 \pm 0.007$	$3.84E-02$	

Gases. In this theory, the molecular effusion out of a small orifice in an otherwise sealed container is related to the vapor pressure of the compound in the container [5]:

$$P^{\text{vap}} = m/W_0 A_0 (2\pi RT/M)^{1/2}, \quad (2)$$

where  $m$  is the mass loss rate of compound from the container (or cell),  $A_0$  the orifice area,  $M$  the molecular weight of the compound, and the Clausing factor,  $W_0$ , is a measure of the probability that a molecule entering the orifice from inside the cell escapes through the orifice to the exterior of the cell (hence it takes values between 0 and 1). The Clausing factor can be calculated based solely upon geometrical factors (see equation (3)) or it may be back calculated from mass effusion data for compounds of known vapor pressure contained in the cell of interest. In our case, the effusion cell is fabricated of 001 gauge stainless steel foil with a single round orifice of approximately (0.6 to 0.8) mm drilled in its cover. The orifice diameter is measured using an optical microscope and scale accurate to 0.05 mm. These dimensions may be used to calculate the Clausing factor using the equation recommended in [6]:

$$W_0 = 1/(1 + 3/8r), \quad (3)$$

where  $l$  is the effusion length (*i.e.* cell material thickness) and  $r$  the orifice radius. The calculated Clausing factors of our cells ranged from 0.96 to 0.98. These calculated values compared very favorably to those obtained by back-calculation from effusion rate data on compounds of known vapor pressure.

We used an effusion apparatus as described elsewhere [4]. Briefly, the effusion cell is suspended on one arm of a Cahn 2000 microbalance with a 1 g capacity, accurate to  $\pm 0.05$  mg. The temperature is measured with an Omega type K thermocouple, accurate to  $\pm 0.1$  K, which sits directly above the effusion cell opening and records continuously at the same pre-determined intervals as the mass recording. The thermocouple is periodically calibrated against a NIST-traceable thermometer with a 0.1 K accuracy. The cell is enclosed within a glass vacuum enclosure vessel and is hung on a balance wire, inside a copper capsule painted black to promote heat transfer via radiation. Above the black capsule and oven is a condenser operating between ( $-20$  and  $20$ ) °C, used for condensing the effusing vapors onto the glass walls and maintaining the high vacuum.

## 2.2. Materials examined

The reliable performance of this apparatus was verified using fluorene, anthracene, and pyrene; these results are presented elsewhere [4]. We obtained excellent agreement between our data and available literature data for these well-studied compounds.

All seven hetero-atom-containing compounds were obtained from TCI America at a minimum purity of 0.95 (mass fraction). Their purities and molecular structures are given in table 1. It has been shown [7] that subliming at least 0.06 mass fraction of each compound before commencing data collection is sufficient to remove volatile impurities, and data collection was halted when a mass fraction of 0.06 of starting weight remained in the cell to account for non-volatile impurities. A mass spectrometer showed that for sample mass fraction loss between 0.01 and 0.04 a large amount of volatile impurities are sometimes evolved, whereas above 0.05 fractional mass loss the compound of interest accounts for virtually all of the mass spectrometer signal [7]. In addition, we performed a routine gas chromatograph/mass spectrometer (GC/MS) analysis of a sample of 9-fluorenone (minimum 0.95 mass fraction purity). 9-Fluorenone (20.3 mg) was sublimed in an effusion cell at 328 K until the mass of the compound in the cell reached 18.6 mg (a fractional mass loss of 0.084). The cell was removed and its contents analyzed in a Perkin Elmer Clarus GC/MS using

EPA method 8270D. The sample was shown to be greater than 0.99 (mass fraction) pure with only trace impurities, confirming our original in-stream MS results as presented elsewhere [7]. Each compound was run at least twice with two different effusion cells and data were taken at each temperature in the selected range chosen at random, to avoid any biasing that might be associated with consistent increase or decrease of temperature. We were able to

TABLE 2

Sublimation vapor pressure data obtained for heteroatomic aromatic compounds using the isothermal Knudsen effusion technique.

T/K	$P^{\text{vap}}$ /Pa	T/K	$P^{\text{vap}}$ /Pa
<i>9-Fluorenone</i>			
300.8	0.0121	328.4	0.246
303.6	0.0169	328.6	0.245
307.9	0.0279	330.9	0.311
309.8	0.0365	331.1	0.319
313.0	0.0510	331.9	0.345
313.1	0.0509	336.5	0.528
315.1	0.0616	336.6	0.540
323.0	0.139	337.8	0.596
323.1	0.143	337.9	0.599
324.5	0.159	342.7	0.937
324.7	0.167	342.8	0.952
<i>9-Fluorenone</i>			
326.1	0.0210	344.7	0.144
327.5	0.0244	346.1	0.159
329.8	0.0315	347.4	0.186
331.3	0.0374	351.2	0.276
334.9	0.0512	355.1	0.402
340.9	0.101	358.7	0.560
342.6	0.115	361.9	0.740
343.6	0.123	366.1	1.03
<i>9-Fluorenone oxime</i>			
374.5	0.175	386.2	0.385
376.6	0.198	387.9	0.428
378.5	0.231	389.9	0.474
382.6	0.302	393.8	0.613
383.2	0.317	395.2	0.671
		398.6	0.816
<i>9H-Pyrido[3,4-b]indole</i>			
352.8	0.00570	374.4	0.0545
363.8	0.0174	378.2	0.0753
367.9	0.0256	381.8	0.103
368.1	0.0272	382.0	0.107
370.3	0.0337	382.2	0.108
371.4	0.0416	385.4	0.141
371.5	0.0416	385.9	0.155
374.1	0.0503	389.2	0.218
		389.4	0.229
<i>Anthraquinone</i>			
346.0	0.00449	380.1	0.149
359.9	0.0209	385.4	0.267
360.9	0.0220	385.8	0.263
362.7	0.0252	386.8	0.305
367.4	0.0410	392.7	0.493
369.9	0.0542	392.8	0.494
377.6	0.119	393.4	0.519
379.2	0.144	399.2	0.872
		399.9	0.948
<i>Phenoxazine</i>			
329.7	0.0281	346.9	0.196
336.7	0.0594	348.2	0.220
340.9	0.102	352.9	0.345
340.9	0.102	353.1	0.363
344.9	0.164	356.7	0.483
345.1	0.164	360.9	0.748
		364.5	1.07
<i>Phenoxathiin</i>			
304.2	0.0861	311.9	0.217
308.7	0.143	318.2	0.453
311.4	0.209	323.0	0.771
311.5	0.207	324.5	0.927

reproduce the measured vapor pressures no matter the temperature path followed.

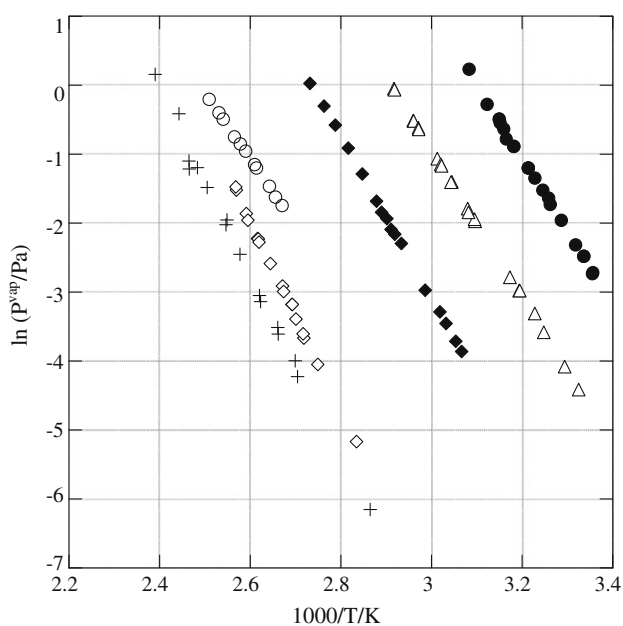
### 3. Results

Data were taken over a temperature range specific to each compound. The mass loss rate from the effusion cell must be great enough to permit its accurate determination outside of the range of balance noise. This determined the minimum temperature for each compound. Each sample is kept below its melting point such that only sublimation vapor pressures are measured. The rate of mass effusing from the cell ranged from  $(10^{-8}$  to  $10^{-6})$   $\text{g}\cdot\text{s}^{-1}$ , depending on the orifice size. This yielded vapor pressures between (0.004 and 1.07) Pa for the seven compounds measured, as detailed in table 2.

Table 1 presents the results of fitting the data with the Clausius–Clapeyron equation (equation (1)) along with the statistical significance of these results; a 95% confidence interval was calculated via linear regression for each set of experimental results. The enthalpy and entropy values presented here are calculated using the slope and intercept of the Clausius–Clapeyron equation for the temperature range indicated in table 1 and no corrections have been made to any other standard conditions.

#### 3.1. Fluorene derivatives

This laboratory previously reported the vapor pressure and enthalpy of sublimation of pure fluorene in the temperature range of (298 to 324) K; the enthalpy of sublimation was  $87.1 \pm 1.9$   $\text{kJ}\cdot\text{mol}^{-1}$  [4]. Here we examined three derivatives of fluorene containing oxygen and nitrogen substituent groups: 9-fluorenone, 9-fluorenone, and 9-fluorenone oxime. All heteroatom substituents were located on the 9-carbon position of the five-member ring of fluorene, providing an excellent opportunity to compare the effect of a particular substituent group on this parent PAH. Data are shown in figure 1, along with some earlier reported data on the parent compound and another related compound (9-fluorene-carboxylic acid [8]).



**FIGURE 1.** Vapor pressure as a function of temperature for fluorene and its substituted derivatives. ●, Fluorene [4]; △, 9-fluorenone; ◆, 9-fluorenone; ○, 9-fluorenone oxime; ◇, 9H-Pyrido[3,4-b]indole; and +, 9-fluorene-carboxylic acid [8].

The enthalpy of sublimation of 9-fluorenone is  $88.5 \pm 3.7$   $\text{kJ}\cdot\text{mol}^{-1}$ , measured between (301 and 343) K, and is only slightly higher than fluorene and actually the same within the limits of experimental uncertainty. Verevkin [9] reported an enthalpy of sublimation for 9-fluorenone of  $91.7 \pm 7.6$   $\text{kJ}\cdot\text{mol}^{-1}$  in the temperature range of (323 to 349) K while Hansen and Eckert [10], using a gas transpiration method between (298 and 343) K, found an enthalpy of sublimation of 9-fluorenone of  $92.3 \pm 1.2$   $\text{kJ}\cdot\text{mol}^{-1}$ . Both of these results fall within the limits of uncertainty for our results.

The regression lines for fluorene and 9-fluorenone in figure 1 appear parallel and indeed their slopes are almost identical, indicating very similar enthalpies of sublimation. It is the entropy of sublimation that shows a significant influence of the ketone group in 9-fluorenone. The value of  $\Delta S_{\text{sub}}/R$  for 9-fluorenone is  $31.0 \pm 3.7$ , compared to 32.9 for fluorene, corresponding to entropies of sublimation of (0.258 and 0.273)  $\text{kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for 9-fluorenone and fluorene, respectively. The lower vapor pressures of the ketone-form PAC are thus mainly attributable to a lower entropy change on vaporization compared to the fluorene.

Pure fluorene exhibits herringbone stacking, stabilized by van der Waals forces [11]. X-ray diffraction studies have shown that 9-fluorenone assumes similar packing to fluorene [12]. The small decrease in vapor pressure and thus sublimation entropy, indicate only a slightly more disordered solid phase than in fluorene.

At 326 K the vapor pressure of 9-fluorenone is almost an order of magnitude lower than 9-fluorenone. The low vapor pressures of this compound required measurements in a temperature range considerably higher than that for 9-fluorenone and fluorene – between (326 and 366) K. In this temperature range, the sublimation enthalpy of 9-fluorenone is  $97.4 \pm 2.5$   $\text{kJ}\cdot\text{mol}^{-1}$ , and sublimation entropy is  $0.267$   $\text{kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , indicating the lower vapor pressure for 9-fluorenone as compared to fluorene is mainly driven by enthalpic effects. The enthalpy of sublimation of 9-fluorenone is considerably higher than that of either 9-fluorenone or fluorene, but its entropy of sublimation is only slightly higher than 9-fluorenone and slightly lower than fluorene. While we do not have structural data with which to verify this, it is our belief that the higher enthalpy of sublimation for 9-fluorenone likely has to do with existence of hydrogen bonding interactions in this compound.

The temperature range required to take data on 9-fluorenone oxime was higher than that required for the above compounds; an appreciable mass loss was not observed until temperatures exceeded 375 K (the oxime derivative also has a much higher melting temperature, ca. 466 K as compared with the parent fluorene, 385 K). Hence, 9-fluorenone oxime shows an even lower vapor pressure than the above compounds. The calculated enthalpy of sublimation was  $79.6 \pm 1.2$   $\text{kJ}\cdot\text{mol}^{-1}$  over the temperature range of (375 to 399) K, consistent with the much lower slope of the Clausius–Clapeyron plot shown in figure 1 for this compound as compared with the others discussed above. Meanwhile, the entropy of sublimation of 9-fluorenone oxime is  $0.240$   $\text{kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . In this case, the sublimation enthalpy and entropy are both significantly lower than those for the fluorene, though it needs to be emphasized that these values were not obtained in the same temperature range. The reader is again cautioned that the reported enthalpies and entropies are for the temperature range of measurement, and have not been corrected to a common standard basis (in some cases, the data necessary to make such a correction were unavailable). Nonetheless, these results seem to suggest that the oxime compound exists in a somewhat more disordered phase than the other fluorene derivatives.

Figure 1 also shows previously reported results for 9-fluorene-carboxylic acid (melting point 498 K) where even lower vapor pressures are seen for the carboxyl-substituted compound than for the oxime compound [8]. The carboxyl compound gave an enthalpy of sublimation of  $110.2$   $\text{kJ}\cdot\text{mol}^{-1}$  and entropy of

0.264 kJ · K<sup>-1</sup> · mol<sup>-1</sup>. Here again it is likely to be the influence of a strong hydrogen-bonding group on the 9-position of fluorene that determines a higher enthalpy of sublimation, which is the main factor leading to lower vapor pressures than pure fluorene.

Finally, figure 1 also shows the vapor pressure data for 9H-pyrido[3,4-b]indole, a heterocyclic compound with a similar structure to fluorene in which nitrogen replaces the 2 and 9 carbons of the parent fluorene. Its enthalpy of sublimation is 114.5 ± 1.2 kJ · mol<sup>-1</sup> and entropy of sublimation is 0.281 kJ · K<sup>-1</sup> · mol<sup>-1</sup>, both substantially higher than for fluorene. These are likely attributable to intermolecular hydrogen bonding in the 9H-pyrido[3,4-b]indole that result in a higher enthalpy, and with that, higher entropy of sublimation associated with the greater configurational requirements in the solid phase.

### 3.2. Anthracene derivatives

Anthracene has an enthalpy of sublimation of 98.5 ± 3.3 kJ · mol<sup>-1</sup> and an entropy of sublimation of 0.271 kJ · K<sup>-1</sup> · mol<sup>-1</sup> as measured in our laboratory over the temperature range of (322 to 348) K [4]. The vapor pressure of anthraquinone, with keto groups at both the 9 and 10 carbon positions, is considerably lower than that of pure anthracene, and gives an enthalpy of sublimation of 115.0 ± 5.0 kJ · mol<sup>-1</sup> and an entropy of sublimation of 0.287 kJ · K<sup>-1</sup> · mol<sup>-1</sup> in the temperature range of (346 to 400) K. Measurements on anthraquinone by Bardi *et al.* [13] in the temperature range of (397 to 471) K gave an enthalpy of 107.8 kJ · mol<sup>-1</sup> and an entropy of sublimation of 0.269 kJ · K<sup>-1</sup> · mol<sup>-1</sup>, both slightly lower than those measured here. These measurements were still well below the melting point of 558 K [14]. A decline in sublimation enthalpy with an increase in temperature is to be expected, and the temperature range investigated by Bardi *et al.* was significantly higher than that investigated here.

Pure anthracene, like fluorene, also assumes a herringbone-packing structure [15]. Evidence suggests that anthraquinone also assumes herringbone packing [16] with a slightly greater layer thickness than anthracene due to the presence of the oxygen groups on the molecule [17]. There is a large increase in interaction

energy associated with the interaction of the oxygen functional groups in the anthraquinone.

The replacement of anthracene's 9-carbon with nitrogen and 10-carbon with oxygen, creating phenoxazine, had a much less significant impact on the vapor pressure than anticipated. Phenoxazine, whose molecular structure is shown in table 1, has an enthalpy of sublimation 103.9 ± 2.3 kJ · mol<sup>-1</sup>, only slightly higher than that of pure anthracene, and an entropy of sublimation of 0.286 kJ · K<sup>-1</sup> · mol<sup>-1</sup>, again only slightly higher than anthracene. As seen in figure 2, the vapor pressures of anthracene and phenoxazine are fairly close; at 348.2 K the vapor pressure of anthracene is 0.263 Pa [4] and that of phenoxazine is 0.220 Pa.

Phenoxathiin is an analog of phenoxazine with sulfur and oxygen in the central ring, and its vapor pressure is significantly higher than that of anthracene. Because of the oxygen and sulfur substituents, phenoxathiin is not a planar molecular. As compared to anthracene, phenoxathiin has a slightly lower enthalpy and higher entropy of sublimation, 96.3 ± 2.2 kJ · mol<sup>-1</sup> and 0.296 kJ · K<sup>-1</sup> · mol<sup>-1</sup>, respectively, in the measured temperature range of (304 to 325) K. While the enthalpy of sublimation of phenoxathiin is comparable to that of pure anthracene, the entropic favorability of its sublimation results in its greater volatility as seen in figure 2 and tables 1 and 2. A recent article by Monte *et al.* [18] presents the vapor pressure of phenoxathiin in the temperature range of (318 to 373) K. Since the melting point of phenoxathiin is 328.8 K [19], if we consider only their data for phenoxathiin in the solid phase and apply the Clausius–Clapeyron equation, we obtain an enthalpy of sublimation for their data between (318 and 328) K of 96.2 ± 3.6 kJ · mol<sup>-1</sup> and an entropy of sublimation of 0.296 ± 0.31 kJ · K<sup>-1</sup> · mol<sup>-1</sup>, in excellent agreement with our data.

Hence, it appears that the higher volatility of this compound compared to anthracene is associated with the significant entropic favorability of the vaporization process. Fitzgerald *et al.* [20] note that the O, S, and H atoms have close intermolecular approaches making “straightforward an understanding of the absence of disorder in this structure.” Thus the solid phase is a tight structure, with a lower degree of disorder possible than is characteristic of the anthracene to which it is compared.

It is interesting to compare the results from phenoxathiin to thianthrene, a compound in which two sulfur atoms link the ben-

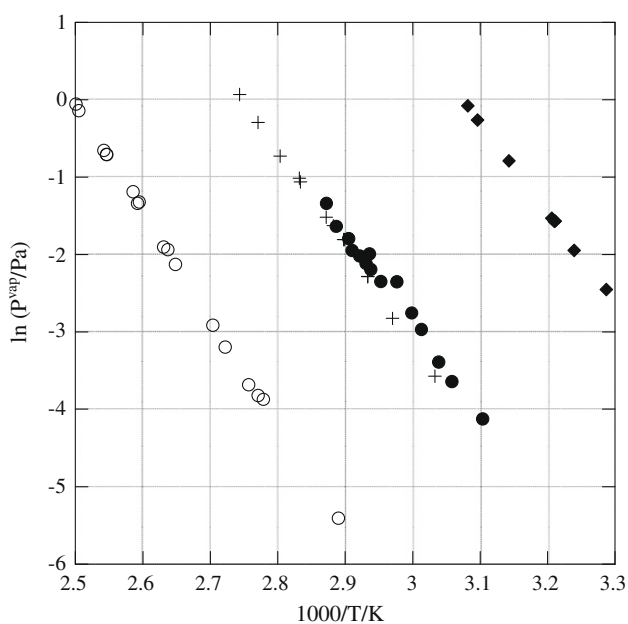


FIGURE 2. Vapor pressure as a function of temperature for anthracene and related compounds. ●, Anthracene [4]; +, phenoxazine; ○, anthraquinone; and ◆, phenoxathiin.

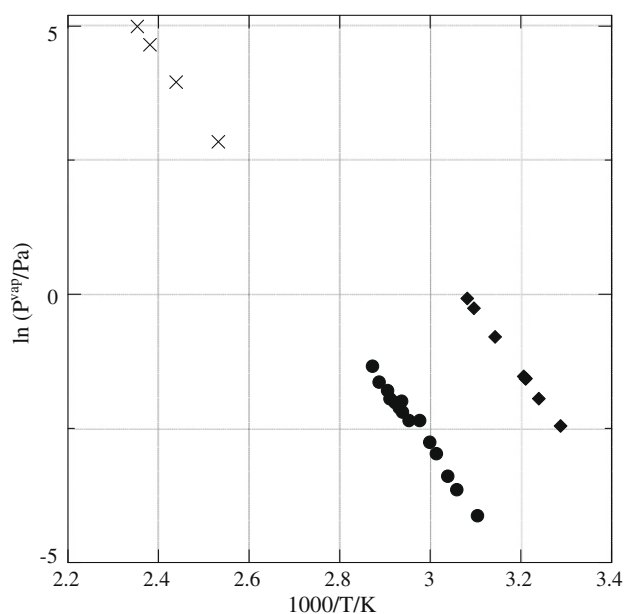


FIGURE 3. Vapor pressure as a function of temperature for anthracene and related compounds. ●, Anthracene [4]; ◆, phenoxathiin; and ×, thianthrene [20].

zene rings as compared to the one sulfur and one oxygen atom linkage of phenoxathiin. Steele *et al.* [16] report a sublimation/vaporization enthalpy for thianthrene of  $71.4 \text{ kJ} \cdot \text{mol}^{-1}$  and  $0.209 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for the entropy, both much lower than for phenoxathiin. However, these data actually span the melting point of thianthrene, as the temperature range of measurement was from (395 to 639) K; the melting point of thianthrene is 429 K [21]. Examining the Steele *et al.* data from below the melting point, the enthalpy of sublimation was  $99.9 \text{ kJ} \cdot \text{mol}^{-1}$  and entropy of sublimation is  $0.277 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , a slightly higher enthalpy and entropy of sublimation than anthracene and slightly higher enthalpy and much lower entropy than phenoxathiin. Figure 3 is a Clausius–Clapeyron plot of phenoxathiin, thianthrene and anthracene, showing the slightly higher slope (enthalpy) for thianthrene than phenoxathiin. Of course, because the Steele *et al.* measurements were taken at a considerably higher temperature range than those for phenoxathiin (and we are unable to locate reliable heat capacity data to correct for temperature range) we note that these compounds would likely have rather similar vapor pressures in the same range of temperature, since they exhibit similar enthalpies and entropies of sublimation; this is apparent from the extrapolation of the data in figure 3.

#### 4. Conclusions

The present work shows that heteroatomic substitutions or substituents in polycyclic aromatic molecules can drive vapor pressure in different directions, depending upon the relative contributions of enthalpy and entropy. For the heteroatom-containing fluorenes and anthracenes, the vapor pressure tends generally to decrease as molecular weight (or size of substituents group) increases, as expected. Crystalline structure and the ability to form intermolecular bonding interactions are critical in determining the vapor pressure of a given compound at any temperature. In certain cases, it is the enthalpic contribution associated with formation of hydrogen bonding interactions that dictates a decrease in vapor pressure. In other cases, it is the greater degree of order or disorder introduced into the solid structure that is the main determinant of change in the vapor pressure. There does not appear to be a consistent trend in terms of the effects of substitutions

on changes in enthalpy or entropy of sublimation; enthalpic or entropic effects depend upon molecule-specific factors.

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#### References

- [1] G. Rieveschi Jr., F.E. Ray, *Chem. Rev.* 23 (1938) 287–389.
- [2] M.A.V. Ribeiro da Silva, M.L.C.C.H. Ferrão, A.J.M. Lopes, *J. Chem. Thermodyn.* 25 (1993) 229–235.
- [3] V. Oja, E.M. Suuberg, *J. Chem. Eng. Data* 43 (1998) 486–492.
- [4] J.L. Goldfarb, E.M. Suuberg, *J. Chem. Eng. Data* 53 (2008) 670–676.
- [5] M. Knudsen, *The Kinetic Theory of Gases*, Methuen & Co., Ltd., London, 1934.
- [6] M.A.V. Ribeiro da Silva, M.J.S. Monte, L.M.N.B.F. Santos, *J. Chem. Thermodyn.* 38 (2006) 778–787.
- [7] J.L. Goldfarb, E.M. Suuberg, *J. Chem. Thermodyn.* 40 (2008) 460–466.
- [8] J.L. Goldfarb, E.M. Suuberg, *Environ. Toxicol. Chem.* 27 (2008) 1244–1249.
- [9] S.P. Verevkin, *Thermochim. Acta* 310 (1998) 229–235.
- [10] P.C. Hansen, C.A. Eckert, *J. Chem. Eng. Data* 31 (1986) 1–3.
- [11] G. Klebe, F. Diederich, *Phil. Trans. Roy. Soc. Lond. A* (1993) 37–48.
- [12] H.R. Luss, D.L. Smith, *Acta Cryst. B* 28 (1972) 884–889.
- [13] G. Bardi, R. Gigli, L. Malaspina, V. Piacente, *J. Chem. Eng. Data* 18 (1973) 126–130.
- [14] J.R. Donnelly, L.A. Drewes, R.L. Johnson, W.D. Munslow, K.K. Knapp, G.W. Sovocool, *Thermochim. Acta* 167 (1990) 155–187.
- [15] G.R. Desiraju, A. Gavezzotti, *Acta Cryst. B* 45 (1989) 473–482.
- [16] M. Slouf, *J. Mol. Struct.* 611 (2002) 139–146.
- [17] L. Tamam, H. Kraack, E. Sloutskin, B.M. Ocko, P.S. Pershan, M. Deutsch, *Thin Solid Films* 515 (2007) 5631–5636.
- [18] M.J.S. Monte, L.M.N.B.F. Santos, C.A.D. Sousa, M. Fulem, *J. Chem. Eng. Data* 53 (2008) 1922–1926.
- [19] W.V. Steele, R.D. Chirico, S.E. Knipmeyer, A. Nguyen, *J. Chem. Thermodyn.* 25 (1993) 965–992.
- [20] L.J. Fitzgerald, J.C. Gallucci, R.E. Gerkin, *Acta Cryst. C* 47 (1991) 381–385.
- [21] M.M. Mayer, W.J. Howell, D.L. Tomasko, C.A. Eckert, *J. Chem. Eng. Data* 35 (1990) 446–449.

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