Review of Sublimation Thermodynamics of Polycyclic Aromatic Compounds and Heterocycles

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This review details sublimation vapor pressure and thermodynamic data on 85 polycyclic aromatic compounds and heterocycles from the early 1900s through 2012. These data were collected using a variety of vapor pressure measurement techniques, from effusion to gas saturation to inclined-piston manometry. A brief overview of each measurement technique is given; these methods yield reproducible sublimation vapor pressure data for low volatility organic compounds such as polycyclic aromatic compounds and heterocycles. Several conclusions can be drawn from this literature survey, specifically that there remains a dearth of data on the sublimation thermodynamics (and fusion thermodynamics) of heteroatomic high molecular weight aromatic compounds, inhibiting a holistic understanding of the effect of specific heteroatoms and substituent position on the thermodynamics of these compounds. However, we can clearly see from the data that there are a variety of potential intermolecular interactions at work that generally tend to increase the enthalpy of sublimation and decrease the vapor pressure of a substituted polycyclic aromatic compound/ polycyclic heterocycles versus its parent compound.

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INTRODUCTION

The rise of the manufactured gas plant in the 19th century, which ushered America into the industrialized world, helped spur developments in organic chemistry that led to the detection of polycyclic aromatic compounds (PAC) and heterocycles (PH), key byproducts comprising coal tar. Since then, these compounds remain some of the most keenly scrutinized aromatics [1]. Polycyclic aromatic hydrocarbons (PAH) are high molecular weight organic compounds consisting of two [2] or more fused aromatic rings sharing a pair of carbon atoms that generally result, on a large scale, from the incomplete combustion of coal, fossil fuels, and from other anthropogenic sources. PAH are characterized by low aqueous solubilities and low vapor pressures. Both of these properties tend to decrease as the molecular weight of the molecules increases, although structural isomers often display different thermodynamic properties.

Polycyclic aromatic compounds result when one or more of the aromatic rings' hydrogen atoms are substituted by a heteroatom—often a halogen, oxygenated, methyl, or other group. PH (in this case, we will consider those with two or more fused rings) are similar in backbone to PAH, but one or more of the fused rings' carbons is replaced by another atom or branched group. PAC and PH are known for their carcinogenic nature and ubiquitous presence within the environment. Their occupancy results from a number of factors, most readily from diffuse combustion sources, such as open burning, as well as from tar byproducts entering land and water through dumping and migration from waste containment. Sediments are a common environmental location with high concentrations of PAC and PH; contaminants' origins are often suspected to be atmospheric deposition resulting from incomplete combustion of fossil fuel and biomass. Other potential sources in sediments include oil spills, accidental and intentional dumping of coal tar, asphalt, oil, and creosote [2–5]. The substitution of heteroatoms on PAH strongly influences the vapor pressure and thermodynamics of the parent compounds because of newly introduced molecular interactions, thereby affecting risk assessment estimations.

Although many researchers have pioneered advances in PAC and PH synthesis and reactions, we know relatively little about the basic thermodynamic properties of many of these compounds. One reason for the dearth of data on the vapor pressures of PAC and PH is the difficulty in performing such measurements. Many direct methods of vapor pressure measurement are often not applicable as the high temperatures required for such measurements can degrade these relatively high molecular weight cyclic compounds. Furthermore, the data that do exist in the literature are spread out over a myriad of sources and genres, depending on the original research group performing the measurements. This review presents sublimation thermodynamic data on a variety of PH and PAC from a litany of sources published over the past century to identify gaps in the literature and trends among these substituted compounds. A variety of relatively recent reviews on the thermodynamics of PAH, some of which extend into substituted compounds and heterocycles, present a considerably larger amount of thermodynamic data (including fusion and vaporization data) than what is presented herein (see, e.g., [6,7]). However, the goal of this review is to present a survey of experimental sublimation data (not including model predictions) on PAC and PH with naphthalene, fluorene, anthracene, phenanthrene, pyrene, and

acenapthene parent compounds (2, 3, and 4 fused ring compounds) to discuss the impact of different heteroatomic substituents and locations within the parent compound.

BACKGROUND

Polycyclic aromatic compounds and heterocycles often exist in the solid phase at ambient conditions. As such, sublimation thermodynamic data are essential to predicting their environmental fate and transport, especially their partitioning between the gas and soil phase, as well as their ability to form particulate matter. For example, Henry's law constants, estimated with vapor pressure data in combination with aqueous solubility data, are often used to model the equilibrium of dissolved organics in water with their atmospheric concentrations. Similar calculations are extended to nonaqueous phase liquids to determine volatilization potential of such systems. The compiled vapor pressure data of the compounds presented here were taken using a variety of measurement techniques. When available, the techniques used to gather each data are listed in the tables. As low vapor pressure measurement techniques have evolved over the past century, it is important to have a basic familiarity of each-they are described (in brief) in the succeeding paragraphs. To provide an example of the reproducibility of vapor pressures and thus enthalpies and entropies of sublimation using these methods, Table 1 details measurements for anthracene and the respective experimental method used to collect each data set. The enthalpy of sublimation over the average temperature given in the reference was corrected to the standard enthalpy of sublimation at 298.15 K according to the method proposed in Roux et al. [6] such that the corrected standard enthalpy of sublimation, $\Delta_{sub}H^{\circ}_{m}$ (298.15 K), as a function of measured enthalpy of sublimation over the average temperature range of measurement, \overline{T} , is equal to

$$\Delta_{\text{sub}} H_m^{\circ}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = \Delta_{\text{sub}} H_m^{\circ}(T) + \{0.75 + 0.15 [C_{p,m}(s, 298.15 \text{ K})]_{\text{estim}}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}\} \quad (1)$$

• $(\bar{T}/\text{K} - 298.15)/1000$

The estimated solid heat capacity, $C_{p,\text{solid}}$, for anthracene used was 209 J mol⁻¹ K⁻¹. To provide a basis of comparison, we found the mean of the corrected values. The average standard enthalpy of sublimation for anthracene, found to be 100.6 kJ mol⁻¹ for these values, was used to determine the percent difference from the mean for each measurement. As Table 1 shows, the coupled-column liquid chromatography measurement by Sonnefeld, Zoller, and May [8] is an outlier with an enthalpy of sublimation almost 9% less than the average value (average calculated without this outlier). The other methods used—Knudsen effusion, torsion effusion, calorimetry, and gas saturation—all yield enthalpy of sublimation values within $\pm 5\%$ of the mean.

The data reported in this review were taken using both direct and indirect vapor pressure measurement techniques in closed and open systems. Static, or closed systems, such as the inclined piston manometer, viscosity, ion, and capacitance gauges, relies on the sublimed vapor achieving a measurable equilibrium with its condensed sample. Conversely, techniques such as effusion and transpiration represent dynamic systems with continuous sublimation where the vapor pressure is related to the mass loss or other measurable quantity within this system.

Static measurement techniques

Ion gauge. An ion gauge consists of three electrodes (anode, cathode, and collector of positive ions) to measure the amount of positive ionization produced by an electron stream. The anode produces an accelerating field, such that electrons ionize the gas molecules with which they collide, and the positive ions produced are collected on the third, negatively charged, collector electrode. This positive

Table 1

Sublimation enthalpies of anthracene	as a function of measurement tech	nique ^a compared with avera	age value of 100.6 kJ mol ⁻	¹ at 298.15 K.
		1 1		

T _{min} /K	T _{max} /K	$\Delta_{ m sub}$ H/kJ mol $^{-1}$	$\begin{array}{c} \Delta_{sub} \mathrm{H^\circ/kJmol^{-1}}\\ (298\mathrm{K}) \end{array}$	% difference with average in $\Delta_{sub}H^{\circ}$ (298 K)	Vapor pressure measurement method	Reference
283	323	91.7	91.9	-8.7	Coupled-column liquid chromatography	[8]
313	363	102.6	103.9	3.2	Gas saturation	[53]
318	363	100.0	101.3	0.7	Knudsen effusion	[50]
322	348	98.5	99.7	-1.0	Knudsen effusion	[24]
338	361	100.4	102.0	1.4	Torsion effusion	[54]
340	360	98.8	100.5	-0.1	Knudsen effusion	[28]
342	353	98.5	100.1	-0.6	Knudsen effusion	[55]
353	432	101.0	104.0	3.3	Calorimetry	[56]
354	399	94.6	97.1	-3.5	Gas saturation	[57]
358	393	94.7	97.2	-3.4	Gas saturation	[58]

^aSublimation enthalpies corrected to 298 K according to Roux et al. 2008 [6] (using an estimated solid heat capacity of 209 J mol⁻¹ K⁻¹); ref [8] not included in average.

ionization current is a function of the electron current, anode voltage, collector (negative) voltage, and the pressure of the gas; fewer ions are produced by low-density gases. The number of ions produced is proportional to the gaseous molecular density multiplied by the electron current emitted from the filament, and therefore, the pressure is estimated by measuring the ion current. The ratio of the electron current used, I-, to positive current produced, I+, is given as follows:

$$\frac{I+}{I-} = \alpha \beta L_e \, \bar{P}_i = KP \tag{2}$$

where the factors α , β , L_e , and $\overline{P_i}$ (effective ionization efficiency) are dependent on both the pressure, P, and the electron emission current, I-, such that K is a constant of these factors and is actually therefore an observable quantity. The coefficients describing the ionization are pressure and electron current dependent; α ($\alpha \le 1$) describes the fraction of effective ionizing agents and β ($\beta < 1$) describes the fraction of ions that are consumed within the ionization region, also a function of gauge dimensions, L_e , and molecular free path. While an ionization gauge actually measures atomic concentration, it is directly calibrated for pressure when another (often McLeod) gauge is used as a reference standard [9–11].

Viscosity gauge. Viscosity gauge measurements are founded on Knudsen's kinetic theory of gases, based on the gas momentum transfer between a moving part of the gauge and a stationary surface [12]. For an ideal gas at equilibrium, the viscosity is given as follows:

$$\eta = \frac{1}{3}\rho\lambda\bar{\nu} \tag{3}$$

where ρ is the density of the gas, λ the mean free path of a gas particle, and \bar{v} the average velocity of the gas particle. If the mean free path is similar in dimension to the system, the viscosity of the gas will decrease as its density (or pressure) is lowered. The rotor slows at a rate proportional to the gas pressure, square root of molecular weight, inverse square root of the absolute temperature, and an effective accommodation coefficient to account for rotor surface roughness and tangential motion of molecules colliding with the rotor surface [12]. Measurements can either be taken in a continuous mode, such as with the oscillating quartz gauge, or a discrete mode [13].

The spinning rotor gauge is an example of a discrete mode of the viscosity gauge, which appears quite frequently in the literature to measure vapor pressures of high molecular weight organic compounds such as PAC and PH. Fremerey [14] developed a spinning rotor gauge that suspends a freely rotating steel ball by permanent magnets and magnetic coils whose excitation current may be electronically adjusted. At a desired frequency, the excitation is stopped, and the magnetism remaining in the ball induces an electric voltage in a coil, such that the frequency can be measured as a function of time. The pressure, P, is related to the decrease in frequency, \bar{v} , as a function of time, by

$$P = \frac{\pi \rho_{\text{ball}} r \bar{v}}{10 \alpha t} ln \frac{v(t)}{v_0} \tag{4}$$

where r and ρ_{ball} are the radius and density of the ball, respectively, v(t) and v_0 the frequency of the ball at time t and at the beginning of the measurement, and α is an accommodation coefficient, specific to the gas. Of course, many modifications to Fremerey's original design are found in the literature, but all generally work off of this principle. For example, Van Ekeren et al. [15] compare the vapor pressures for naphthalene and trans-diphenylethene measured using both a spinning rotor gauge and torsion effusion, showing excellent agreement between both the static and dynamic techniques. Their apparatus positions a spinning rotor measuring head in a thermostated steel cylinder, with the sample held in a container sitting within a liquid thermostat regulated within 0.01 K. Ribeiro da Silva et al. [16] also present a comparison of sublimation vapor pressures of copper(II) β-diketonates measured via Knudsen effusion, torsion effusion, and Fremerey's (MKS Instruments) spinning rotor gauge. The standard molar enthalpies of sublimation measured for benzoic acid were within 0.1% across each measurement technique.

Ruzicka et al. [17] used a static Capacitance gauge. apparatus to directly measure the sublimation vapor pressure of naphthalene. These data are reported in Table 2. This apparatus can measure pressures from 0.1 to 1333 Pa up to 313 K. Following a vacuum purge of the system, the sample is immersed in a thermostat, and the vapor pressure is measured via a capacitance diaphragm absolute gauge MKS Baratron type in the chamber above the sample, heated to prevent condensation. This is a very similar experimental setup as the spinning rotor gauge described earlier. However, the gauge pressure is the measured vapor pressure. While this incarnation of the static method is quite applicable to compounds with moderate to high vapor pressures, the low sublimation vapor pressures of many two-ring and higher PAC and PH do not allow for the use of such a static apparatus.

A static apparatus presented by Monte et al. enables measurements in the 0.4–133 Pa range from 253 to 413 K and in the 3–1300 Pa range from 253 to 453 K using a capacitance diaphragm gauge [18–20]. The sample cell resides in a cylindrical cavity within a thermostated vessel, plumbed via heated lines to the pressure gauge. A turbomolecular pump evacuates the system between measuring cycles. When the system has reached a sufficiently low pressure—on the order of 10^{-5} Pa–the pressure above the condensed phase is recorded until stability is reached. Data from the Monte apparatus agree well with those taken by the same group using Knudsen effusion for a variety of PAH [18–20]. For

			Vanor	nressure (lata on polvevelie aro	matic comp	ounds w	ith nanł	ithalene as th	he narent comp	annd. ^a			
			v apu	bicesate	ada oli polycyche alo			iui iiapi		ne parent comp	-niin			
	CAS Registry	Molecular	Minimum	Temp	Experimental	P^{vap}	Clausi Clape equat	ius- yron ion		$C_{p, \text{ solid}}$	$\Delta H^\circ_{ m sub}$	Melting		
Compound	no.	weight g mol ⁻¹	purity %	range K	method	(298 K) Pa	в	q	$\Delta ar{H}_{ m sub}$ kJ mol $^{-1}$	(298 K) kJ K ⁻¹ mol ⁻¹	(298 K) kJ mol ⁻¹	point K	Structure	Reference
Naphthalene C ₁₀ H ₈	91-20-3	128.2	>99	250–353	Static apparatus/ torsion effusion	1.07E+01	31.97	8.82	73.3 ± 0.6	165.8	72.6	354	\bigcirc	[17,59]
2-Bromonaphthalene C ₁₀ H ₇ Br	580-13-2	207.1	>99	280–328	Knudsen effusion	8.36E-01	32.27	9.67	80.4 ± 0.7			331	Br	[35,60]
2-Chloronaphthalene C ₁₀ H7Cl	91-58-7	162.62	>99	280–329	Knudsen effusion	2.49E+00	31.37	9.076	75.5 ± 0.6	235.6	78.9	332	o V	[35,61,62]
l-Bromo-2-naphthoic acid C ₁₁ H ₇ BrO ₂	20717-79- 7	251.1	>98	340-401	Knudsen effusion	7.63E-06	32.21	13.11	109.0 ± 2.7			464	e → H O H O H O O O H O O O O O O O O O O O O O	[40]
1-Naphthylacetic acid C ₁₂ H ₁₀ O2	86-87-3	186.2	66<	343–373	Transpiration	1.25E-04	35.14	13.15	112.3 ± 0.9			406) H	[63]
2-Naphthylacetic acid C ₁₂ H ₁₀ O ₂	581-96-4	186.2	66<	343-372	Transpiration	3.08E-05	38.84	14.67	124.6 ± 1.0			415	He contraction of the contractio	[63]
1,4-Dibromonaphtha- lene C ₁₀ H ₆ Br ₂	83-53-4	285.96	88	297–322	Knudsen effusion	2.04E-02	32.77	10.925	90.8 ± 1.7				ăă	[24]
2 -Acetylnaphthalene $C_{12}H_{10}O$	93-08-3	170.2	Frac Sub	295–316	Viscosity gauge	7.43E-02	32.87	10.57	87.9 ± 2.6			329.0	0	[64]
1,8-Dimethylnaphtha- lene $C_{12}H_{12}$	569-41-5		66'66	328–336	Inclined piston manometer	5.66E-03	27.04	9.6	79.8 ± 2.3	242.8	81.1	335.0		[22,48,65]
2,3-Dimethylnaphtha- lene $C_{12}H_{12}$	581-40-8	156.2	Frac Sub >99.9	279–301 333-373	Viscosity gauge Inclined piston manometer	4.38E-01 3.22E-03	31.49 27.45	9.63 9.89	80.1 ± 1.7 82.2 ± 1.8	215 215	79.8 84.0	378.5		[64,66] [64,66]

Table 2

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			99.95	348–383	Autabatic calorineuy Inclined piston	2.95E-03	28.3	10.17	$\begin{array}{c} 86.3\\ 84.6\pm1.5\end{array}$	203.55 203.55	87.9 86.7	383.3		[48] [22,48]
Dimethy Inaphtha-	582-16-1	156.2	99.95	333–368	Inclined piston	4.16E-03	28.41	10.1	84.0 ± 1.7	251.85	86.0	370.0	\geqslant	[22,67,68]
C12H12				340	manometer Adiabatic calorimetry				84.8	251.85	86.8	368.8	Ъ	[48,67]
aphthol H ₈ O	90-15-3	144.2	6.09<	297–313	Knudsen effusion	6.64E-02	34.1	10.97	91.2 ± 2.4	166.9	91.4	368.0		[69–71]
laphthol h ₈ O	135-19-3	144.2	9.99.9	305-324	Knudsen effusion	1.94E-02	34.08	11.33	94.2 ± 2.7	172.8	94.6	394.0	H	[69–71]
iitronaphthalene { ,H ₇ NO ₂	36-57-7	173.2		305-321	Knudsen effusion	7.21E-02	35.39	11.33	94.2 ± 0.5			329.0	°	[71,72]
Naphthoquinone H ₆ O ₂	130-15-4	158.2	<i>79</i> <	308-342	Torsion and weighing effusion	6.82E-02	33.808	10.875	90.4 ± 1.9			397		[73]
Naphthalenediol :	571-60-8	160.1	>97	381	Torsion and weighing effusion	1.17E-05	36.52	14.266	118.6±1.9			470	ББ Z	[73]
inoxaline 1 ₆ N ₂	1-19-0	130.1	9.99<	365-372	Micro calorimetery						66.6			[39]
nazoline 1 ₆ N ₂	253-82-7	130.1	9.99<	365-372	Micro calorimetery						76.6		z	[39]
halazine 1 ₆ N ₂	253-52-1	130.1	>99.9	365–372	Micro calorimetery						82.3		Z-Z	[39]
yanoquinoline H ₆ N ₂	1436-43-7	154.2		312-326	Knudsen effusion	2.97E-02	34.34	11.281	93.8 ±4.5				z	[74]
yanoquinoline H ₆ N ₂	34846-64- 5	154.2		312-326	Knudsen effusion	3.47E-02	34.25	11.208	93.2 ±4.5				z	[74]

example, Monte et al. find an enthalpy of sublimation of crystalline fluorene (corrected to 298 K) using the Knudsen effusion technique over the 292.2–320.1 K range of $88.55 \pm 0.23 \text{ kJ mol}^{-1}$. The enthalpy of sublimation of a fluorene sample from the same lot was measured using the static apparatus described herein (corrected to 298 K) over the temperature range of 312.89-378.50 K and found to be $87.26 \pm 0.14 \text{ kJ mol}^{-1}$ [20]. For the sake of comparison, using their Knudsen effusion apparatus, Goldfarb and Suuberg report an enthalpy of sublimation of fluorene (corrected to 298 K) measured over the 298–324 K range of $88.1 \pm 1.9 \text{ kJ mol}^{-1}$ [21].

Inclined piston manometry. An inclined piston manometer balances a known weight, W, of a free piston declined from the horizontal by a known angle, θ , against the pressure exerted by the vapor of the sample. Following system evacuation, the sample is placed in a Pyrex bulb immersed in a thermal reservoir. The temperature is held constant and measured with a thermocouple as the weight and torsion angle are recorded. The vapor pressure is calculated accordingly:

$$P = \left(\frac{g}{g_{\rm std}}\right) \frac{(W \sin\theta)}{A} \tag{5}$$

where A is the area of the piston and g the acceleration of gravity [22].

Dynamic system measurement techniques

Knudsen (weighing) effusion. The Knudsen effusion technique enables the indirect measurement of vapor pressure by measuring the molecular leak rate from an effusion cell through a small orifice assuming that thermal and chemical equilibrium exist within the sample cell. The rate of molecular effusion through the pinhole leak (measured as the mass loss rate of sample from the cell) equals the rate at which molecules would strike an area of wall equal to the area of the hole, if the hole were not present. At low pressures (below approximately 1 Pa), the mean free path of the molecules is large compared with the diameter of the orifice; the intermolecular collisions in the vapor phase at the orifice are negligible [23]. The Knudsen effusion equation relates the vapor pressure of the compound, P, to the mass loss, m, per unit time, t, through the orifice of area A_0 , to the molecular weight of the effusing species, M, at absolute temperature T using the universal gas constant, R.

$$P = \frac{m}{tA_0} \sqrt{\frac{2\pi RT}{M}} \tag{6}$$

Various implementations of this technique exist in the literature (see, e.g., [24–28]).

Torsion effusion. In the torsion effusion technique, an effusion cell with two effusion holes of the same diameter is suspended from a long thin wire and exerts a torque on the wire because of the effusing molecules.

This torque is directly proportional to the vapor pressures, such that

$$P = C'I \tag{7}$$

where C' is the apparatus' constants and I is the electric compensation current. The effusion cell is suspended on the wire in such a way that the two effusing gas streams twist the wire in the same direction. This method is advantageous in that only a small amount of material is required, and, as opposed to the Knudsen effusion method, the molecular weight of the material is not necessary to calculate the vapor pressure. This method has been combined with weighing effusion to allow for the confirmation of the vapor phase composition (monomeric, dimeric, etc.) by calculating the ratio of the pressures measured simultaneously at a given temperature. [29,30]

Gas saturation/transpiration. Gas saturation, also known as transpiration, is an indirect dynamic measurement of vapor pressure where an insoluble inert gas is passed over the vaporizing sample. A generator column is filled with a pure analyte or an inert support material onto which the analyte is coated. The analyte can be coated in several ways; in one, an uncoated support material is packed into a column, the column filled with an analyte solution of known (relatively high) concentration, the solvent is evaporated, and the column is conditioned by purging with an inert gas at elevated temperature. A second method can be used whereby the support material is precoated and dried, and then packed in the column, followed by a conditioning step to remove trace impurities. When a gas (nitrogen, air) flows over the column at given temperatures, it carries away the vapor in equilibrium with the condensed phase that volatilizes according to its vapor pressure at that temperature.

The compound's saturation vapor pressure, P, is determined via measuring the amount of material transported by a known amount of carrier gas using the equation:

$$P = \frac{P^{\text{atm}} \cdot n_i}{(n_i + n_c)} \approx \frac{P^{\text{atm}} \cdot n_i}{n_c}$$
(8)

where P^{atm} is the atmospheric pressure, n_i is the molar flow rate of the material vaporizing, and n_c is the molar flow rate of the carrier gas, such that $n_c >> n_i$. The concentration of organic compounds in the saturated carrier gas may be determined using an FID, infrared analysis, UV spectroscopy, gas chromatography, and liquid chromatography. Regardless of the method of detection, the temperature and flow rates of the carrier gas and sample are experimental values, controllable with a high degree of precision. It was noted by Bell and Groszek [31] in their work that oxygenated molecules yield lower vapor pressures than expected from hydrocarbons of the same carbon number. In addition, hydrocarbons containing chlorine and sulfur suffered a lack of consistency. It is proposed that these effects tail off as molecular weight and carbon number to substituent ratio increases. Transpiration is applicable to measuring vapor pressures from about 10^2 to 10^{-6} Pa [8,31,32].

Coupled-column liquid chromatography (gas saturation and HPLC). Coupled-column liquid chromatography is a commonly used incarnation of the transpiration technique. In this method, a gas saturation system is coupled to an HPLC. In the gas saturation system, as described earlier, an inert gas flows through a column packed with either the pure compound of interest or with an analyte-coated inert support. In this case, the HPLC is directly coupled to the vapor saturator column, decreasing experimental time as the entire analyte volume, not an aliquot, is used to measure the concentration of the vaporized sample. The HPLC column is calibrated with standard solutions of the analyte and is connected to the outlet of the generator using purified nitrogen (or other inert) for flow of the analyte and removal of the solvent from the trap [8].

Data. We begin with compounds having a naphthalene backbone, composed of two fused aromatic rings with first heteroatomic, then heterocyclic substitutions, then move on to fluorene, acenaphthene, anthracene, and phenanthrene derivatives (three-ring systems) through to pyrene, and other four or more ring systems. The unsubstituted PAH values for each *parent* compound are generally those from sources recommended in the compilation by Roux et al. [6]. To standardize the data across compounds and experimenters, Tables 2–8 detail the sublimation vapor pressure data reduced to the Clausius–Clapeyron form over the temperature range measured (when suitable data was available), such that

$$\ln(P/Pa) = a - b \cdot 10^3 (K/T) \tag{9}$$

where P is the vapor pressure in Pascal at a given temperature T in Kelvin. The tables also give the vapor pressure at 298.15 K (as measured or extrapolated from the Clausius-Clapeyron equation) for each compound as a relative basis of comparison across compounds. The enthalpy of sublimation of the compound is determined from the slope of the linear Clausius–Clapeyron plot of ln P versus inverse temperature and the entropy at P = 1 Pa, from the intercept; $\Delta_{sub}S = a/R$. Data are presented as the sublimation enthalpy of the compound over the temperature range measured in kilojoules per mole with a 95% confidence interval (when available). If available, the measured solid molar heat capacity is used to standardize the sublimation enthalpies to 298.15 K as described by Roux et al. [6] in eq. 1. While estimated molar heat capacities of the solid phase compounds at 298.15 K can be found with a group additivity method (see, e.g., [33]), the uncertainties introduced in these calculations and then carried through the standardization of sublimation enthalpy are of questionable use to this discussion. Here, we note that there is a distinct lack of molar heat capacities present in the literature for these compounds, hindering the usability of the available thermodynamic data.

Melting points are given in Tables 2–8, when available. Again, we note a lack of data in the literature on the melting points of many PAC and PH compounds. Also detailed in these tables are the molecular structure, molecular weight, and Chemical Abstract Service (CAS) registry number for each compound. In addition, the data tables give the minimum purity of the compound used by each experimenter (when available), as well as the method of experimentation (when available). As many of these compounds are difficult to synthesize, and measurement techniques are laborious and time-consuming, the experimental sublimation thermodynamics of many of these compounds do not appear in multiples in the literature (that the author could find). When available, replicate data are provided.

Two-ring systems: naphthalene. Naphthalene is the simplest and smallest fused benzene ring aromatic compound and is often associated with wood burning and forest fires. Its halogenated species frequently result when halogens are present in the mixture during combustion, such as in flame retardants [34]. As Figure 1 and Table 2 show, the vapor pressure of the substituted naphthalenes decreases significantly as the size and number of halogen substituents increases; the vapor pressure of 1,4-dibromonaphthalene [17] and one order of magnitude lower than a mono-bromine substitution as measured by Verevkin [35].

The enthalpy of sublimation for pure naphthalene is approximately 73.3 kJ mol^{-1} in the temperature range of 258-314 K [17]. The enthalpy of sublimation of 2-bromonaphthalene measured by Ribeiro da Silva, Ferrão, and Lopes [36] was $81.2 \pm 1.0 \text{ kJ mol}^{-1}$ at 280–328 K, in good accord with that $(80.4 \pm 0.68 \text{ kJ mol}^{-1})$ measured by Verevkin [25]. These data show an increase in enthalpy of approximately 10% (or 7–8 kJ mol⁻¹) with the substitution of a single bromine atom onto the 2-position of naphthalene. On the other hand, Verevkin measured the enthalpy of sublimation of 2-chloronaphthalene to be 75.5 ± 0.631 kJ mol⁻¹[35], showing a very slight increase as compared with the parent naphthalene. Hence, the limited influence of single halogen substituents, as also noted for anthracene, cannot be generalized to this aromatic ring compound. While it is the case here that a single chloro-substituent does not influence the enthalpy very much, in this case, the single bromo-substituent does. The enthalpy of sublimation of 1,4-dibromonaphthalene is $90.8 \pm 1.7 \text{ kJ mol}^{-1}$, an increase of 17.5 kJ mol^{-1} , or about 24% over pure naphthalene. Thus, we note the effect of each bromine substituent is in the range of $8-9 \text{ kJ mol}^{-1}$, roughly consistent with the influence on enthalpy of sublimation of the addition of two bromines on anthracene, as seen in Table 3 and discussed in the following paragraphs.

Polycyclics containing oxygen functional groups, such as aldehydes, nitro, and carboxyl groups, can result from

		jo transford	Kelerence	[6,75]	[24,75]	[24,75]	[24,75]	[24,75]	[24,75]	[40,75]	[40,75]	[40,75]
		C	ourucine		ă.	ăă	ă- ă-ă		ō-ō		de la	о
		Melting	k	491.0	376.0	481.0	495.0	496.0	484.0	380.0	509.0	492.0
	compound.	ΔH°_{sub}	kJ mol ⁻¹	101.9								
	e as the parent e	$C_{p, \text{ solid}}$	(290 K) kJ K ⁻¹ mol ⁻¹	209								
	th anthracen	م م	∆π _{sub} kJ mol ^{−1}	98.5 ± 3.3	100.5 ± 1.8	116.7 ± 3	114.2 ± 2.8	99.29 ± 2.7	113.9 ±4.5	100.6 ± 3.9	134.8 ± 3.4	120.1 ± 3.8
e	unds wi	sius- eyron ation tants	q	11.85	12.09	14.035	13.733	11.942	13.702	12.1	16.22	14.45
Table	compo	Clau Clape equé cons	а	32.59	33.2	34.26	33.57	31.28	35.24	32.05	36.16	33.42
	aromatic	p ^{vap}	(290 N) Pa	7.65E-04	6.30E-04	2.66E-06	3.68E-06	1.52E-04	2.17E-05	0.00019	1.2E-08	2.9E-07
;	a on polycyclic	Experimental	memou	Knudsen effusion	Knudsen effusion	Knudsen effusion	Knudsen effusion	Knudsen effusion	Knudsen effusion	Knudsen effusion	Knudsen effusion	Knudsen effusion
,	ssure dat	Temp	range K	322–348	316–368	358-408	359–392	331–372	316-376	329–363	401-421	385-420
	Vapor pres	Minimum	httmd %	66	95	86	98	>98	>96	66 <	>98	>97
		Molecular	$g \mod^{-1}$	178.2	257.13	336.02	336.02	212.67	247.12	206.2	222.2	222.2
		CAS	Kegisury no.	120-12-7	1564-64-3	3278-82-8	523-27-3	17135-78-3	605-48-1	642-31-9	613-08-1	723-62-6
			compound	Anthracene $C_{14}H_{10}$	9-Bromoanthracene C ₁₄ H ₉ Br	1,5-Dibromoanthracene C ₁₄ H ₈ Br ₂	9,10-Dibromoanthracene C ₁₄ H ₈ Br ₂	2-Chloroanthracene C ₁₄ H ₉ Cl	9,10-Dichloroanthracene C ₁₄ H ₉ Cl	9-Anthraldehyde C ₁₅ H ₁₀ O	2 -Anthracenecarboxylic acid $C_{15}H_{10}O_2$	9 -Anthracenecarboxylic acid $C_{15}H_{10}O_2$

Journal of Heterocyclic Chemistry

Anthraquinone	84-65-1	208.21	>98	346–400 Kn	udsen	6.93E-06 34.53	13.83	115.0 ± 5.0	240	117.7		>)=0 >	[45,76]
C14H8U2			6.66	en 377–395 Kn	udsen	1.61E-06 32.22	13.577	112.9 ± 0.2	240	116.1			[77,76]
				eur 376.15 Kn	udsen	1.68E-04 33.576	12.595	104.7	240	107.6		=0	[78,76]
Anthrone C ₁₄ H ₁₀ O	90-44-8	194.23	66.66	en 346–365 Kn eff	udsen udsen usion	3.49E-04 34.64	12.695	105.6 ± 0.8				o o	[77]
9 -Nitroanthracene $C_{14}H_9NO_2$	602-60-8	223.2		355–378 Kn effi	udsen usion	6.77E-05 35.87	13.55	112.7 ± 0.3				Č –Ž O	[72]
9-Methylanthracene C ₁₅ H ₁₂	779-02-2	192.3		329–345		3.96E-03 35.04	12.09	100.5 ± 3.8			354.0		[79,80]
$9,10$ -Dimethylanthracene $C_{16}H_{14}$	781-43-1	206.3		363–378		8.55E-05 34.76	13.15	109.3 ± 3.1					[62]
2 -Ethylanthracene $C_{16}H_{14}$	52251-71-5	206.3		343–359		6.03E-04 35.04	12.651	105.2 ± 0.8					[42]
1,5-Dihydroxyanthraquinone $C_{14}H_8O_4$	117-12-4	240.2		410-503 Kn effi	udsen usion	3.07E-07 34.35	14.705	122.3 ± 2.8				о	[81]
1,8-Dihydroxyanthraqui- none C ₁₄ H ₈ O ₄	117-10-2	240.2		373-456 Kn effi	udsen usion	6.29E-06 35.147	14.043	116.8±3.2				H O H H H H H H H H H H H H H H H H H H	[81]
9-Butylanthracene C ₁₈ H ₁₈	1498-69-7	234.33	Vac Sub	234–293 Kn effi	udsen usion	9.72E-04 37.55	13.257	110.2 ± 1.1			320.0		[82]
Phenoxazine C ₁₂ H ₉ NO	135-67-1	183.21	>95	330–365 Kn eff	udsen usion	5.07E-04 34.36	12.5	103.9±2.3			429.85		[45,83]

Sublimation of PAC

(Continued)

Journal of Heterocyclic Chemistry DOI 10.1002/jhet

	Reference		[45,84]	[77,84] [85,84]	[77]	[77,86]	[41,43]	[42,43]	[50]
	Structure		S S S	S S S	o		× ×		
	Melting	K	328.8	429.6	486.6	448.3	383.4	451.6	
	$\Delta H^{\circ}_{ m sub}$ (298 K)	kJ mol ⁻¹	96.8	107.0		105.8	90.6	96.8	
	$C_{p, m solid}$	kJ K^{-1} mol ⁻¹	214	220 220		226	205	234	
	$\Delta ar{H}_{ m sub}$	$kJ mol^{-1}$	96.3±2.2	105.1 ± 0.6 99.1 ± 3.5	110.9 ± 1.2	103.9 ± 0.6	89.5 ± 0.2	92.8±1.6	108.1 ± 1.6
e 3 inued)	sius- eyron ation stants	þ	11.58	12.641 11.914	13.343	12.497		11.16	13.005
Tabl (Conti	Clau Clap equi	а	2 35.6	4 34.9 4 32.99	34.46	4 34.47	~	3 32.12	5 34.218
	P^{vap} (298 K)	Pa	3.84E-00	5.42E-0⁄	3.31E-00	5.72E-02	6.56E-03	4.85E-03	8.08E-05
	Experimental method		Knudsen effusion	Knudsen effusion Transpiration	K nudsen effusion	Knudsen effusion	Knudsen effusion	Inclined piston manometry	Knudsen effusion
	Temp range	ĸ	304–325	344–364 358–427	369–387	342–362	333	390-430	334–381
	Minimum purity	%	>98	9.99	98.3	99.7	66	66<	66
	Molecular weight	g mol ⁻¹	200.26	216.322	212.27	196.2	179.22	180.2	209.21
	CAS Registry no.	•	262-20-4	92-85-3	492-22-8	90-47-1	260-94-6	92-82-0	46492-08-4
	Compound		Phenoxathiin C ₁₂ H ₈ OS	Thianthrene C ₁₂ H ₈ S ₂	Thioxanthone C ₁₃ H ₈ OS	Xanthone C ₁₃ H ₈ O ₂	Acridine $C_{13}H_9N$	Phenazine C ₁₂ H ₈ N ₂	Benz[g]isoquinoline- 5,10-dione C ₁₃ H ₇ O ₂ N

J. L. Goldfarb

Vol 50

te as the parent compound.	$C_{p, \text{ solid}} = \Delta H_{o}^{\circ}$ Melting $C_{p, \text{ solid}} = \Delta H_{o}^{\circ}$ Melting $C_{p, \text{ solid}}$ $D_{effective}$	b (298 K) (298 K) point Structure Keterence -1 kJ K ⁻¹ mol ⁻¹ kJ mol ⁻¹ K	19 388.0 (1) [21]	1-1 [87]	3.8 354 (87,80)	3.4 357.0 2 9 [40]	4.6 503.0 0 OH [40]	3.7 (45) 5.1 (53)	2.5	1.2 N ^{OH} [45]	3.0 428.0 428.0 1401
luorene as the parent compound.	$\Delta \tilde{E}$ C_{p} solid ΔH°_{sub} Melting	ΔH_{sub} (298 K) (298 K) point J mol ⁻¹ kJ K ⁻¹ mol ⁻¹ kJ mol ⁻¹ K	38.1±1.9 388.0	0.0 ± 1.7	354 3.8 3.4	00.0 ± 3.4 357.0	10.2 ± 4.6 503.0	88.5 ± 3.7 22.3 ± 5.1	77.4±2.5	<i>1</i> 9.6±1.2	l(4.2±3.0 428.0 428.0 b)
aromatic compounds with f	Clausius- Clapeyron equation constants	298K) Pa a b k	.58E-02 32.85 10.6 8	.07E-02 32.86 10.83 9	.96E-03 35.04 12.09 10	.26E-04 33.27 12.03 10	86E-06 31.7 13.25 1	87E-03 30.98 10.64 8 59E-02 33.13 11.107 9	97E-04 32.06 11.72 9	.71E-02 28.82 9.57 Y	.65E-05 35.89 13.74 1
por pressure data on polycyclic a	num Temp Experimental	ity range method (2 6 K	97 298–324 Knudsen 6. effusion	285–317 Transpiration 3.	285-317 Transpiration 3.	-95 338–356 Knudsen 8. effusion	.97 349–418 Knudsen 2. effusion	-98 301–343 Knudsen 8. effusion 1. Transpiration 1.	-95 326–366 Knudsen 6. effusion	.97 375–399 Knudsen 3. effusion	-99 349–384 Knudsen 3. effision
Va	CAS Registry Molecular Minir 	no. weignt puri g mol ⁻¹ %	86-73-7 166.2	523-37-7 180.2	730-37-6 180.2	0084-90-3 194.2 >	989-33-9 210.2 >	486-25-9 180.2 >	689-64-1 182.22 >	< 157-52-0 195.22 >	607-57-8 211.2 >
		Compound	Fluorene C ₁₃ H ₁₀	9-Methyl-fluorene 2 C ₁₄ H ₁₂	1-Methyl-fluorene C ₁₄ H ₁₂	2-Fluorenecarboxalde- 30 hyde C ₁₄ H ₁₀ O	9-Fluorenecarboxylic 1 acid C ₁₄ H ₁₀ O	9-Fluorenone C ₁₃ H ₈ O	9-Fluorenol C ₁₃ H ₁₀ O	9-Fluorenone oxime 2 C ₁₃ H ₉ NO	2-Nitrofluorene C.,H.NO.

November 2013

Table 4

(Continued)

	$C_{p, \text{ solid}} = \Delta H_{\text{sub}}^{\circ}$ Melting (298 K) (298 K) point Structure F	kJ K ⁻¹ mol ⁻¹ kJ mol ⁻¹ K	[8] ZHU-	194 103.1 194 [8	Its	217.8 95.8 362.5 189.	238.2 99.1 341 (89)	199.01 79.8515293 355	198.3 92.0386183 371.9 53. 89.9 379.8 194.9 194.3 198.3 92.2592028 185.
Table 4 (<i>Continued</i>)	Clausius- Clapeyron equation constants $\Delta \bar{H}_{ m sub}$	a b kJmol ⁻¹	54.69 14.865 123.6	32.38 12.2 101.4±1.1	33.825 13.769 114.5 ±2.0	33.54 11.42 94.9 ± 0.3	34.95 11.83 98.4 ± 0.3	30.63 9.513 79.1 ± 3.6	32.87 10.97 91.2 ± 6.4 (Extrapolated 89.9 ± 0.0 measurement) 32.74 10.903 90.6 ± 2.8
	Temp Experimental P ^{vap} range method (298 K)	K Pa	308-342 1.2E+02	347–364 Knudsen 1.92E-04 effusion	353389 Knudsen 4.20E-06 effusion	313–333 Knudsen 8.38E-03 effusion	310–329 Knudsen 8.67E-03 effusion	303-343 Transpiration	303-348Transpiration2.74E-01298.15Inclined piston1.94E-02manometrymanometry336-366336-366Transpiration
	Molecular Minimum weight purity	g mol ⁻¹ %	181.2 >98	167.21 >99.9	168.19 >98	181.23 >99.9	195.26 >99.9	168.19 99.9	184.26 >97 >99.9
	CAS Registry no.		Aminofluorene $153-78-6$ $_{3}H_{11}N$	J-Carbazole 86-74-8 2H ₉ N	J-Pyrido[3,4-b]indole 244-63-3 1H ₈ N ₂	Methylcarbazole 1484-12-4 $_{3}H_{11}N$	Ethylcarbazole 86-28-2 4H ₁₃ N	benzofuran 132-64-9 2H ₈ O	benzothiophene 132-65-0 2H ₈ S

Journal of Heterocyclic Chemistry

Table 5

	Reference		[21,71,95]	[24]
	Structure			ă-
	Melting	K	367	
.pur	$\Delta H^\circ_{\rm sub}$	kJ mol ⁻¹	84.8	
ie parent compou	Ϋ́́Η	kJ mol ⁻¹	78.73 ± 2.24	87.36 ± 2.64
thene as th	sius- syron ttion tants	q	9.47	10.508
h acenaph	Claur Clape equa	а	30.59	32.37
impounds wit	devq 708 K)	Pa	3.05E-01	5.55E-02
clic aromatic co	Experimental method		Knudsen effusion	Knudsen effusion
ı on polycy	Temp	K	299–320	296–321
or pressure data	Minimum	76 %	66	>94
Vap	Molecular weight	g mol ⁻¹	154.211	233.1
	CAS Benistry no	meran no.	83-32-9	2051-98-1
	Commented		Acenaphthene C ₁₂ H ₁₀	5-Bromoacenaphthene C ₁₂ H ₉ Br

incomplete combustion in the presence of oxygen or oxygen-containing compounds [37]. They are also the products of photooxidation reactions occurring through several mechanistic pathways [38]. Figure 2 shows the effect of adding various heteroatomic groups to naphthalene. In each case, the vapor pressure of the parent compound is decreased and enthalpy of sublimation increased relative to the parent PAH. The type of substituent (halogenated, oxygenated) significantly impacts the sublimation behavior. The vapor pressure of 2-naphthol is more than three orders of magnitude less than that of pure naphthalene, whereas the addition of two methyl groups (seen through 2,3- and 2,6-dimethylnaphthalene) lowers the vapor pressure by two orders of magnitude. Interestingly, the sublimation enthalpies for these dimethyl naphthalenes are quite similar despite the difference in methyl positions on the parent compound, whereas the vapor pressure of 2naphthol is one-third of what the vapor pressure of 1naphthol is at 298.15 K.

The substitution of nitrogen compounds within the aromatic rings-such as for the quinolones and quinoxolines-has a varying effect on the sublimation vapor pressure. Interestingly, when the nitrogens replace adjacent carbons (pthalazine), we see an increase in enthalpy of sublimation of almost 10%. However, when the nitrogens replace carbons leaving one ring-carbon between the two substitutions (quinazoline), the enthalpy of sublimation is only slightly higher (less than 5 kJ mol^{-1}), and when the nitrogens replace carbons at the 1 and 4 positions (quinoxaline), Ribeiro da Silva and Matos find a lower enthalpy of sublimation-by more than 10%-as compared with the parent naphthalene [39].

Three-ring systems: anthracene. Anthracene routinely in mixtures and appears tarry soot-common environmental pollutants. Pure anthracene is widely characterized in the literature and as such is often used as a calibration standard for low vapor pressure measurements. Its heteroatom-containing counterparts are being increasingly investigated by a number of researchers, as evidenced in Table 3. Interestingly, we see that the substitution of one bromine atom to anthracene at the 9position has a very small impact on the vapor pressure relative to pure anthracene. It cannot be assumed a priori that substitution of a larger halogen atom for a hydrogen atom will automatically change the sublimation behavior of a given PAH, although the impact of substitution of a chlorine at the 2-position does have a significant effect, in contrast to what we observe for napthalene. It cannot be concluded from these results alone whether it is the influence of chlorine versus bromine or the 2 versus 9 positions substitution that makes a significant difference.

The substitution of a carboxyl group onto anthracene at the 2 versus 9 positions also makes a significant difference in vapor pressure and enthalpy of sublimation. The

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Table 6	compounds
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	data
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		F	Vapor pressu	ure data on po	olycyclic aromat	ic compour	nds with pi	henanthrene	as the parent cor	npound.			
Compound	CAS Registry no.	Molecular weight	Minimum purity	Temp range	Experimental method	P^{vap} (298 K)	Clausius Clapeyrc equation constant	in n s ∆H _{sub}	$C_{p, m \ solid} (298 m \ m K)$	$\Delta H^\circ_{ m sub} (298{ m K})$	Melting	Structure	Reference
		$\mathrm{g}\mathrm{mol}^{-1}$	%	K		Pa	ab	kJ mol ⁻	$^{-1}$ kJ K ^{-1} mol ^{-1}	kJ mol ⁻¹	K		
$Phenanthrene \\ C_{14}H_{10}$	85-01-8	178.23	9.99	313-333	Knudsen effusion	1.98E-02	33.03 11.(<pre>11 91.5 ±0</pre>).4 220.6	92.4	374	([27,48]
4-Methylphenanthrene C ₁₅ H ₁₂	832-64-4	192.26	>98	295–300 200–290	Ebulliometer			93.4	263.1	122.8	(Triple point) 324.9		[46]
$2,7$ -Dimethylphenan-threne $C_{16}H_{14}$	1576-69-8	206.28			Knudsen effusion			106.8 ±0	.8		395399		[47]
4,5-Dimethylphenan- threne $C_{16}H_{14}$	674-69-9	206.28			Knudsen effusion			104.7 ± 1	6.1				[47]
2,4,5,7-Tetramethylphe- nanthrene $C_{18}H_{18}$	7396-38-5	234.34	>99		Knudsen effusion			114.3 ± 1	Ľ.		383–385		[47]
3,4,5,6-Tetramethylphe- nanthrene $C_{18}H_{18}$	6/8/43	234.34	66 <		Knudsen effusion			133.6 ± 2	8.		343-344		[47]
3.4 -Benzoquinoline (phenanthridine) $C_{13}H_9N$	229-87-8	179.22	99.85 99	288–323 309–437	Knudsen effusion Knudsen effusion	2.11E-03 4.09E-03	31.96 11.5 34.92 12.0	$\begin{array}{ccc} 36 & 94.4 \pm 3 \\ 345 & 100.1 \pm 1 \end{array}$	8.8 201.9 10.1 201.9	94.7 102.5	380	-z	[43,49] [43,50]
5,6-Benzoquinoline (benzo[/Jquinoline) C ₁₃ H ₉ N	85-02-9	179.22	99.87	288–323	Knudsen effusion	4.96E-05	23.88 10.0)7 83.7 ± ²	3.6			Z	[49]
7,8-Benzoquinoline (benzo[h]quinoline) C ₁₃ H ₉ N	230-27-3	179.22	66	293–323	Knudsen effusion	2.20E-04	24.16 9.5	71 80.7 ± 2	2.6 206.4	81.0	324	z	[43,49]

Lable 7 Vapor pressure data on polycyclic aromatic compounds and heterocycles with pyrene as the parent compound.	Clausius- Clapeyron Capeyron equation CAS Registry Molecular Minimum Temp Experimental P ^{vap} constants ΔH^o_{sub} Melting modeling ΔH^o_{sub} Melting Defension modeling ΔH^o_{sub} Melting Defension	$gmol^{-1}$ % K Pa a b $kJmol^{-1}$ K weight putty automotion (270 K) and $kJmol^{-1}$ k molecular relation	129-00-0 202.3 99 322-381 Knudsen 5.40E-04 31.94 11.76 97.79 \pm 3.3 100.3 423.0 for [6,21] effusion	1714-29-0 281.15 94 321-366 Knudsen 1.02E-04 30.86 11.935 99.23±4.3	3029-19-4 230.3 >98 360-393 Knudsen 5.43E-06 32.44 13.28 110.4 \pm 3.8 462.0 (40) effusion	5522-43-0 247.3 >98 379-408 Knudsen 5.82E-07 36.18 15.06 125.2±3.8 425.0 $^{\circ}_{N^+}$ ^{O-} [40] effusion
Vapor pre	CAS Registry Mc no. w		129-00-0 21	1714-29-0 2:	3029-19-4 2	5522-43-0 22
	Commoning	Compound	Pyrene C ₁₆ H ₁₀	1-Bromopyrene C ₁₆ H ₉ Br	1-Pyrenecarboxaldehyde C ₁₇ H ₁₀ O	1-Nitropyrene C ₁₆ H ₉ NO ₂

Table 7

	Deference		[78]	[78,96]	[55]	[54,97]	[66,86]	[50]
	Cruichirea	20000						S
Vapor pressure data on polycyclic aromatic compounds with four or more fused rings.	Melting	k		446.1	442.4		462.8	
	$\Delta H^{\circ}_{\mathrm{sub}}$	kJ mol ⁻¹		115.5		134.0		
	۰ <i>H</i> V	kJ mol ⁻¹	152.2	114.9	135.0 ± 2.6	127.2 ± 1.3	105.4	111.9±1.2
	sius- syron ttion tants	q	18.306	13.816	16.236	15.296		13.462
	Clau Clape equa	а	36.401	35.821	39.68	35.21		34.058
	$P^{\rm vap}$	Pa	1.35E-11	2.64E-05	3.72E-07	9.99E-08		1.5E-05
	Experimental		Knudsen effusion	Knudsen effusion	Knudsen effusion	Knudsen effusion	Transpiration	Knudsen effusion
	Temp	K	492.15	398.15	377-400	256-379	313-453	325–373
	CAS Registry. Molecular Minimum No. weight purity gmol ⁻¹ % 641-13-4 306.3136				Vac. Sub	Vac. Sub	6.66	66
			306.3136	230.2607	268.35	256.341	216.2772	234.32
			641-13-4	82-05-3	56-49-5	56-56-4	238-84-6	239-79-7
	Commonind	Compound	Anthranthrone C ₂₂ H ₁₀ O ₂	Benzanthrone C ₁₇ H ₁₀ O	20- Methylcholanthrene C ₂₁ H ₁₆	9,10-Dimethyl-1,2- benzanthracene C ₂₀ H ₁₆	1,2-Benzofluorene C ₁₇ H ₁₂	1,2- Benzodiphenylene sulfide C ₁₆ H ₁₂ S

Table 8

1258



Figure 1. Clausius–Clapeyron plot showing the effect of halogenation on the vapor pressures of pure naphthalene. •, Naphthalene [16]; \Box , 2-chloronaphthalene [34]; **a**, 2-bromonaphthalene [34]; and •, 1,4-dibromonapthalene [23].



Figure 2. Clausius–Clapeyron plot showing the effect of various substituents on the vapor pressures of pure naphthalene. **•**, Naphthalene [16]; •, 1-naphthol [68]; +, 2-naphthol [68]; \boxtimes (half-shaded box), 2-acetylnaphthalene [63]; **o**, 1,4-naphthoquinone [53]; •, 2,3-dimethylnaphthalene [63]; X, 2,6-dimethylnaphthalene [63].

enthalpy of sublimation of 2-anthracenecarboxylic acid is over 10% higher than that of 9-anthracenecarboxylic acid [40]. Although there are data available in the literature on a range of anthracene-based PAC, there are few data available with the same substituent on different carbon positions. We also see a range of effects for heterocycles of anthracene; the replacement of one nitrogen atom for one carbon atom at the 9-position (acridine) lowers the enthalpy of sublimation by approximately 10% [41–44], whereas the substitution of two nitrogen atoms at the 9 and 10 carbon positions to make phenazine has a negligible effect on the enthalpy of sublimation, although the vapor pressure increases owing to entropic effects [42,44].

The addition of a nitro Three-ring systems: fluorene. group at the 2-carbon position of fluorene increases the enthalpy of sublimation by more than 25% (approximately 26 kJ mol^{-1}), as seen in Table 4. The replacement of the carbon in position 9 of fluorene by addition of a carboxyl group increases the enthalpy of sublimation by 21.9 kJ mol^{-1} , an increase of approximately 25%. We also see a vapor pressure depression of over four orders of magnitude [44]. As compared with the addition of a nitro group to this same parent molecule, the addition of a carboxylic group shows a comparable increase in the enthalpy of sublimation. What is vastly different is the effect on entropy of sublimation. The interactions of the nitro groups clearly require a more ordered condensed phase, and the release of this order upon sublimation results in a large entropy benefit. On the other hand, the carboxylic groups, while being involved in energetically similar interactions in the condensed phase, can do so without requiring a greater degree of order. Consequently, the nitro substituted compound is more volatile than the carboxylic compound, despite the fact that the nitro group addition increases the energetic favorability of the condensed phase. The addition of an aldehyde group to fluorene also has a rather large impact on vapor pressure, although not nearly as large as that from the addition of a nitro or carboxyl substituent. The aldehyde addition increases the enthalpy of sublimation by 11.9 kJ mol⁻¹ whilst modestly increasing the entropy of sublimation $(\Delta_{sub}S/R)$ increased by $0.4 \text{ kJ mol}^{-1} \text{ K}^{-1}$) [44]. In this instance, the effect of the substitution is more dominated by enthalpy effects, without much in the way of compensating entropic effects.

Three-ring systems: acenaphthene. As Figure 3 shows, the vapor pressure of 5-bromoacenaphthene is decreased considerably as compared with acenaphthene. In Table 5, we see an 8-9 kJ mol⁻¹ influence of the single bromosubstituent on the sublimation enthalpy versus the parent compound. This is the extent of experimental data available (that the author could locate) on substituted acenapthene in the literature.

Three-ring systems: phenanthrene (methylphenanthrenes and the benzoquinolines). The impact of successive addition of methyl groups to phenanthrene highlights the critical role that substituent position plays on the resulting sublimation vapor pressures, as demonstrated in Table 6. Chirico et al. [46] note that the interaction between the 4-methyl group and the 5-position hydrogen of 4-methylphenanthrene



Figure 3. Vapor pressures of \blacksquare 5-bromoacenaphthene and \blacklozenge 1-bromopyrene as compared with parent PAH: • acenaphthene and \blacktriangle (triangle) pyrene [20,23].

contributes at least 22 kJ mol^{-1} to the enthalpy of sublimation at 400 K, attributed to a hindered rotation effect. Interestingly, Karnes et al. [46] find similar enthalpies of sublimation for 2,7-dimethylphenanthrene and 4,5-dimethylphenanthrene, despite the potential rotational effects noted by Chirico. However, for 2,4,5,7-tetramethylphenanthrene, Karnes et al. measure an enthalpy of sublimation of approximately 114 kJ mol⁻¹, whereas for 3,4,5,6-tetramethylphenanthrene, it was reported as 134 kJ mol⁻¹. The potential rotational and other steric effects of the adjacent methyl groups in the 3,4,5,6-tetramethylphenanthrene likely cause this substantially higher enthalpy of sublimation.

Table 6 also details the impact of substituting one nitrogen atom for a carbon within the phenanthrene ring, yielding a series of benzoquinolines. The enthalpy of sublimation corrected to 298 K of phenanthrene is approximately 92.4 kJ mol⁻¹. The enthalpy of sublimation of 3,4-benozoquinoline, corrected to 298 K, measured by different groups, ranges from 94.7 to 102.5 kJ mol⁻¹, whereas for 7,8-benzoquinoline, it drops to 81.0 kJ mol⁻¹ and for 5,6-benzoquinoline (in the range of 288–323 K, heat capacity data not available) was reported as 83.7 kJ mol⁻¹ [27,43,48–50]. This series of substitutions clearly illustrates the importance of substituent position of heteroatom on the vapor pressure behavior.

Four-ring systems: pyrene. 1-Bromopyrene shows a considerably decreased vapor pressure as compared with the parent pyrene, as seen in Table 7. In this case, the enthalpy effect of the single bromo-substituent is only modest, as it was for anthracene. It appears that the decrease in vapor pressure is dictated by the slight increase in enthalpy of sublimation, along with a slight decrease in

entropy of sublimation upon substitution (as noted through the *a* constant in the Clausius–Clapeyron equation in the tables). The addition of a larger carboxyl group on the same carbon increases the enthalpy of sublimation by approximately 10%, and an even larger effect—a 25% increase in ΔH_{sub} —is found by adding a nitro group to the 1-carbon of the parent pyrene molecule [6,21,24,40]. Given the absence of solid heat capacity data for the substituted compounds, it is difficult to draw more accurate conclusions.

Other systems of four or more rings. Table 8 provides data on substituted PAC with four or more fused rings available in the literature. Because of the lack of data on PAC and PH as large as these, the only conclusion we can form from looking at this assortment is that they also follow the trend that as the compound itself increases in molecular weight and number of benzene rings, the vapor pressure decreases and enthalpy of sublimation tends to increase.

The impact of intermolecular interactions. At atmospheric pressures and temperatures, intermolecular interactions play a relatively minor role in vapor phase behavior; the vapors often behave like ideal gases. However, in the liquid or solid phase, it is intermolecular interactions that bind a component to that phase. Consequently, the enthalpy changes upon vaporization and sublimation are a result of breaking intermolecular attractive bonds within the condensed phase. The higher the degree of attraction between molecules, the higher the required enthalpy change and the lower its fraction within the gas phase at equilibrium at a given temperature.

van der Waals forces are significant intermolecular attractions that create dispersive attractions between the molecules of a compound or compounds. All substances, regardless of their polarity, experience varying degrees of these instantaneous electron displacements, producing momentary electron-rich and electron-depleted pockets, creating intermolecular attraction between these regions. The size and shape of each molecule determine the intensity of the van der Waals forces. Long, straight chain molecules experience greater dispersion forces than conglomerates of aromatic rings, as straight chain molecules arrange larger temporary dipoles and can situate themselves closer together than shorter, agglomerated molecules. The direct relationship between the strength of van der Waals attraction forces to molecular size partially explains the experimentally observed trend between larger molecular size and decreasing sublimation vapor pressure.

Dipole–dipole interactions operate over a relatively long range; the potential energy of a pair of dipoles varies as $1/r_{ij}^3$, the inverse of the cube of the molecular separation between molecules *i* and *j* [51]. These charge imbalances, in addition to the van der Waals forces, result in attraction to a molecule's surroundings.

In addition to van der Waals forces and dipole-dipole interactions, organic compounds also experience induced dipole interactions resulting from polar structures, a potentially large contributing factor to PAC and PH behavior. Weakly attractive, induced dipole forces are the result of a polar characteristic in one molecule inducing a dipole in another, nonpolar, molecule (or molecular region) by disturbing the arrangement of electrons in the nonpolar species. A result of varying electronegativities of the assorted atoms in organic compounds includes organic structures with dissimilar atoms bound to one another having regions that are always deficient or enriched in electrons. These induced dipoles have a significant but not uniform impact on the vapor pressure and enthalpy of sublimation of a given compound.

For example, replacing a hydrogen in a PAH with a halogen, such as bromine or chlorine, increases the enthalpy of sublimation, as seen in the bromo- and chloro-naphthalenes and anthracenes. This trend does not necessarily follow the trend in electronegativity of the substituent group. Fluorene's electronegativity is greater than chlorine's, which is greater than bromine's. Increasing the size of the halogen and its ability to polarize increases the van der Waals and induced dipole attractions, yet the enthalpies of sublimation of 9,10dibromoanthracene and 9,10-dichloroanthracene are within the limits of error $(114.2 \pm 2.8 \text{ vs } 113.9 \pm 4.5 \text{ kJ mol}^{-1})$, respectively, over similar temperature ranges). Other functional groups, such as carboxyl groups, strongly increase the enthalpy of sublimation, as they offer dipole interaction possibilities. However, this is also strongly dependent on the location of the substituent group-the enthalpy of sublimation of 2-anthracenecarboxylic acid is 134.8 ± 3.4 kJ mol⁻¹ (over 401-421 K), whereas for 9-anthracenecarboxylic acid, the enthalpy of sublimation is only $120.1 \pm 3.8 \text{ kJ mol}^{-1}$ (over 385–420 K), compared with anthracene's at 98.5 ± 3.3 (over 322-348 K). Of course, it cannot be overlooked that adding any number of atoms to a basic aromatic structure will increase its interaction possibilities per mole, simply by virtue of introducing more van der Waals type interactions.

A third intermolecular interaction that strongly influences the vapor pressure and enthalpy of sublimation of organic compounds is hydrogen bonding, arising from the significant electronegativity differences between hydrogen and oxygen, nitrogen, and fluorene. Molecules with oxygen, nitrogen, and/or fluorene-containing substituents can interact with available hydrogens on neighboring molecules. Existence of hydrogen bonds results in significantly increased heats of sublimation over those expected when accounting for van der Waals and dipole attractions alone. The attraction due to any single hydrogen bonding interaction can add upwards of $10 \,\text{kJ}\,\text{mol}^{-1}$ to the total enthalpy of vaporization and significantly more to the enthalpy of sublimation for simple mono-aromatic compounds. For example, Almeida and Monte [52] recently demonstrated that a single hydrogen bond contributes 27 kJ mol^{-1} to the enthalpy of sublimation of benzoic acid and some of its derivatives.

The forces that act on organic molecules—van der Waals forces, dipole-dipole attractions, and hydrogen bondingare somewhat additive in their impact on the enthalpy of sublimation and vapor pressure. Successive substitution of hydrogens on parent PAH molecules will virtually always increase their enthalpies of sublimation. However, as we see clearly here, the overall impact on the enthalpy of sublimation is not a linear function of the number of substituent groups alone; it also depends upon the position of substituents on the parent molecule, the size and shape of the molecule, and other groups already present on the parent molecule. Structural elements of organic compounds give rise to the electronic forces that operate on a molecule and its neighbors. These attractive forces tend to keep molecules in their condensed phases, lower their vapor pressures, and raise their enthalpies of sublimation and melting points.

SUMMARY

The compiled data are intended to encourage improved thermodynamic model development and identify areas in the literature with gaps in experimental data. Although many techniques such as group contribution methods, quantitative–structure property relations, UNIFAC, and others are quite adept at predicting the sublimation vapor pressures and enthalpies/entropies of sublimation for nonsubstituted PAH, these models do not often tackle, or if they do they suffer greatly, compounds with heteroatomic substitutions.

In any system in which equilibrium exists between a condensed and a vapor phase, the propensity towards sublimation is controlled by the magnitude of the enthalpy and entropy of sublimation. It was noted that successive addition of halogens to PAH generally increases the enthalpy of sublimation and decreases the vapor pressure as compared with the parent compound. In the case of the smaller naphthalene, the difference in vapor pressures appears to be due more to enthalpic considerations, whereas for the larger anthracene, the difference is more attributable to entropic effects, as observed through the Clausius-Clapeyron equation as applied to sublimation vapor pressures. The results for pyrene and acenaphthene paint a mixed picture. These results warn that a simple group contribution approach, in which a halogen substitution is correlated with a particular, easily calculated effect on enthalpy, is unlikely to be successful. However, among the PAC composed of only fused benzene rings (naphthalene, anthracene, and pyrene), the relative effect of halogen addition decreases as the parent compound's molecular size increases. Larger thermodynamic effects occur with the addition of two halogens, although it appears from the dibrominated anthracenes that the carbon position to which the halogens are substituted does not strongly influence the change in vapor pressure.

We can see from this data that simply accounting for a given molecule's substitution by changes in molecular weight alone is not sufficient to describe changes in sublimation thermodynamics—nor is a one-size-fits-all substitution parameter for each atom or molecule (nitrogen, oxygen, carboxyl, etc.). Rather, the heteroatom substitution is likely a function of various inter- and intra-molecular interactions specific to both the geometry of the parent molecule and heteroatom substituted.

This collection of data on PAC and heterocycles highlights the lack of thermodynamic data available on these compounds to present a holistic picture of their sublimation thermodynamics. Although sublimation vapor pressure data are increasingly appearing in the literature for PAC and PH, there is still a gaping hole when it comes to fusion thermodynamics as well as solid-phase molar heat capacities.

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