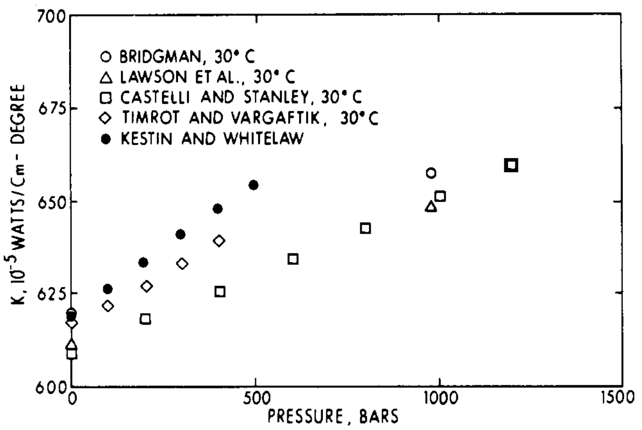

Figure 4. Comparison of historic pressure data at 30°C with experimental results

where K is given in W/cm-deg, P is the pressure in bars, and T is the temperature in degrees centrigrade. The values generated by this equation have a standard error of $\pm 1.5 \times 10^{-5}$ W/cm-deg or ±0.25% from the experimental data.

Discussion

Direct comparison of the data given by Equation 5 with that reported in the literature is only partly possible because most data for high pressure cover higher temperature ranges, and that for lower temperatures is restricted to low pressures.

Powell's (5) review and analysis of all the atmospheric pressure determinations has resulted in a set of "most probable" values for water. These data are shown in Figure 3 in comparison to our atmospheric values as determined from Equation 5. Our results are systematically about 0.5–1% lower than those "most probable" values cited by Powell. Although the origin of this discrepancy is unknown, no special effort was made to resolve this difference since we are primarily concerned with the effect of pressure on the thermal conductivity.

Previous experimental determinations of the thermal conductivity of water at high pressure have been conducted by Timrot and Vargaftik (*8*), Bridgman (*1*), and Lawson et al. (*3*); however, the overlap with our data is sparse. Figure 4 shows the data of Timrot and Vargaftik (*8*), Bridgman (*1*) [corrected in accordance with the recommendations of Riedel (*6*)], Lawson et al. (*3*), and our results for a temperature of 30°C.

Included in Figure 4 are the recommended values of thermal conductivity of water proposed by the Sixth International Conference on the Properties of Steam as reported by Kestin and Whitelaw (*2*). These values were calculated from a formula that covers the pressure range from saturation to 500 bars and temperatures from 0° to 300°C to a tolerance of ±2%. This tolerance just incorporates our values at atmospheric pressure, but as the pressure is increased, the discrepancy between our data and the values computed from the equation of Kestin and Whitelaw increases (Figure 4).

The reason for this behavior is that the Kestin and Whitelaw equation is designed to cover a large, nonlinear range of thermal conductivity. This possibly sacrifices some accuracy at the low end of the temperature scale, which is of but limited interest to power engineers, for greater accuracy at higher temperatures. Also, the data on which the equation is based are unstated.

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Vaporization Characteristics of 9-Phenylanthracene

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Equilibrium vapor pressures of solid (352–428K) and liquid (435–507K) 9-phenylanthracene were derived from torsion effusion and vapor-phase spectrophotometric absorbance measurements. The condensation coefficient on the solid was virtually unity. Molar absorptivities of the vapor were evaluated, and thermodynamic constants for the vaporization process were derived.

In connection with their studies of the solubilization of a series of similar hydrocarbons in DNA solutions, Craig and Isenberg (*5*) expressed an interest in the vaporization thermodynamics of 9-phenylanthracene. We also considered the kinetics of vaporization of such a large molecule to be of general interest and have undertaken a torsion effusion and a spectrophotometric study of the vapor pressure as a function of temperature. The large value of the molar absorptivity of the molecule in the vicinity of 242 mμ provides an opportunity for study of the temperature dependence of the absorbance of the saturated vapor at concentrations also suitable for effusion studies. By substantial variation of effusion orifice areas, information can be derived about the magnitude of the condensation coefficient on the solid; thermodynamic data derived from the two methods may be compared for consistency and provide a further test of the reliability of the effusion method (*20*).

Experimental

The torsion effusion apparatus was described previously (*15, 19*). Pyrex effusion cells were suspended by 1 or

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2-mil tungsten wires, from 66 to 70 cm in length, the diameter depending upon the specific cell used and the desired sensitivity. Sample temperatures, controlled within ±1°, were taken to be those indicated by calibrated thermocouples placed in a fixed dummy cell adjacent to the freely suspended cell. The validity of this assumption was verified by Rice and Gregory (*15*).

The total steady state pressure in the cell, P_s, was evaluated from the angular deflection θ with the proportionality constant determined by measurement of the vapor pressure of zinc (*1, 15*), by use of the equation (*15*)

$$\log_{10} P(\text{torr}) = 9.8765 - 6893.9T^{-1} - 0.19211 \log_{10} T - 0.0002622T$$

Two effusion orifices, approximately the same size and located on opposite sides at opposite ends, were formed in each cell. Cells had internal diameters ca. 1.4 cm and were ca. 4 cm long; orifice areas and apparatus constants are summarized below:

Cell	Orifice area (total) × 10^3 cm^2	$k \times 10^3$ torr rad^{-1}, $P = k\theta$
1	7.18	8.35 ± 0.15
2	90.9	15.2 ± 0.1
4	2.05	37.3 ± 0.3
5	46.0	2.13 ± 0.04

Absorbance measurements were made with a Cary 14H spectrophotometer. A description of the furnace and the quartz sample cells has been provided by Hilden (*8*) and Hilden and Gregory (*9*). To prevent condensation of vapor on the windows, the latter were kept about 2° above the temperature of the condensed phase (in a small side arm on the cell). The vapor could be fully condensed in the side arm, without disturbing the temperature of the cell windows, by insertion of a cold finger into the furnace; this procedure was convenient for calibration of the cell at various temperatures by comparison against a reference cell.

Samples of 9-phenylanthracene (Aldrich Chemical) were supplied by Craig and Isenberg of Oregon State University. They purified the material by double-vacuum sublimation. Samples sufficient to fill the effusion cells to about half volume were introduced directly without further treatment. Similarly, samples were inserted into Pyrex side arms attached to the quartz absorption cells via graded seals. The cells were then evacuated to a pressure of 10^{-6} torr and baked (350–400°) for several hours before sealing off the Pyrex extensions. Then an appropriate amount of 9-phenylanthracene, ca. 0.01 gram, was sublimed into each cell; the excess remained in the side arm which was then sealed off, leaving a small extension compatible with the furnace dimensions. Four different samples were used to study the vapor pressure; three additional samples were studied as superheated vapors to observe the variation of the absorbance of a fixed amount of sample with temperature. Cell path lengths of 1, 2.5, 5, and 10 cm, respectively, were used (*18*).

A differential thermal analysis experiment was carried out on 9-phenylanthracene over the temperature range of the vapor-pressure measurements on the solid phase. No evidence to indicate the existence of phase transitions in this interval was observed.

Results and Discussion

Effusion studies. Steady state effusion pressures were virtually independent of the choice of cell orifice area. Results are compared graphically in Figure 1. The data for each cell were first fitted to equations of the form $\log_{10} P(\text{torr}) = A - BT^{-1}$ by least squares; following is a list of the constants derived from the separate sets of data with the cell number, A, B, and the temperature (K) range indicated in that order: 1, 14.332, 6383 (357–378°); 2, 13.546, 6093 (361–368°); 4, 13.261, 5976 (368–395°); 5, 13.323, 6017 (352–364°). The combined data for all cells give the least-squares constants A = 13.981 and B = 6252, and the corresponding free energy equation $\Delta G° = 28{,}600 - 50.8T$ for the range 352–395K.

The lack of significant variation of the steady state pressure when the effusion orifice area is increased by a factor of 45 indicates that the condensation coefficient of solid 9-phenylanthracene is virtually unity. It appears that orientation requirements for accommodation of this large molecule on the surface do not hinder the condensation process. It has been pointed out by a number of workers that factors such as polarity, surface reactions, or significant changes in molecular geometry seem most likely to result in a small condensation coefficient (*14, 17*).

Absorbance studies. Representative spectra of 9-phenylanthracene over the wavelength intervals studied are shown in Figure 2. Initially, values of the absorbance $A = \log_{10} I_0/I$, at the peaks at 242 and at 353 mμ for each cell containing an excess of the condensed phase, were selected as measures of the concentration and were fitted by use of a least-squares treatment to an equation of the form $\log_{10} AT = C - BT^{-1}$. The results at 242 m$\mu$, measured over the temperature range 380–396K, gave a B constant identical within experimental error to that derived from the torsion effusion results for cell 4 in the same temperature range. Thus, it was assumed that the species absorbing light and the species effusing from the effusion cell were identical and that this species is the monomer. Dimers are not to be expected in the vapor phase in appreciable concentration because of steric hindrance (*3*). Hence, by use of the pressures indicated by

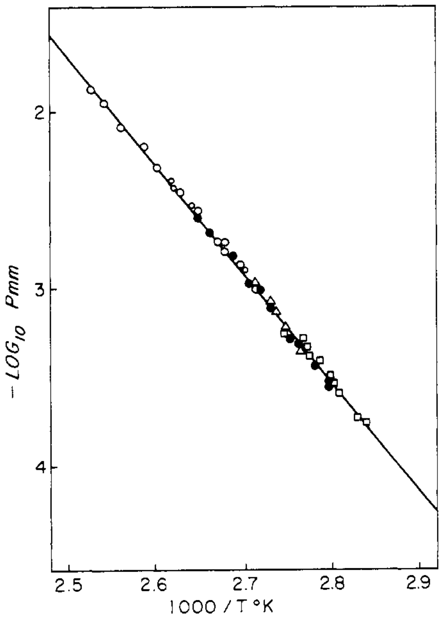

Figure 1. Torsion effusion vapor pressures for 9-phenylanthracene(s) = 9-phenylanthracene(g)
● Cell 1 (1-mil fiber)
△ Cell 2 (2-mil fiber)
○ Cell 4 (1-mil fiber)
□ Cell 5 (1-mil fiber)
— Equilibrium pressures predicted by least-squares treatment of all effusion data

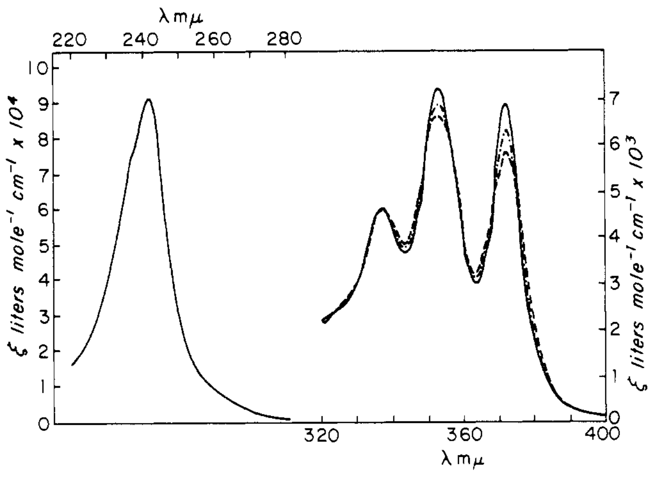

Figure 2. Apparent molar absorptivity vs. wavelength for 9-phenylanthracene vapor

—— 200° (220–280 mμ)
—— 150°
–·–·– 200° (320–400 mμ)
------ 250°

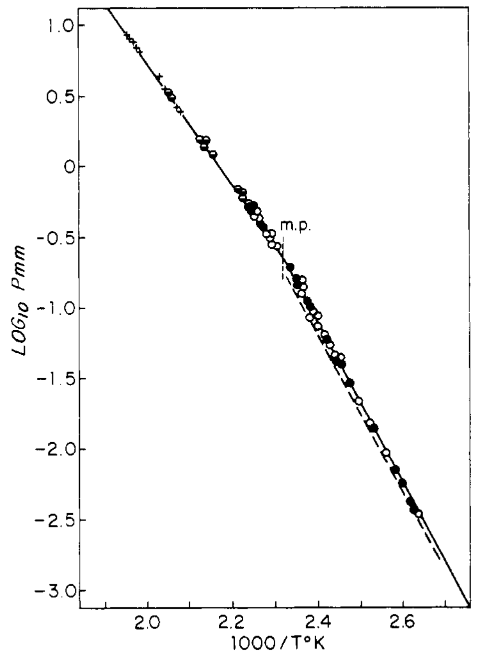

Figure 3. Vapor pressures evaluated from absorbance data for 9-phenylanthracene

○ Sample A
● Sample B
⊖ Sample C
+ Sample D
----- Klochkov (*12*)

the torsion effusion results, apparent molar absorptivities at 242 mμ may be calculated for each temperature of the corresponding Cary 14H study.

The absorbance of several samples of vapor at constant concentration, i.e., pressures below the saturation vapor pressure (no condensed phase present), was also measured between 170° and 250°. No significant change in the absorbance at 242 mμ was observed with change of temperature in this interval. This behavior was also assumed characteristic of the temperature region of the torsion data, and the measured torsion pressures were used to evaluate the molar absorptivity at 242 mμ; this yielded an average value of 91,050 l. mol^{-1} cm^{-1}.

The molar absorptivities at 353 mμ could then be evaluated at various temperatures from the concentrations indicated by the absorbance at 242 mμ. However, values at 353 mμ were temperature dependent, decreasing by approximately 1% when the temperature increased by 10° in the range 473–523K. The magnitude of the change is indicated for a 100° interval in Figure 2. Values ranged from 6980 at 200° to 6660 at 250°. The peak maxima for the vapor were shifted toward shorter wavelengths, and the molar absorptivities were somewhat lower than have been reported for the liquid phase, as may be seen in the following comparison: [λ max; molar absorptivity (l. mol^{-1} cm^{-1})]: vapor at 200° (242 mμ; 91,050) (353 mμ; 6980); in ethanol (255.5 mμ; 144,600) (*4*) (256 mμ; 123,000) (*13*) (364.5 mμ; 12,600) (*4*) (365 mμ; 9340) (*13*); in CH_2Cl_2 (259 mμ; 135,000) (*6*) (368 mμ; 9340); in C_6H_{12}-Bu_2O (255 mμ; 251,000) (*10*) (366 mμ; 15,870) (*10*).

Assuming that the temperature dependence of ε max at 353 mμ has the same temperature coefficient in the range 404–509K as observed for the superheated vapor in the range 473–523K, apparent molar absorptivities in the range of the equilibrium vapor studies were again derived and apparent vapor pressures subsequently evaluated from absorbances measured at this wavelength.

Least-squares treatment of the separate sets of data at the two wavelengths gave the following constants for expressions of the form $\log_{10} P(\text{torr}) = A - BT^{-1}$; the cell path length, wavelength, *A*, *B*, and temperature range follow in order: for solid ⇄ gas; 10 cm, 242 mμ, 13.285, 5985 (380–396K); 10 cm, 353 mμ, 12.702, 5752 (409–427K); for liquid ⇄ gas; 10 cm, 353 mμ, 10.129, 4646 (435–446K); 1 cm, 353 mμ, 9.464, 4340 (450–485K); 1 cm, 353 mμ, 9.325, 4276, (479–507K). A general correlation of all the Cary 14H results is shown in Figure 3. The only previous vapor-pressure study for this compound found in the literature is that of Klochkov (*12*), who used a manometer similar to that of Rodebush and Coons (*16*) in the pressure range 0.01–0.5 torr. Our results are about 10% higher than his; the heats compare favorably.

For a combined correlation of all torsion effusion and Cary 14H data, estimated values of $\Delta C_P°$ of −20 and −23 cal deg^{-1} mol^{-1} for the vaporization of the solid and liquid 9-phenylanthracene, respectively, have been used. These values are consistent with a comparison of our observed heats of vaporization and an estimated heat of vaporization at the normal boiling point of 417° of 15 kcal mol^{-1}, based on the Fishtine equation (*7*). The combined data have been correlated by a least-squares treatment in the form $\log_{10} P(\text{torr}) = A - BT^{-1} + \Delta C_P° R^{-1} \log_{10} T$.

For solid → vapor (353–428K), with an assumed $\Delta C_P° = -20$,

$$\log_{10} P(\text{torr}) = 43.790 - 7716T^{-1} - 10.065 \log_{10} T \quad (\sigma = 0.0174)$$

which gives:

$$\Delta G° = 35{,}308 + 20T \ln T - 187.2T \quad \text{kcal mol}^{-1}$$

$$\Delta H° = 35{,}308 - 20T \quad \text{kcal mol}^{-1}$$

$$\Delta S° = 167.2 - 20 \ln T \quad \text{cal deg}^{-1}\ \text{mol}^{-1}$$

Based on the scatter of data, the uncertainty in $\Delta H°$ is estimated as ±0.6 kcal mol^{-1}, and from σ, the uncertainty in $\Delta G°$ as ±0.25 kcal mol^{-1}; correspondingly, the entropy change is uncertain by ±2.0 eu.

For liquid → vapor (435–507K), with an assumed $\Delta C_P° = -23$,

$$\log_{10} P(\text{torr}) = 45.559 - 6770T^{-1} - 11.575 \log_{10} T \quad (\sigma = 0.0072)$$

which gives:

$$\Delta G^\circ = 30{,}980 + 23T \ln T - 195.3T \quad \text{kcal mol}^{-1}$$

$$\Delta H^\circ = 30{,}980 - 23T \quad \text{kcal mol}^{-1}$$

$$\Delta S^\circ = 172.3 - 23 \ln T \quad \text{cal deg}^{-1}\,\text{mol}^{-1}$$

Estimated uncertainties are ±0.3 kcal mol and 0.1 kcal in ΔH° and ΔG°, respectively, and ±1.0 eu in ΔS°. The equations lead to predicted values of $\Delta H^\circ = 15.1$ kcal mol^{-1} and $\Delta S^\circ = 21.9$ eu at the normal boiling point. At the melting point of 155°, the value, $\Delta H^\circ = 5.6 \pm 1$ kcal mol^{-1}, is derived.

Thermodynamic data found in the literature for vaporization of polycyclic aromatic hydrocarbons have generally been measured in different temperature ranges and are difficult to compare without knowledge of the heat capacities of the phases involved. The results of the present study seem reasonably in accord with expectation. A comparison with perylene ($C_{20}H_{12}$), a symmetrical, planar polycyclic aromatic hydrocarbon, is of interest; this substance may be supposed to be more closely packed in the crystal than the nonplanar 9-phenylanthracene ($C_{20}H_{14}$) (2); the former is reported to have an enthalpy of sublimation of 31 kcal and an entropy of sublimation of 52.5 cal deg^{-1} mol^{-1} (at a mean temperature of 140°) (*11*). Both these values are somewhat larger than those predicted by the equations derived for 9-phenylanthracene at 140° (27 and 46.7, respectively). The latter may be expected to have lower values if steric factors reduce the lattice energy and increase the entropy in the solid state.

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Prediction of Saturated Vapor Densities for Nonpolar Substances

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A relationship was developed capable of predicting saturated vapor densities for a variety of nonpolar substances. Data available in the literature for 25 substances were correlated to produce a relationship between the reduced saturated vapor density, $\rho_{R(v)}$, and the reduced temperature, T_R, reduced pressure, P_R, and z_c, the critical compressibility factor. For the 276 points considered, an average deviation of 1.9% resulted for T_R up to 0.985 and included helium (12 points, average deviation 4.3%) and hydrogen (12 points, average deviation 2.6%). An attempt to use this relationship for polar substances such as methyl alcohol, ethyl alcohol, ammonia, sulfur dioxide, and water produced an average deviation of 2.7% for 42 data points and therefore should be acceptable for most applications.

The saturated vapor density of a substance represents a point on the saturated vapor envelope of a PVT surface and therefore depicts the limiting value of a gaseous isotherm just before condensation is initiated. Thus, the saturated vapor state becomes the point of intersection between a super-heated gas isotherm and the corresponding vaporizing liquid isotherm.

Cailletet and Mathias (5) in their pioneering work in 1886 attempted to relate the saturated liquid and saturated vapor densities with temperature. Their efforts resulted in the formulation of the empirical "rectilinear diameter rule" which states that the mean saturated density is linearly dependent on temperature:

$$\tfrac{1}{2}(\rho_l + \rho_v) = mT + k \tag{1}$$

which in reduced form becomes

$$\tfrac{1}{2}(\rho_{R_l} + \rho_{R_v}) = sT_R + t \tag{2}$$

where $s = mT_c/\rho_c$ and $t = k/\rho_c$. At the critical point, $\rho_{R(l)} = 1$, $\rho_{R(v)} = 1$, at $T_R = 1$ produces the relation, $1 = s + t$. Substituting for t in Equation 2 produces

$$\tfrac{1}{2}(\rho_{R_l} + \rho_{R_v}) = 1 - s(1 - T_R) \tag{3}$$

In 1957 Guggenheim (*16*) related the difference between the reduced saturated liquid and vapor densities to the reduced temperature as

$$\tfrac{1}{2}(\rho_{R_l} - \rho_{R_v}) = \tfrac{7}{4}(1 - T_R)^{1/3} \tag{4}$$

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