Vapor Pressures and Derived Enthalpies of Vaporization for Some Condensed-Ring Hydrocarbons

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Experimental values of vapor pressure for seven condensed-ring aromatic hydrocarbons (acenaphthene, phenanthrene, fluorene, and 1,8-, 2,3-, 2,6-, and 2,7-dimethylnaphthalene) in solid and liquid states were measured in the range 0.1–25.8 mm Hg by means of the inclined-piston deadweight gage. Enthalpies of sublimation and vaporization were derived at the melting temperature and 125°C by application of the Clapeyron relation.

Hydrocarbon fractions in heavy ends of petroleum or shale oil, natural tars, and oils derived from the liquefaction of coal are composed largely of hydrogen-deficient condensed-ring molecular systems. Because many of the pure compounds that are members of these systems are low-pressure solids at room temperature, the amount of reliable physical and thermodynamic data available for them, compared to that for alkane hydrocarbons (*1–3, 8, 11–13*), is sparse. This paper is based on part of a comprehensive thermodynamic investigation on polynuclear aromatic compounds performed by the Bureau of Mines as American Petroleum Institute Research Project 62.

No experimental vapor-pressure values are reported in the literature in the ranges of the present investigation. However, Nelson and Senseman (*10*) report high-temperature measurements on liquid phenanthrene, and Mortimer and Murphy (*9*) report high-temperature measurements on liquid phenanthrene, acenaphthene, and fluorene. We found no literature measurements on the dimethylnaphthalenes in the range of the present measurements; however, Driesbach (*6*) does give a few calculated values, based apparently on normal boiling points, which are only in fair agreement with present values.

Materials

The samples of phenanthrene and 2,3-dimethylnaphthalene were purchased from James Hinton Co. and used without further purification. Acenaphthene was provided by courtesy of D. L. Camin, Sun Oil Co. Fluorene and 1,8-dimethylnaphthalene were synthesized and zone-refined by the Hydrocarbons Synthesis Project, American Petroleum Institute, E. J. Eisenbraun, Director, Oklahoma State University; and 2,6- and 2,7-dimethylnaphthalene were obtained by courtesy of D. L. Camin and J. A. Hedge, Sun Oil Co., and zone-refined by the Hydrocarbons Synthesis Project referred to above. The purities of the samples given in column 2, Table I (except for 2,3-dimethylnaphthalene) were determined from measurements of the lowering of the melting point as a function of fraction melted observed during calorimetric heat capacity studies in this laboratory as part of API Research Project 62 on "Thermodynamics of Hydrocarbons from Petroleum."

Experimental Methods

The inclined-piston manometer described by Douslin and McCullough (*4*) and Douslin and Osborn (*5*) provides a primary determination of static pressure. Briefly, the method (Figure 1) consists of balancing the known weight, W, of a free piston declined from the horizontal by a measured angle, θ, against the pressure exerted by the vapor of the sample. From the

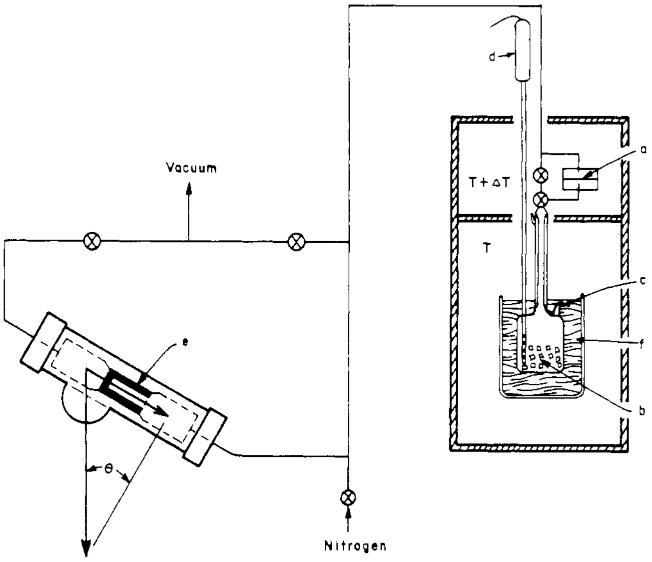

Figure 1. Inclined-piston vapor-pressure apparatus
- a. Null diaphragm
- b. Sample
- c. Seal-off
- d. Platinum thermometer
- e. Piston
- f. Mercury or gallium reservoir

Table I. Enthalpy of Sublimation, ΔH_{sub}, and Vaporization, ΔH_{vap}, Derived from Clapeyron Relation, kcal mol^{-1}

Substance	Min purity, mol %	Triple point,[a] K	ΔH_{sub}, TP[b]	ΔH_{vap}, TP[b]	ΔH_{fusion}[a]	ΔH_{vap}, 398.15K
Acenaphthene	99.98	366.559	19.70	14.56	5.13	14.14
Phenanthrene	99.99	372.385	(20.85)[c]	16.92	3.93	16.39
Fluorene	99.99	387.943	19.54	(14.86)[c]	4.68	...
1,8-Dimethylnaphthalene	99.99	336.328	(19.02)[c]	15.25	3.77	14.27
2,3-Dimethylnaphthalene	99.9+	...	19.37	14.30	...	14.21
2,6-Dimethylnaphthalene	99.95	383.317	19.71	14.01	5.99	13.81
2,7-Dimethylnaphthalene	99.95	368.812	19.89	14.21	5.58	13.82

[a] Determined calorimetrically by H. L. Finke and J. F. Messerly of the energy relations research group, Bartlesville Energy Research Center, Bureau of Mines. [b] TP = triple point. [c] Derived with the aid of ΔH_{fusion}, column 6.

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area and weight of the piston, the angle of declination, θ, and the acceleration of gravity, the vapor pressure is calculated as a primary quantity, $p = (g/g_{\text{std}})(W \sin \theta)/A$. The apparatus was modified for operations above room temperature by inserting a sensitive null diaphragm, a, and nitrogen gas column between the sample, b, and the piston face, e. Corrections were applied, when significant, for the nitrogen gas head and the sample vapor head between the null diaphragm and the surface of the liquid or solid sample.

The sample was placed in a Pyrex glass bulb which was immersed in a mercury or gallium reservoir, f, in a thermostated bath controlled to 0.001K. A positive temperature increment in the upper part of the thermostated bath prevented condensation of sample on the underside of the null diaphragm.

Outgassing of the sample and the Pyrex bulb was done before the sample was placed in the thermostated bath. Initially, the sample as pea-size chunks of solid crystalline material was placed into an L-shaped tube that extended well away from the Pyrex bulb but was sealed directly to it on a side of the bulb opposite from the thermometer reentrant well. The Pyrex bulb with neck and valve was baked out for 48 hr at about 200°C under a high vacuum, while the sample inside the L-shaped tube was refrigerated with Dry Ice. When the baking was completed, the assembly was tilted, allowing the chunks of sample to enter the sample bulb. The L-shaped tube was then sealed off close to the surface of the bulb indicated by the small protuberance, c, left from the sealed-off tube. Occasionally during the course of the measurements, the sample was cooled and the entire system pumped for a short period to remove any inert gas that might have been desorbed after the initial outgassing operation described above.

Temperatures were measured with a precision of 0.001° on the International Temperature Scale [T, K = t, °C (Int., 1968) + 273.15] (*7*) by use of a 25-ohm platinum resistance thermometer that had been calibrated by the National Bureau of Standards and checked at the triple-point temperature of a certified benzoic acid cell. Periodic observations of the ice-point resistance of the thermometer showed no significant change. The resistance of the thermometer was measured to a precision of 2×10^{-5} ohm with a high-sensitivity galvanometer and Mueller G-2 bridge, the coils of which had been compared and adjusted to a standard resistor calibrated at the National Bureau of Standards.

Results

The unsmoothed experimental vapor pressures determined on liquid and solid phases of the samples are in Table II. Measurements were always begun at the lowest temperature, on the solid phase, and thereafter taken at regularly increasing temperatures through the fusion and into the liquid phase. Because of small amounts of impurities, the vapor-pressure curve at the solid-liquid transition was never exceptionally sharp and was displaced downward 0.01 to 0.10K from the triple-point temperature representing 100% pure material.

The extension of the present phenanthrene data to higher temperatures on a log p vs. $1/T$ plot brings them into fair agreement with the high-temperature results of Mortimer and Murphy (*9*) and Nelson and Senseman (*10*). However, the results reported by Mortimer and Murphy do not show the curvature that is characteristic of the present results or of those of Nelson and Senseman, which both lie reasonably well on a single convex line. Also, an extension to higher temperatures of the present acenaphthene data along the convex curvature of the line intersects the higher temperature data of Mortimer and Murphy (*9*). Consequently, Mortimer and Murphy's data, which are represented by a straight line, would, if extrapolated to the present temperature range, predict significantly higher values than those presently observed.

From the slopes of the experimental lines on log p vs. $1/T$

Table II. Experimental Vapor Pressures (mm Hg[a]) Determined by Inclined-Piston Manometry

Acenaphthene		Phenanthrene		Fluorene		1,8-Dimethylnaphthalene		2,3-Dimethylnaphthalene		2,6-Dimethylnaphthalene		2,7-Dimethylnaphthalene	
t, °C	p	t, °C	p	t, °C	p	t, °C	p	t, °C	p	t, °C	p	t, °C	p
Solid		Liquid		Solid		Solid		Solid		Solid		Solid	
65.000	0.149	100.000	0.228	75.000	0.113	55.000	0.111	60.000	0.105	75.000	0.402	60.000	0.149
70.000	0.231	105.000	0.309	80.000	0.167	57.500	0.136	65.000	0.165	80.000	0.611	65.000	0.232
75.000	0.351	110.000	0.410	85.000	0.242	60.000	0.170	70.000	0.254	85.000	0.927	70.000	0.356
80.000	0.529	115.000	0.552	90.000	0.356	62.500	0.213	75.000	0.382	90.000	1.367	75.000	0.548
85.000	0.787	120.000	0.720	95.000	0.512			80.000	0.574	95.000	1.988	80.000	0.830
90.000	1.151	125.000	0.936	100.000	0.744	Liquid		85.000	0.852	100.000	2.888	85.000	1.237
92.500	1.388	130.000	1.208	105.000	1.061			90.000	1.237	105.000	4.116	90.000	1.820
93.195	1.463	135.000	1.554	110.000	1.500	65.000	0.256	95.000	1.782	110.000	5.782	95.000	2.639
		140.000	1.987	114.000	1.943	70.000	0.357	100.000	2.537				
Liquid		145.000	2.515			75.000	0.493			Liquid		Liquid	
		150.000	3.156			80.000	0.672	Liquid					
95.000	1.612					85.000	0.904			111.000	6.037	96.000	2.812
100.000	2.108					90.000	1.206	105.000	3.445	115.000	7.305	100.000	3.460
105.000	2.732					95.000	1.585	110.000	4.413	125.000	11.500	105.000	4.441
110.000	3.513					100.000	2.075	115.000	5.633	130.000	14.224	110.000	5.678
115.000	4.485					105.000	2.694	120.000	7.196	135.000	17.476	115.000	7.186
120.000	5.666					110.000	3.463	125.000	8.994	140.000	21.303	120.000	9.035
125.000	7.118					115.000	4.421	130.000	11.277	145.000	25.816	125.000	11.279
130.000	8.883					120.000	5.616	135.000	13.902				
135.000	11.019					125.000	7.063						
140.000	13.572					130.000	8.824						
						135.000	10.955						
						140.000	13.525						

[a] 1 mm Hg = 0.1333224 kN/m^2.

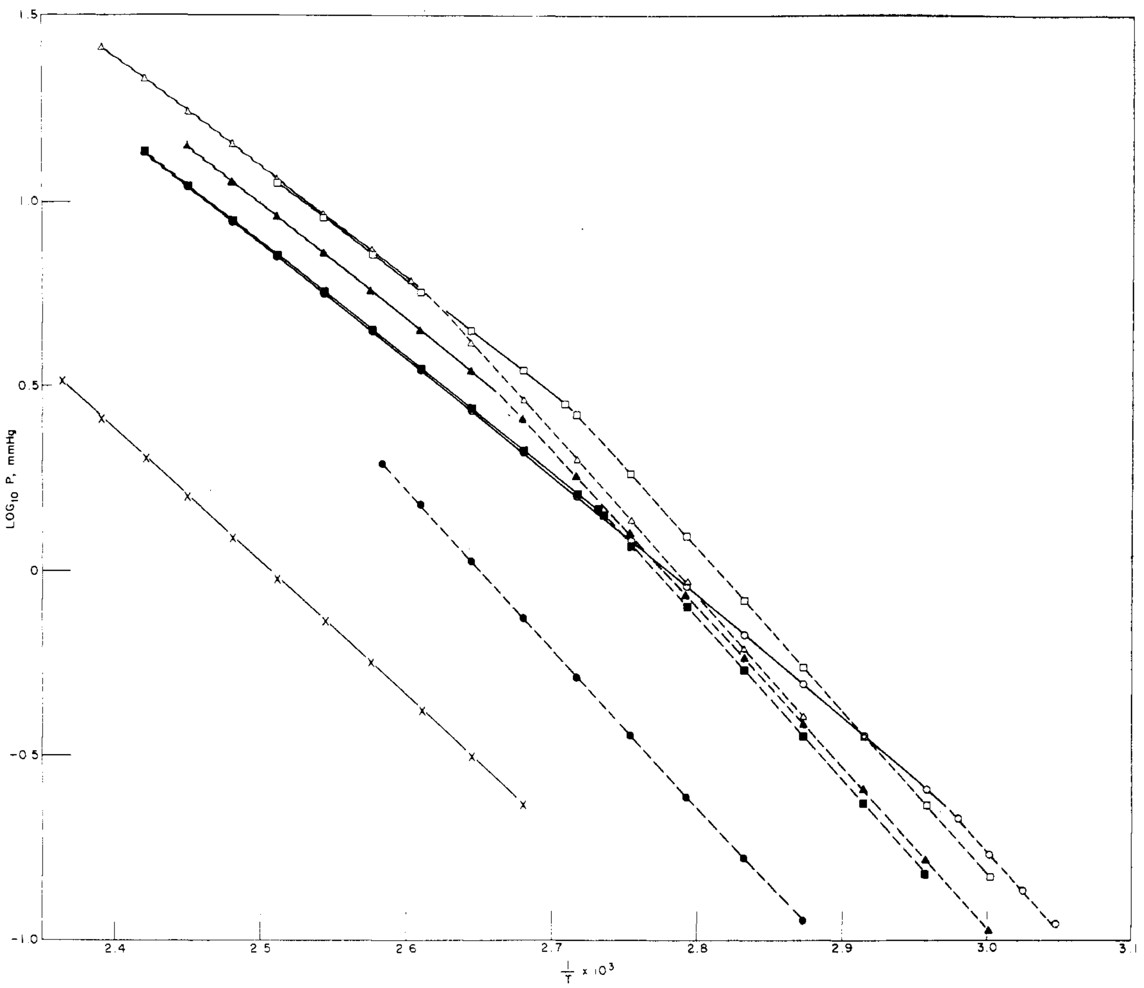

Figure 2. Vapor-pressure relations for solid and liquid phases of condensed-ring aromatic hydrocarbons

○ 1,8-Dimethylnaphthalene
▲ 2,3-Dimethylnaphthalene
△ 2,6-Dimethylnaphthalene
□ 2,7-Dimethylnaphthalene
■ Acenaphthene
● Fluorene
X Phenanthrene
— Liquid
- - Solid

plots (Figure 2), enthalpies of sublimation or vaporization at the melting temperature and at 125°C were determined by the Clapeyron relation (Table I). It is difficult to obtain a reliable extrapolation to 25°C of the vapor pressures or derived values of the enthalpies of vaporization, although the slopes of solid and liquid phases of the various compounds seem quite regular. The behavior of 1,8-dimethylnaphthalene is quite noticeable because its pressure is lower than that of the other dimethylnaphthalenes in the liquid and higher in the solid. For phenanthrene, fluorene, and 1,8-dimethylnaphthalene, the calorimetric enthalpy of fusion was used to obtain either ΔH_{sub} or ΔH_{vap} not derivable solely from the vapor-pressure results. For acenaphthene, 2,6-, and 2,7-dimethylnaphthalene, the differences between calorimetrically measured and vapor-pressure-derived values for the enthalpies of fusion are small.

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