Table V. Value of C for Different Hydrocarbon Groups

Hydrocarbon Group	Constant
Cyclohexane	515
Bicyclohexyl	535
Dicyclohexanes, separated by straight chains	568
Dicyclohexanes, separated by branched chains	515
Indan, hexahydro-	520
Naphthalene, decahydro-	545
Paraffin	550

ACKNOWLEDGMENT

Permission from WADD, Wright-Patterson Air Force Base, Ohio, to publish these data is appreciated. We thank Robert C. Reid of the Massachusetts Institute of Technology for helpful discussion and advice.

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RECEIVED for review June 22, 1962. Accepted September 14, 1962. This work was performed under the direction of Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio, on Contract **AF 33(616)-5799.**

Vapor Pressure of Naphthalene

Thermodynamic Consistency with Proposed Frequency Assignments

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New vapor pressure measurements for solid naphthalene in the submicron region are presented. With present knowledge of the normal modes of vibration of the $C_{10}H_8$ molecule, a value $\Delta H_0^0 = 18.30 \pm 0.05$ kcal./mole may be deduced for the process of sublimation. From this and values of the vapor pressure of the liquid, the free energy function is derived up to 500° K. At 25° the free energy function is 63.21 ± 0.08 kcal./mole. The success of various vibrational frequency assignments in correlating vapor pressure and heat of vaporization data is discussed. Many previous vapor pressure data for the solid are shown to be grossly in error.

THE FORMIDABLE task of assigning values to the 48 fundamental vibrational frequencies of the naphthalene molecule has been attempted by a number of spectroscopists in recent years. Although a good deal of progress has been made in this matter, as evidenced by recent normal coordinate calculations (*10*, *28*), it is not yet possible to calculate the thermodynamic functions of the ideal gas at elevated temperatures with even moderate accuracy by statistical methods. By combining each of seven recently reported frequency assignments with certain pertinent thermodynamic data, values of the free energy function may be derived with fair accuracy up to 500° K., and an improved value of the heat of sublimation at 25° may be obtained. In this connection previous values of the vapor pressure of the solid are critically evaluated and new measurements are presented in the range^{-5} to 10^{-3} mm. of mercury. The derived values of the free energy functions allow a calculation of the vapor pressure of the solid up to the melting point with an estimated ±5% uncertainty. Naphthalene may therefore provide a convenient test substance for low pressure manometers such as the Knudsen effusion cell.

EXPERIMENTAL

The vapor pressures of naphthalene, ice, benzene and carbon tetrachloride were measured between 10^{-5} and 10^{-3} mm. with a Knudsen gage. The construction of the gage and the method of correcting for nonlinearity of response have been described elsewhere (*22*). The latter three substances served to determine the gage sensitivity (deflection per unit pressure) to ±3% on the basis of their accurately calculated vapor pressures (*21*). As a result of this method of calibration, it was discovered that the McLeod gage previously used for calibrating (*22*) was reading correct relative pressures but 20% low in absolute pressure. This may have been caused by the streaming of mercury vapor into the isolating cold trap (*24*). The usual sources of error expected in the determination of very low vapor pressures were exhaustively explored. They could account only for the scatter of the data, which was somewhat greater than the precision of the Knudsen gage. In particular, care was taken to prevent rapid changes in the temperature of the solid samples; this was especially advisable for ice (*11*). Although the decision to base the calibration on calculated vapor pressures was grounded on evidence independent of the substance naphthalene, the resulting values of the vapor pressure of naphthalene fit the over-all thermodynamic picture well.

The napthalene sample was sublimed in vacuo into a small glass bulb connected to a break-seal through a length of 3 mm. I. D. glass tubing. The sample was then sealed, and the bulb with its break-seal was sealed onto the Knudsen gage. This constituted the measuring system and was isolated from the vacuum system by a magnetically operated, greaseless ball and socket joint, situated inside the vacuum system. There was no stopcock grease exposed inside the measuring system itself. The gage was evacuated for several weeks before the sample bulb was opened. An ultimate vacuum of 10^{-6} mm. was obtained. The calibration substances were distilled directly into a similar sample bulb already attached to the gage without benefit of the break-seal procedure.

A conventional cryostat consisted of a double-walled, cylindrical borosilicate glass flask filled with pentane and immersed in liquid nitrogen. The flask could be evacuated to control heat transfer to the coolant, and a heater immersed in the pentane provided a fine control of the temperature. A copper cylinder, just fitting inside the flask, helped eliminate extreme temperature gradients. A certain gradient was desirable to assure that the condensed phase of the sample was in the coolest region in contact with the vapor. A copper constantan thermocouple, calibrated at the dry-ice point, was wrapped around the sample bulb to permit determination of the temperature of the sample to ±0.03°. To this precision the temperature of the sample could be held constant for at least 5 minutes before a slow drift set in. Additional vapor pressure measurements, in which common freezing mixtures were used to control the temperature of the sample, gave results in agreement with those obtained using the above cryostat.

The whole of the temperature gradient between the sample and the gage occurred over the 3 mm. I. D. tubing below the break-seal. This relatively small bore assured a thermal transpiration effect approaching the Knudsen limiting law, $P_2/P_1 = (T_2/T_1)^{1/2}$. The actual calculation of the effect was made using a modified Liang equation (*7*) with a special low pressure correction (*26*). It should be pointed out that Figure 2 of reference 26 applies only where $T_1 = 77.8°$ K, and $T_2 = 297.1°$ K. and must be scaled for other temperature conditions. The scaling formula used here was

$$R/R_L = [(R/R_L) \text{ of ref. } 26] \times (1 - R_0)/[1 - (77.8/297.1)^{1/2}]$$

The deviation of P_2/P_1 from the limiting law was always small and could be neglected for water, because of the small value of the collision diameter of the H_2O molecule, and in the case of naphthalene, because of the small value of the transpiration effect itself.

Commercial naphthalene, 1% thianaphthene (*4*), was recrystallized from ethanol and purified by zone-melting. Although thianaphthene forms solid solutions with naphthalene, the phase diagram is favorable for purification by fractional crystallization (*18*). The melting point of the purified sample was measured from a cooling curve to be 80.10° corresponding to 99.7 mole % pure.

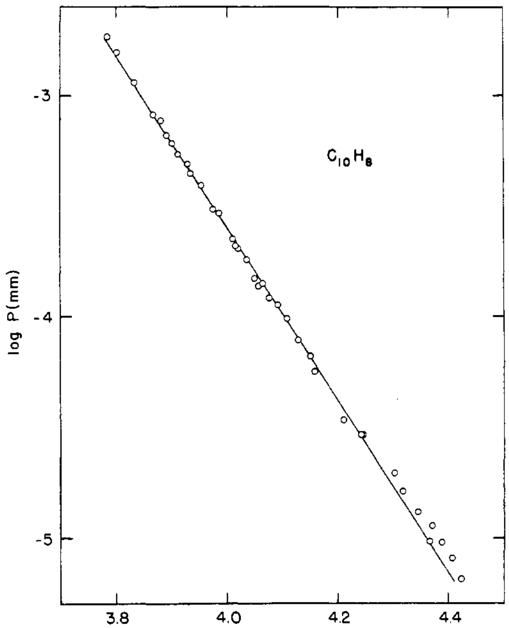

Figure 1. Naphthalene vapor pressure data of this work

Benzene was purified by distillation followed by fractional freezing: m.p. = 5.51°, 99.97 mole % pure. Carbon tetrachloride was purified by distillation: $n_D^{25.7} = 1.4568$, estimated 99.9 mole % pure based on carbon disulfide impurity. Ordinary distilled water was used.

Smoothed values of the vapor pressure of naphthalene were obtained from the best straight line drawn through the data (log P vs. $1/T$). The estimated reliability of P is ±5% in the middle of the range and somewhat less at either extreme. The results are shown graphically in Figure 1 and quoted here at four points,

T.° K.	$1000/T$	log Pmm.
230	4.348	0.046 – 5
240	4.167	0.747 – 5
250	4.000	0.396 – 4
260	3.846	0.995 – 4

DISCUSSION

To compare the present results with the numerous vapor pressure measurements of previous workers, use was made of the relationship between the standard Gibbs free energy of vaporization (ΔG^0) and the vapor pressure (P),

$$\Delta G^0 = -RT \ln P - BP = \Delta(G^0 - \mathrm{H}_0^0) + \Delta H_0^0 \quad (1)$$

where the vapor is assumed to obey the equation of state, $PV = RT + BP$. The constancy of the quantity ΔH_0^0, as calculated from Equation 1, forms a criterion of the accuracy to which the remaining terms in the equation are known. There is a rather large uncertainty in the value of the free energy function of ideal gaseous naphthalene over the temperature range of interest, due to the uncertainty in the frequency assignment. However, the resulting inconstancy in ΔH_0^0 should manifest itself in no more than a smooth drift whith temperature for any one particular

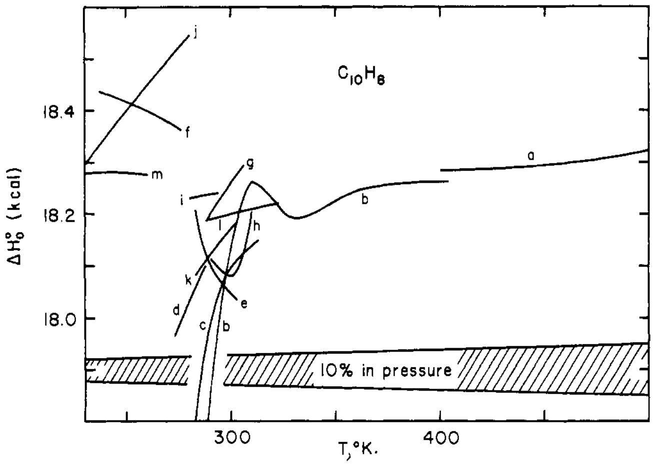

Figure 3. Values of Δ_0^0 of sublimation of naphthalene

—Calculations from Equation 1 with vapor pressure data a and m cited in Figure 2, using seven different vibrational frequency assignments.

○Calculations from Equation 2 with the colorimetric value of the heat of vaporization.

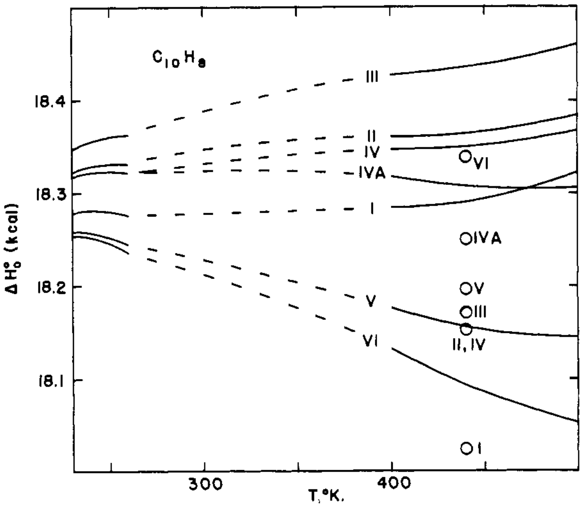

Figure 2. Values of ΔH_0^0 of sublimation of naphthalene calculated from Equation 1 with frequency assignment **I** and the following vapor pressure data: *a (9), b (1), c (5), d (25), e (33), f (3), g (34), h (29), i (8), j (13), k (30), l (12),* and *m,* this work

assignment. From the way in which the vibrational contributions to the free energy increase with temperature this drift should probably, but not necessarily, be monotonic. The accurately known vapor pressure values in the millimeter range for the liquid (*9*) between 400 and 500° K. help establish this drift. In the low pressure range, therefore, erroneous vapor pressure data can be expected to yield inconsistent values of ΔH_0^0.

On this basis vapor pressure data for the solid, drawn from eleven sources in the literature (*1, 3, 5, 8, 12, 13, 25, 29, 30, 33, 34*) were compared with the values reported here. The vibrational frequency assignment of Luther and co-workers (*16, 17*), hereafter designated as **I**, was arbitrarily chosen for the calculation of the free energy function of the ideal gas, along with the constants, $\sigma = A \times B \times C = 1.6651 \times 10^{112}$ g.^{3} cm.^{6}, and the usual harmonic-oscillator-rigid-rotor approximation. The thermodynamic functions of the solid were taken from the most recent measurments (*20*). The heat capacity of the liquid was extrapolated to 500° K. with the equation, $C_{sat} = 19.212 + 0.092572\ T$ (*20*). Comparing this relation with earlier measurments (*2, 31*), it is estimated that the value of $(G^0 - H_0^0)$ for the liquid is uncertain to ±25 cal./mole at 500° K. The second virial coefficient (B) has been calculated from the Berthelot equation using the critical constants (*27*), $T_c = 753°$ K., $P_c = 41$ atm., and B(cc./mole) $= 106[1 - 6(753/T)^2]$. The results of the calculation of ΔH_0^0 are given graphically in Figure 2. Because of the disparity even among more recent data on the vapor pressure of the solid, only the values reported here were included in subsequent calculations.

The calculation of ΔH_0^0 was repeated for each of six other frequency assignments; **II**, McClellan a nd Pimentel (*19*); **III**, Lippincott and O'Reilly (*15*); **IV**, Mitra and Bernstein (*23*); **IVA**, the alternate assignment of Mitra and Bernstein (*23*); **V**, Freeman and Ross (*10*) with the out-of-plane frequencies of assignment **VI**; **VI**, Scully and Whiffen (*28*) with the uncertain A_u mode set at 195 cm.$^{-1}$. The results are plotted in Figure 3. Dashed lines join the curves based on the vapor pressure of the liquid with those based on the vapor pressure of the solid reported here for each frequency assignment. From the low temperature region a value, $\Delta H_0^0 = 18.30 \pm 0.05$ kcal./mole, is deduced. This choice is clearly reasonable even in the absence of low pressure data.

From the calorimetric value of the latent heat of vaporization at 440.9° K. (*6*), a value, $\Delta H_{440}^0 = 11.134 \pm 0.030$ kcal./mole, may be derived for the enthalpy of vaporization to the ideal gas at 440.0° K. Values of ΔH_0^0 calculated at this temperature from the relation

$$\Delta H_0^0 = \Delta H^0 - \Delta(H^0 - H_0^0) \qquad (2)$$

have been included in Figure 3. The enthalpy function for the ideal gas is more sensitive to the choice of frequencies than is the free energy function, and it is not surprising that the values of ΔH_0^0 obtained from Equation 2 differ by as much as 250 cal. from those obtained from Equation 1. This difference corresponds to the term $T\ \delta\ S^0$, where $\delta\ S^0$ is, in turn, the difference between the calorimetric and spectroscopic entropies of the ideal gas. On an entropy basis, assignments **IVA** and **V** are best because they yield the smallest values of δS^0 at 440° K. Of these two **IVA** is to be preferred because it yields a more constant value of ΔH_0^0 from vapor pressure data.

From the derived value of the constant ΔH_0^0 a new set of free energy functions of the ideal gas have been calculated with Equation 1. For the region between 260 and 400° K., where there is a lack of dependable vapor pressure data, assignment **I** has been used as a guide in interpolation. The results are tabulated in Table I with interpolated values in parenthesis. Values of ΔG^0 of vaporization or sublimation and of P, calculated with the aid of the values in Table I, will be more accurate than the uncertainty in ΔH_0^0 would indicate, because of internal consistency with experimental values of P. An uncertainty of ±5% in the values of P

Table I. Free Energy Function of Ideal Gaseous Naphthalene

T, ° K.	$(H_0^0 - G^0)/T^a$, Cal./Mole - ° C.
250	60.44
273.15	(61.78)
298.15	(63.21)
300	(63.31)
350	(66.14)
400	68.95
450	71.74
500	74.48

[a] Estimated uncertainty is ± (50/T).

reported here and less than ±1% in P for the liquid, lead to a reasonable assignment of ±5% to values of P calculated in the intermediate range. For ΔG^0 this corresponds to $\pm 0.1T$ cal. or ±30 cal. at 25°.

From the standard heat of formation of solid naphthalene at 25° (*32*), and the entropies and free energy functions of hydrogen and graphite (*14*), the standard free energy of formation of the ideal gas was calculated up to 500° K. (Table II).

In spite of the uncertainty in the enthalpy function of the ideal gas, it is possible to derive a somewhat more accurate value of the heat of sublimation at 25° than the recently quoted value of 17.50 ± 0.25 kcal./mole (*32*). The calculation was made both with Equation 2 and with the alternate relationship,

$$\Delta H^0_{440} = \Delta H^0_{298} + \Delta(H^0 - H^0_0)_{440} - \Delta(H^0 - H^0_0)_{298}$$

The difference in the results of these two calculations (Table III) may be traced, approximately, to the average value of $T\delta S^0$ at 400° K. for the seven frequency assignments considered.

Table II. Standard Free Energy of Formation of Ideal Gaseous Naphthalene

T, ° K.	ΔG^f, Kcal./Mole
298.15	53.58 ± 0.39
350	50.23
400	47.09
450	44.00
500	40.92

Table III. Heat of Sublimation of Solid Naphthalene and Heat of Formation of Ideal Gaseous Naphthalene at 25° in Kcal./Mole

Frequency Assignment	$\Delta(H^0 - H^0_0)_{298}$	$\Delta,\Delta(H^0 - H^0_0)\vert^{440a}_{298}$
I	−0.842 ±	−6.048 ± 0.050[b]
II	−0.836	−6.184
III	−0.800	−6.237
IV	−0.842	−6.176
IVA	−0.879	−6.238
V	−0.940	−6.123
VI	−0.990	−6.215
Average	−0.876 ± 0.052[c]	−6.174 ± 0.072[c]
	$\Delta H^0_0 = 18.300 \pm 0.050$	$\Delta H^0_{440} = 11.134 \pm 0.030$
	$\Delta H^0_{298} = 17.424 \pm 0.072$	$\Delta H^0_{298} = 17.308 \pm 0.078$

$\Delta H^0_{298} = 17.37 \pm 0.08$

$\Delta H^f_{298}(\text{c}) = 18.75 \pm 0.38$

$\Delta H^f_{298}(\text{g}) = 36.12 \pm 0.39$

[a] $\Delta H^0 - H^0_0)_{440} - \Delta(H^0 - H^0_0)_{298}$.

[b] Estimated uncertainty in enthalpy of the liquid above 25°.

[c] Average deviation.

ACKNOWLEDGMENT

The author wishes to express appreciation to the Rich Electronic Computer Center at the Georgia Institute of Technology for use of the Burroughs 220 in making the necessary statistical thermodynamic calculations and to J. L. Whitten for assistance in programming.

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Received for review May 25, 1962. Accepted September 5, 1962.