The Thermodynamic Properties to 700 K
of Naphthalene and 2,7-Dimethylnaphthalene

Topical Report

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EXECUTIVE SUMMARY

Hydrogen management will be a critical issue for refiners as a result of the 1990 Amendments to the U.S. Clean Air Act. The problem stems from a reduction in hydrogen production and an increase in consumption. The addition of oxygenates to gasoline, as mandated for certain geographic areas at certain times of the year, will mean that less octane is required from the reformer, lowering the severity of the operation and, hence, the amount of hydrogen formed. Also the mandate reducing aromatics content to 25 per cent (20 per cent by proposed California state regulations) will result in a further reduction of reformer operating severity, hence, severely reducing hydrogen production. Another contribution to the problem in managing hydrogen results from increased hydrogen consumption to meet benzene specifications and reduced T90 in gasoline, and lower sulfur levels in diesel. To exacerbate the problem, as heavier crudes are introduced to the refinery, the importance of catalytic hydroprocessing will increase. Hydroprocessing can be a hydrogen guzzler.

In August 1990 the U.S. Environmental Protection Agency (EPA) announced that it is taking steps to cut the sulfur content of diesel fuel by 80 per cent -- from 0.25 weight per cent to 0.05 weight per cent -- effective October 1, 1993. In addition, the level of aromatics in diesel fuel has been the topic of several regulatory efforts in California and by the federal government. However, there exists some question of whether the proposed maximum aromatics content can be achieved and whether the aromatics content decreases concomitantly with decreases in sulfur content due to increased severity of processing conditions. In NIPER topical report NIPER-468, this problem was used as a "simple" example of thermodynamics at work in the "real world" of the process-design engineer. By introducing the concept of "crossover temperature," the report outlined, through applied thermodynamics, how to meet the conditions necessary for efficient attainment of the low aromatics levels required with concomitant sulfur level reduction.

The goal of the research programs in thermodynamics at the National Institute for Petroleum & Energy Research (NIPER), funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Extraction and Process Technology (AEPT), is the determination of the conditions under which heavier feedstocks can be processed to produce the wide slate of fuels required by modern society at prices which maintain the economic competitiveness of the U.S.A., but not conflicting with environmental regulations. The results from the thermodynamic property measurements made in these research programs are made available to the petroleum industry via NIPER topical reports and the peer-reviewed scientific literature.

The research is published in two types of reports. Type One, of which this is an example, details the thermochemical and thermophysical property measurements made on the representative polycyclic aromatic and hydroaromatic compounds. Type Two Reports apply the experimental information detailed in Type One Reports to thermodynamic analyses of key reaction networks involving the aromatics [e.g., derivation of the optimum conditions for formation of hydroaromatics (naphthenes), or design of hydroaromatic solvents which efficiently shuttle hydrogen to sites where the "nascent" hydrogen can be used to break asphaltenes down into smaller molecules, etc.]. Thermodynamic analyses, based on accurate information, can be used to set the boundaries (e.g., temperature range, pressure range, etc.) for efficient processing of materials, and to provide insights for the design of cost-effective methods for aromatic removal, or hydrogen shuttling.

The results reported here derive from the portion of the program providing accurate experimental thermochemical and thermophysical properties for "key" polycyclic aromatic and hydroaromatic compounds present in heavier feedstocks. This report details the thermochemical and thermophysical properties, measured at NIPER, for naphthalene and 2,7-dimethylnaphthalene. It is surprising, considering the large body of research into the Exxon Donor Solvent process, that the thermodynamic properties of both the donor (tetralin) and the product of donation (naphthalene) remain unknown at high temperature. Uncertainties in the calculated entropies of naphthalene led reviewers of the available literature in 1986 to conclude that the calorimetrically derived values of the ideal-gas entropy were not precise enough to allow evaluation of the various vibrational assignments. The results obtained in this research should help eliminate most of the uncertainty.

The property measurements reported here can be used by the process-design engineer to simulate -- on paper, without costly pilot plant experimentation -- the effects of changes in conditions on the operation of the process plant. Because the data has known uncertainty intervals, the process-design engineer can use it with the confidence that the results of the simulation will be reproduced in the pilot plant.

ABSTRACT

Measurements leading to the calculation of the ideal-gas thermodynamic properties are reported for naphthalene and 2,7-dimethylnaphthalene. Experimental methods included adiabatic heat-capacity calorimetry, vibrating-tube densitometry, comparative ebulliometry, and differential-scanning calorimetry (d.s.c.). The critical temperature and critical density were determined experimentally for each compound and the critical pressures were derived from fitting procedures. Vapor-pressure measurements reported in the literature were compared with the results obtained in this research. Enthalpies of vaporization and sublimation were derived from the experimental measurements and compared with literature results. New self-consistent equations for the variation of sublimation pressure with temperature for naphthalene and 2,7-dimethylnaphthalene were derived. Literature values for entropies and enthalpies of the liquid phases and energies of combustion were combined with the present results to derive entropies, enthalpies, and Gibbs energies of formation for the ideal gases for selected temperatures between 298.15 K and 700 K. The ideal-gas properties for naphthalene were compared with values obtained using statistical mechanics with various fundamental vibrational frequency assignments available in the literature. A scheme to estimate the ideal-gas thermodynamic functions for alkylnaphthalenes was updated. The barrier to methyl-group rotation in 2,7-dimethylnaphthalene was shown to be of the same order of magnitude as that published for toluene. Values for ideal-gas entropies for 2-methylnaphthalene in the temperature range 300 K to 700 K were estimated.

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GLOSSARY

This report is written with close adherence to the style adopted by The Journal of Chemical Thermodynamics. A complete description of the style can be found in the January 1992 issue of the journal. This glossary summarizes the main points with respect to the symbol usage.

Throughout this report only SI units are used in reporting thermodynamic values. All values are given in dimensionless units, i.e., physical quantity = number X unit; for example, $\rho/(\text{kg}\cdot\text{m}^{-3})$ rather than " ρ (kg/m^3)" or " ρ kg/m^3 ". Molar values, i.e., intensive functions, are denoted by the subscript "m", e.g., $C_{\text{sat},m}$, whereas extensive functions do not have the subscript. In addition, since thermodynamic values are pressure dependent, they are reported in terms of a standard pressure p° , which in this report is 101.325 kPa (one atmosphere).

M = molar mass in $\text{g}\cdot\text{mol}^{-1}$

T = temperature in Kelvin

p = pressure in Pascals (Pa)

ρ = density in $\text{kg}\cdot\text{m}^{-3}$

$\Delta_c U_m^\circ$ = molar energy of combustion

$\Delta_c U_m^\circ/M$ = energy of combustion per gram

$\Delta_c H_m^\circ$ = molar enthalpy of combustion

$\Delta_f H_m^\circ$ = molar enthalpy of formation

$\Delta_l^g H_m$ = molar enthalpy of vaporization, hence the subscript l (for liquid) and superscript g (for gas)

$\Delta_l^g V_m$ = change in molar volume from the liquid to the real vapor

$C_{v,m}$ = molar heat capacity at constant volume

$C_{p,m}$ = molar heat capacity at constant pressure

$C_{\text{sat},m}$ = molar heat capacity at saturated pressure

μ = chemical potential

n = number of moles of substance

V_x = volume of d.s.c. cell at a temperature T/K .

C_x^{II} = two-phase heat capacity at cell volume V_x

C_V^{II} = two-phase heat capacity at constant volume

$C_V^{\text{II}} (p = p_{\text{sat}})$ = two-phase heat capacity along the saturation line

V_l = molar volume of the liquid

T_c = critical temperature

p_c = critical pressure

ρ_c = critical density

T_r = reduced temperature = T/T_c

p_r = reduced pressure = p/p_c

ρ_r = reduced density = ρ/ρ_c

$\lg$ = $\log_{10}$

ω = acentric factor = $[-\lg(p_x/p_c) - 1]$; p_x is the vapor pressure at $T_r = 0.7$

$\Delta_0^T S_m^o$ = molar entropy at temperature T/K (relative to the entropy at $T = 0\text{ K}$)

$\Delta_0^T H_m^o$ = molar enthalpy at temperature T/K (relative to the crystals at 0 K)

$\Delta_{\text{comp}} S_m$ = molar entropy of compression of a gas

$\Delta_{\text{imp}} S_m$ = gas imperfection term

$T \rightarrow 0$ = Zero Kelvin

To avoid listing units in tables, entropies are reported as divided by the gas constant R , and enthalpies and Gibbs energies are generally reported divided by the product of the gas constant and temperature, $R \cdot T$. Units of time are s (seconds), h (hours), and d (days).

1. INTRODUCTION

Within the petroleum industry, the use of catalytic hydroprocessing is increasing.⁽¹⁾§ Its application continues to grow as crudes become heavier and the range of specialty products increases. Over time its use can only continue to increase with the anticipated processing of oil shale, tar sands, and eventually the products of the liquefaction of coal. Important areas within catalytic hydroprocessing include the hydrogenation of aromatics, hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO). This report is the product of research funded by the U. S. Department of Energy's (DOE) Office of Fossil Energy, Advanced Extraction & Process Technology Program (AEPT). Within a portion of that research program, the thermochemical and thermophysical properties are determined for "key" aromatics and hydroaromatics present in the spectrum of fossil-fuel materials. The results of the thermodynamic-property measurements will be used to provide insights into the reaction networks and relative reactivities of polycyclic aromatics and hydroaromatics within the complicated processes operating in hydroprocessing.

Hydroaromatic (hydrogen donor) compounds will play an important role in the development of processes for the spectrum of fossil-fuel materials from heavy petroleum through coal. For example, in the processing of some heavy petroleums and *all* coal liquids the naphtha fraction will contain relatively large amounts of two-ring aromatics, which have a strong tendency to form coke on catalysts during reforming. A simplistic answer to the problem would be cutting the naphtha at 300 °F rather than 375-400 °F. Since that would decrease the naphtha yield and make the process uneconomical, hydrocracking of the two-ring structures via the formation of hydroaromatics may be a better answer to the problem. The comments of Fisher and Wilson⁽²⁾ then become relevant.

"Predictive schemes are available using group additivity concepts for calculating thermodynamic properties of complex aromatic molecules. Such schemes must rely on accurately measured thermochemical data for the calculation of reliable group additivity values. The lack of such data for the bicyclic and tricyclic species present in these distillates argues against attempting to predict their free energy values."

For the "simple" single-ring aromatics, Fisher and Wilson were able to use the available thermodynamic data to conclude, "thermodynamic limitations to saturation of

§ References are listed in numerical order at the end of this report.

aromatics were found to predominate at the higher temperatures, and complete conversion in synthetic distillates was only achieved well removed from thermodynamic constraints." When the thermodynamic constraints are unknown, or can only be estimated within large error bands, for the larger systems so important to the alternate crudes, how can the process-design engineer know what is "well removed" from them?

Several groups have reported in the recent literature the presence of a coal-resid synergy.⁽³⁻¹¹⁾ An understanding of the reason(s) for this synergy could transform coal-liquefaction technology. However, at present no such understanding exists. It may be that the non-donor species (polycyclic aromatic hydrocarbons in all examples to date) react with the donor solvent forming reactive species which engender hydrogenolysis and liquefaction of the coal.⁽⁸⁾ If that is true, then, with the choice of a suitable system, there is the possibility of coal liquefaction at lower temperatures. Also, the hydrogen addition could be tailored to specific sites within the coal structure cutting the formation of light gases (C₁ through C₄), which wastes expensive hydrogen.

Alternatively, it may be possible that the whole synergy is caused by increased solvation effects due to the high operational temperatures.^(9,10) For example, the reaction temperature (425 °C) in the research of Cassidy et al.⁽¹¹⁾ is above the critical temperature of one of the solvent components, decalin, but below the critical temperatures of either naphthalene or tetralin (two of the other major components). Therefore, the physical states of the various mixtures are difficult to specify, especially since the critical temperatures are mostly estimates with large uncertainties. The effect could be just another example of supercritical solvent extraction. In the absence of high-temperature thermodynamic properties on key polycyclic aromatic hydrocarbons and the products of their partial hydrogenation, the basis for the synergy will remain conjecture.

It is surprising, considering the large body of research into the Exxon Donor Solvent process,⁽¹²⁾ that the thermodynamic properties of both the donor (tetralin) and the product of donation (naphthalene) remain unknown at high temperature. Uncertainties in the calculated entropies of naphthalene led Dorofeeva, Gurvich, and Cyvin,⁽¹³⁾ who reviewed the available literature in 1986, to conclude that the calorimetrically derived values of the ideal-gas entropy were not precise enough to allow evaluation of the various vibrational assignments. The results obtained in this research should help eliminate most of the uncertainty.

Naphthalene

2,7-Dimethylnaphthalene

This report details the thermochemical and thermophysical properties, measured at NIPER, for naphthalene and 2,7-dimethylnaphthalene. The properties were measured by adiabatic heat-capacity calorimetry, comparative ebulliometry, vibrating-tube densitometry, and differential-scanning calorimetry. For naphthalene, the results complement earlier low-temperature adiabatic calorimetric measurements⁽¹⁴⁾ reported by this research group in the 1950s. For 2,7-dimethylnaphthalene, the results complement earlier research by low-temperature adiabatic calorimetry,⁽¹⁵⁾ inclined-piston manometry,⁽¹⁶⁾ and combustion bomb calorimetry⁽¹⁷⁾ reported by this research group in the 1970s. Critical properties for both compounds were determined and, in the case of naphthalene, compared with literature values. Standard Gibbs energies of formation in the ideal-gas state were derived for both compounds. All measured or derived thermodynamic-property values were compared with those reported in the literature.

Group-contribution methods are widely used for the estimation of thermodynamic properties when measurements are unavailable. Methyl-group increments in the temperature range 300 K to 700 K were derived in this research and compared with values obtained by statistical mechanics for the corresponding differences for toluene and benzene. The results are in excellent agreement leading to the accurate estimation of the ideal-gas properties of other alkyl-substituted naphthalenes (provided the 1 and 8 positions are not both substituted).

Naphthalene has been recommended as an alternative to ice as reference material for vapor pressure measurements below 1000 Pascals.⁽¹⁸⁾ Many researchers in the environmental chemistry field use naphthalene as a standard to calibrate equipment for the measurement of the vapor pressure of pollutants such as chlorinated dibenzofurans (dioxans).⁽¹⁹⁾ However, the sublimation pressure of naphthalene as a function of temperature was not reliably established (see Discussion section below). Results obtained in this research define, for the first time, *self-consistent* sublimation vapor pressures for naphthalene in the pressure region 0.1 Pa to 995 Pa (250 K to 353.4 K).

2. EXPERIMENTAL

MATERIALS

The sample of naphthalene used in the measurements reported in this research was obtained from British Drug House (Naphthalene OAS; purity >99.9 moles per cent). It was used without further purification. The 2,7-dimethylnaphthalene was a portion of the sample used for low-temperature adiabatic calorimetry,⁽¹⁵⁾ inclined-piston vapor-pressure,⁽¹⁶⁾ and energy of combustion measurements⁽¹⁷⁾ reported by this research group in the 1970s. A mole-fraction impurity of 0.0007 was determined for naphthalene by fractional melting as part of the adiabatic heat-capacity calorimetric studies. The mole-fraction impurity for 2,7-dimethylnaphthalene was determined to be 0.0005 in the earlier measurements.⁽¹⁵⁾ The high purities of the samples were corroborated by the small differences between the boiling and condensation temperatures observed in the ebulliometric vapor-pressure studies.

The water used as a reference material in the ebulliometric vapor-pressure and density measurements was deionized and distilled from potassium permanganate. The decane used as a reference material for the ebulliometric measurements was purified by urea complexation, two recrystallizations of the complex, its decomposition with water, extraction with ether, drying with MgSO_4 , and distillation at 337 K and 1 kPa pressure.

PHYSICAL CONSTANTS AND STANDARDS

Molar values are reported in terms of $M = 128.1735 \text{ g}\cdot\text{mol}^{-1}$ and $156.2273 \text{ g}\cdot\text{mol}^{-1}$ for naphthalene and 2,7-dimethylnaphthalene, respectively, based on the relative atomic masses of 1981^{(20)†} and the gas constant $R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ adopted by CODATA.⁽²¹⁾ The platinum resistance thermometers used in these measurements were calibrated by comparison with standard thermometers whose constants were determined at the National Institute of Standards and Technology (NIST). All temperatures reported are in terms of the ITS-90.^(22,23) Measurements of mass, time, electrical resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

APPARATUS AND PROCEDURES

Densitometry. Densities reported previously by this research group were obtained in a densitometer,⁽²⁴⁾ which had an upper temperature limit of approximately 430 K.

† The 1981 relative atomic masses were used because the CODATA Recommended Key Values for Thermodynamics (reference 53) are based on them.

Studies on high-molecular-weight compounds (three fused rings and greater) required that this upper temperature limit be raised substantially. As a result, a new densitometer was constructed with an upper temperature limit near 550 K (the limit at present is set by that attainable by the constant-temperature bath). The design of the new densitometer is essentially that used successfully by Dr. J. M. Simonson and his colleagues at Oak Ridge National Laboratory for the study of aqueous salt mixtures at high temperatures and pressures. The densitometer and its operation have been described.⁽²⁵⁾

Measurements of the density of benzene were made between 310 K and 523 K to determine the accuracy of the results obtained with the densitometer.⁽²⁶⁾ Results agreed with the values published by Hales and Townsend⁽²⁷⁾ within ± 0.1 per cent. The precision of the measurements was approximately 0.05 per cent.

Ebulliometric Vapor-Pressure Measurements. The essential features of the ebulliometric equipment and procedures are described in the literature.^(28,29) The ebulliometers were used to reflux the substance under study with a standard of known vapor pressure under a common helium atmosphere. The boiling and condensation temperatures of the two substances were determined, and the vapor pressure was derived with the condensation temperature of the standard.⁽³⁰⁾

The precision in the temperature measurements for the ebulliometric vapor-pressure studies was 0.001 K. The precision in pressure is adequately described by:

$$\sigma(p) = (0.001 \text{ K}) \{ (dp_{\text{ref}}/dT)^2 + (dp_x/dT)^2 \}^{1/2}, \quad (1)$$

where p_{ref} is the vapor pressure of the reference substance and p_x is the vapor pressure of the sample under study. Values of dp_{ref}/dT for the reference substances were calculated from fits of the Antoine equation⁽³¹⁾ to vapor pressures of the reference materials (decane and water) reported in reference 30.

Inclined-Piston Vapor-Pressure Measurements. The equipment for the inclined-piston vapor-pressure measurements has been described by Douslin and McCullough,⁽³²⁾ and Douslin and Osborn.⁽³³⁾ Recent revisions to the equipment and procedures have been reported.⁽²⁴⁾ Uncertainties in the pressures determined with the inclined-piston apparatus, on the basis of estimated precision of measuring the mass, area, and angle of inclination of the piston, are adequately described by the expression:

$$\sigma(p) = 1.5 \times 10^{-4} p + 0.2 \text{ Pa}. \quad (2)$$

The uncertainties in the temperatures are 0.001 K. The contributions of the temperature uncertainties to $\sigma(p)$ are insignificant in the range of the measurements.

Adiabatic Heat-Capacity Calorimetry. Adiabatic heat-capacity and enthalpy measurements were made for naphthalene with a calorimetric system described previously.^(24, 34-36) The calorimeter characteristics and sealing conditions are given in table 1.[¶] Energy measurement procedures were the same as those described for studies on quinoline.⁽²⁴⁾ Thermometer resistances were measured with self-balancing a.c. resistance bridges (H. Tinsley & Co. Ltd.; Models 5840C and 5840D). Energies were measured to a precision of 0.01 per cent, and temperatures were measured to a precision of 0.0001 K. The energy increments to the filled calorimeter were corrected for enthalpy changes in the empty calorimeter, for the helium exchange gas, and for vaporization of the sample. The correction to the measured energy for the helium exchange gas was negligible at all temperatures (<0.001 per cent). The sizes of the other two corrections are indicated in table 1.

Differential-Scanning Calorimetry (d.s.c.). Differential-scanning calorimetric measurements were made with a Perkin-Elmer DSC-2. Experimental methods were described previously.⁽³⁷⁻³⁹⁾

3. RESULTS

DENSITY MEASUREMENTS

Measured densities for naphthalene and 2,7-dimethylnaphthalene in the liquid phase at saturation pressure are listed in table 2.

VAPOR-PRESSURE MEASUREMENTS

Vapor pressures for naphthalene and 2,7-dimethylnaphthalene are reported in table 3. Included in table 3 are the results of earlier measurements made by this research group⁽¹⁶⁾ for 2,7-dimethylnaphthalene both above and below the triple-point using the inclined-piston apparatus. All temperatures were adjusted to ITS-90. Following previous practice,⁽²⁹⁾ the results obtained in the ebulliometric measurements were adjusted to common pressures. The common pressures, the condensation temperatures, and the difference between condensation and boiling temperatures ΔT for the samples are reported. For both samples the small differences between the boiling and condensation

[¶] All tables are given at the end of this report.

temperatures (column 6 table 3) indicated correct operation of the equipment and the high purity of the samples.

ADIABATIC HEAT-CAPACITY CALORIMETRY

Naphthalene was studied previously by adiabatic heat-capacity calorimetry in the temperature range 12 K to 370 K,⁽¹⁴⁾ and included replicate determinations of the enthalpy of fusion. The purpose of the new measurements described here was to extend the results for the liquid phase to near the critical temperature. High-precision (± 0.1 per cent) adiabatic calorimetric measurements were completed between the triple-point temperature (353.40 K) and 445 K, and differential-scanning calorimetric studies (± 1.0 per cent) were completed to near the critical temperature (748.4 K). A melting study was performed as part of the adiabatic calorimetry experiments, and was used to determine the sample purity and to confirm the enthalpy-of-fusion value determined previously.⁽¹⁴⁾

Crystallization of the naphthalene sample in the adiabatic calorimeter was initiated by slowly cooling (approximately $2 \text{ mK}\cdot\text{s}^{-1}$) the liquid sample. Complete crystallization was ensured by maintaining the sample under adiabatic conditions in the partially melted state (10 to 20 per cent liquid) for approximately 8 h. No spontaneous warming, which would indicate incomplete crystallization, was observed in this time period. The sample was cooled at an effective rate of $2 \text{ mK}\cdot\text{s}^{-1}$ to crystallize the remaining liquid. As a final step, the sample was thermally cycled between $<280 \text{ K}$ and within 2 K of the triple-point temperature, where it was held for a minimum of 24 h to provide further tempering.

The triple-point temperature T_{tp} and sample purity were determined by measurement of the equilibrium melting temperatures $T(F)$ as a function of fraction F of the sample in the liquid state⁽⁴⁰⁾ for F values between 0.2 and 0.7. Equilibrium melting temperatures were determined by measuring temperatures at approximately 300-s intervals for 0.8 h to 1.5 h after an energy input and extrapolating to infinite time by assuming an exponential decay toward the equilibrium value. The observed temperatures at 1 h after an energy input were invariably within 2 mK of the calculated equilibrium temperatures. No evidence for solid-soluble impurities was found. The mole fraction of impurities was calculated to be 0.0007. The triple-point temperature (353.40 K) and enthalpy of fusion ($18.99 \text{ kJ}\cdot\text{mol}^{-1}$) were in excellent accord with that measured previously;⁽¹⁴⁾ 353.40 K and $18.98 \text{ kJ}\cdot\text{mol}^{-1}$, respectively.

The experimental molar heat capacities under vapor-saturation pressure $C_{\text{sat,m}}$ determined by adiabatic calorimetry are listed in table 4. Values in table 4 were corrected for effects of sample vaporization into the gas space of the calorimeter. The temperature increments were small enough to obviate the need for corrections for non-linear variation of $C_{\text{sat,m}}$. The precision of the heat-capacity measurements was approximately 0.05 per cent. Equilibrium was reached in less than 1 h for heat-capacity measurements in the liquid phase.

Also included in table 4 are molar heat capacities under vapor-saturation pressure $C_{\text{sat,m}}$ determined by adiabatic calorimetry for 2,7-dimethylnaphthalene. These values were determined in earlier research⁽¹⁵⁾ on that compound by this group, but the series-11 values were not published at that time. The 2,7-dimethylnaphthalene results have been converted to ITS-90.

DIFFERENTIAL-SCANNING CALORIMETRY

Critical-Temperature and Critical-Density Measurements. Both naphthalene and 2,7-dimethylnaphthalene were sufficiently stable in the critical region to allow experimental determination of both the critical temperature and critical density for each compound by differential-scanning calorimetry. By employing a single continuous heating rate of $0.333 \text{ K}\cdot\text{s}^{-1}$, sample decomposition was minimized, and the abrupt decrease in heat capacity associated with the conversion from two phases to one phase was observed. Temperatures at which conversion to the single phase occurred were measured for several cell fillings for each compound. Table 5 reports the temperatures at which conversion to a single phase was observed, and the density obtained from the mass of sample and the cell volume. The cell volume was calculated with the equation:

$$V_x(T)/V_x(298.15 \text{ K}) = 1 + ay + by^2 \quad (3)$$

where $y = \{(T/K) - 298.15\}$, $a=3.216\cdot 10^{-5}$, and $b=5.4\cdot 10^{-8}$. A critical temperature of $(749\pm 1) \text{ K}$ and a corresponding critical density of $(310\pm 15) \text{ kg}\cdot\text{m}^{-3}$ were derived graphically for naphthalene with these results as shown in figure 1. For 2,7-dimethylnaphthalene a critical temperature of $(775\pm 2) \text{ K}$ was estimated from the results shown in figure 2. A corresponding critical density of $(255\pm 30) \text{ kg}\cdot\text{m}^{-3}$ was estimated also. This value is low in comparison with that derived with a corresponding-states correlation later in this paper. The difference is probably related to decomposition near T_c . The value derived from the corresponding-states correlation ($296.5 \text{ kg}\cdot\text{m}^{-3}$) was used in all further calculations.

Figure 1. (Vapor + liquid) coexistence region for naphthalene. ρ denotes density. The crosses indicate the range of uncertainty of this research; —, drawn to be consistent with these experimentally determined values: $\blacklozenge$; critical temperature and critical density from reference 42.

Figure 2. (Vapor + liquid) coexistence region for 2,7-dimethylnaphthalene. ρ denotes density. The crosses indicate the range of uncertainty of this research; ----, drawn to be consistent with the experimentally determined values; $\bigcirc$, the critical temperature deduced from the data shown and the critical density derived from the fitting procedure described in the text. See text.

Theoretical Background. The theoretical background for the determination of heat capacities for the liquid phase at vapor-saturation pressure $C_{\text{sat},m}$ with results obtained with a d.s.c. has been described.^(39,41) Measured two-phase (liquid+vapor) heat capacities for a minimum of two fillings, vapor pressures, and reliable liquid-density values are required.

Measurement of Two-Phase (Liquid + Vapor) Heat Capacities. Table 6 lists the experimentally determined two-phase heat capacities $C_{x,m}^{\text{II}}$ for naphthalene and 2,7-dimethylnaphthalene obtained for three cell fillings for each compound. Heat capacities were determined at 20-K intervals with a heating rate of $0.083 \text{ K}\cdot\text{s}^{-1}$ and a 120-s equilibration period between heats. Decomposition limited these measurements to below 745 K for 2,7-dimethylnaphthalene and 720 K for naphthalene.

SIMULTANEOUS FITS TO VAPOR PRESSURES AND TWO-PHASE HEAT CAPACITIES

A simultaneous non-linear least-squares fit to the vapor pressures listed in table 3 and the $C_{x,m}^{\text{II}}$ values given in table 6 was completed. The fitting procedure has been described.^(39,41)

The Wagner equation,⁽⁴³⁾ as formulated by Ambrose,⁽⁴⁴⁾ was used to represent the vapor pressures:

$$\ln(p/p_c) = (1/T_r)[A(1-T_r) + B(1-T_r)^{1.5} + C(1-T_r)^{2.5} + D(1-T_r)^5], \quad (4)$$

where $T_r = T/T_c$. Critical temperatures of 748.4 K and 775 K were used in the fitting procedures for naphthalene and 2,7-dimethylnaphthalene, respectively. The critical pressures were included as variables in the fits. Experimental $C_{x,m}^{\text{II}}$ values were converted to $C_{v,m}^{\text{II}}$ by means of equation (5):

$$C_{v,m}^{\text{II}} = C_{x,m}^{\text{II}} - T/n \{(\partial V_x/\partial T)_x (\partial p/\partial T)_{\text{sat}}\}. \quad (5)$$

Equation (3) was used to calculate $(\partial V_x/\partial T)_x$ and the vapor-pressure fit was used for calculation of $(\partial p/\partial T)_{\text{sat}}$. The values of $C_{v,m}^{\text{II}}$ were used to derive functions for $(\partial^2 p/\partial T^2)_{\text{sat}}$ and $(\partial^2 \mu/\partial T^2)_{\text{sat}}$, as described previously.⁽⁴¹⁾ The form chosen for variation of the second derivative of the chemical potential with temperature was:

$$(\partial^2 \mu/\partial T^2)_{\text{sat}} / (\text{J}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}) = \sum_{i=0}^n b_i(1 - T/T_c)^i. \quad (6)$$

{For compounds where sufficient information was available to evaluate reliably $(\partial^2\mu/\partial T^2)_{\text{sat}}$ [e.g., benzene⁽⁴⁵⁾, toluene⁽⁴⁶⁾], four terms (i.e., expansion to $n=3$) were required to represent the function. Four terms were used in this research.}

Table 7 lists the coefficients determined in the non-linear least-squares fits. Deviations of the measured vapor pressures from the fitted Wagner equation are included in table 3. Values of $C_{\text{sat},m}$ for naphthalene and 2,7-dimethylnaphthalene were derived from $C_{v,m}^{\text{II}}(p=p_{\text{sat}})$ values⁽⁴¹⁾ and densities calculated with the extended corresponding-states equation of Riedel,⁽⁴⁷⁾ as formulated by Hales and Townsend:⁽²⁷⁾

$$(\rho/\rho_c) = 1.0 + 0.85\{1.0 - (T/T_c)\} + (1.6916 + 0.9846\omega)\{1.0 - (T/T_c)\}^{1/3} . \quad (7)$$

Values for T_c , and the acentric factor, ω , listed in table 7 were used in the liquid-phase density calculations. Values for $C_{v,m}^{\text{II}}(p=p_{\text{sat}})/R$ are not listed. Differences between $C_{v,m}^{\text{II}}(p=p_{\text{sat}})/R$ and $C_{\text{sat},m}/R$ are not significant below the normal boiling point and only become large as the critical temperature is approached.⁽⁴¹⁾

Values for the critical density ρ_c for naphthalene and 2,7-dimethylnaphthalene were obtained by adjusting ρ_c to minimize deviations between the values measured (table 2) and calculated with equation (7). Resulting percentage differences are listed in table 2, column 3.

The results for $C_{\text{sat},m}/R$ derived from the d.s.c. measurements are included in table 8 and are footnoted to distinguish them from the adiabatic calorimetric measurements. The estimated uncertainty in the values is 1 per cent.

THERMODYNAMIC PROPERTIES IN THE CONDENSED STATE

Entropies and enthalpies for the liquid phase under vapor saturation pressure relative to that of the crystals at $T \rightarrow 0$ for naphthalene and 2,7-dimethylnaphthalene are listed in table 8. The tabulated values were derived by integration of the smoothed heat capacities for the liquid phase listed in tables 3 and 8, together with the entropy and enthalpy increments from $T \rightarrow 0$ reported previously^(14,15) for the liquid phases at the respective T_{tp} 's. The heat capacities were smoothed with cubic-spline functions by least-squares fits to six points at a time and by requiring continuity in value, slope, and curvature at the junction of successive cubic functions. Due to limitations in the spline-function procedure, some acceptable values from tables 3 and 8 were not included in the fit, while in other regions graphical values were introduced to ensure that the second derivative of the heat capacity with respect to temperature was a smooth function of temperature. The entropy and enthalpy increments from $T \rightarrow 0$ to the triple-

point temperatures were assigned an uncertainty of 0.1 per cent of their values for all the calculations reported here.

DERIVED ENTHALPIES OF VAPORIZATION

Enthalpies of vaporization $\Delta_l^g H_m$ were derived from the Wagner-equation fits by means of the Clapeyron equation:

$$dp/dT = \Delta_l^g H_m / (T \Delta_l^g V_m). \quad (8)$$

$\Delta_l^g V_m$ is the increase in molar volume from the liquid to the real vapor. The Wagner-equation fits were employed to derive dp/dT . Estimates of liquid-phase volumes were made with equation (7) and the critical constants listed in table 7. The uncertainty in the liquid-phase volumes was estimated to be 1 per cent.

Vapor-phase volumes were calculated with the virial equation of state truncated at the third virial coefficient. Second virial coefficients were estimated with the corresponding-states equation of Pitzer and Curl,⁽⁴⁸⁾ and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera.⁽⁴⁹⁾ This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene, toluene, and decane.⁽⁵⁰⁾ Third virial coefficients are required for accurate calculation of the gas volume for pressures greater than 1 bar. Uncertainties in the virial coefficients are assumed to be 10 per cent. Derived enthalpies of vaporization are reported in table 9. For $p > 1$ bar the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived enthalpies of vaporization.

THERMODYNAMIC PROPERTIES IN THE IDEAL-GAS STATE

Enthalpies and entropies at selected temperatures for the ideal gas were calculated using values in tables 8 and 9 and are listed in columns 2 and 4 of table 10. Entropies and enthalpies of compression to 101.325 kPa were calculated based on the virial equation truncated after the third virial coefficient:

$$pV_m = RT + Bp + C'p^2. \quad (9)$$

Formulations used to calculate the entropy and enthalpy of compression, which include the "gas-imperfection corrections," are available in the literature.^(25,51) Required temperature derivatives of virial coefficients were calculated by numerical differentiation of values estimated by the methods of Pitzer and Curl⁽⁴⁸⁾ and Orbey and

Vera.⁽⁴⁹⁾ The gas-imperfection corrections, which are included in the values given in columns 2 and 4 of table 10, are listed separately. Uncertainties in the gas-imperfection correction values are difficult to assess because temperature derivatives of estimated values are involved. An uncertainty of 10 per cent of the calculated correction was assumed.

The derived ideal-gas enthalpies and entropies for naphthalene and 2,7-dimethylnaphthalene were combined with the standard molar enthalpies of formation $\Delta_f H_m^0$ ($C_{10}H_8$, cr) = (77.9±1.2) kJ·mol⁻¹ ("assessed best" value listed in reference 52) and $\Delta_f H_m^0$ ($C_{12}H_{12}$, cr) = -(5.44±1.12) kJ·mol⁻¹ (reference 17) to calculate the enthalpies, entropies, and Gibbs energies of formation listed in columns 6, 7, and 8, respectively, of table 10. The standard molar enthalpies of formation for both compounds were derived using the CODATA values for the enthalpies of formation of CO₂(g) and H₂O(l).⁽⁵³⁾

Enthalpies and entropies for equilibrium hydrogen were determined from JANAF tables.⁽⁵⁴⁾ Values for graphite were determined with the polynomial⁽⁵⁵⁾ used to calculate the values from 298.15 K to 6000 K listed in the JANAF tables. All uncertainties in table 10 represent one standard deviation and do not include uncertainties in the properties of the elements because these cancel in calculations of chemical equilibria. Their inclusion leads to overestimation of the error limits of such calculations.

CALCULATION OF SUBLIMATION PRESSURES

The "third-law" method was employed to calculate sublimation pressures for naphthalene from 250 K to the triple-point temperature. The "third-law" values were calculated from the tabulated entropies and enthalpies for the crystalline solid (table 6 of reference 14), the liquid (table 8), and extrapolated vapor pressures for the liquid phase calculated with the Wagner parameters listed in table 7. The method applied here was the same as that used previously for biphenyl.⁽⁴¹⁾ The sublimation vapor pressures for naphthalene were represented by the equation:

$$\ln(p/p^0) = 21.079 + 1.8850 \times 10^3 (T/K)^{-1} - 4.0191 \times 10^6 (T/K)^{-2} \\ + 6.8892 \times 10^8 (T/K)^{-3} - 4.5834 \times 10^{10} (T/K)^{-4}, \quad (10)$$

in the temperature region 250 K to 353.40 K with $p^0 = 1$ Pa.

Sublimation pressures were calculated for 2,7-dimethylnaphthalene from 315 K to the triple-point temperature. The "third-law" values were calculated from the tabulated entropies and enthalpies for the crystalline solid (table 5 of reference

15), the liquid (table 8), and extrapolated vapor pressures for the liquid phase calculated with the Wagner parameters listed in table 7. The sublimation vapor pressures for 2,7-dimethylnaphthalene were represented by the equation:

$$\ln(p/p^0) = -1.2968 + 3.3660 \times 10^4 (T/K)^{-1} - 2.0835 \times 10^7 (T/K)^{-2} \\ + 4.4302 \times 10^9 (T/K)^{-3} - 3.5514 \times 10^{11} (T/K)^{-4}, \quad (11)$$

in the temperature region 315 K to 368.79 K with $p^0 = 1$ Pa.

4. DISCUSSION

Throughout this section all literature results were converted to ITS-90, when warranted by the accuracy and precision of the measurements. Often, no temperature-scale details were given. In those cases the date of the reference was used to guess the applicable temperature scale. Literature prior to 1949 was assumed to adhere to ITS-27; from 1949 to 1969 inclusive ITS-48; and 1970 to date IPTS-68. For temperatures of interest in this research ITS-27 and ITS-48 are equivalent. Conversions to ITS-90 were accomplished using the tables given by Goldberg and Weir.⁽²³⁾

NAPHTHALENE

Densities Liquid-phase densities under saturation pressure for naphthalene have been reported by several research groups.^(27,56,57) Figure 3 compares the densities obtained in this research (table 2) and the various literature liquid-phase densities with values calculated using extended corresponding states [equation (7) and the parameters listed in table 7]. Agreement between the various measurements is within 0.1 per cent except for those of Shinsaka et al.,⁽⁵⁷⁾ which are approximately 0.3 per cent lower than any other measurements. Shinsaka et al.⁽⁵⁷⁾ noted for several other compounds that their results "tended to be 0.3 per cent lower than earlier values."

As shown in figure 3, the small positive slope in the deviations can be removed by increasing T_c from 748.4 K to 755 K. This shift necessitates a small adjustment in the critical density from 320.0 kg·m⁻³ to 319.6 kg·m⁻³. The critical temperature for naphthalene 748.4 K appears to be well established. The trend in the deviations shown in figure 3 may result from limitations of the corresponding-states correlation.

Figure 3. Comparison of literature density measurements ρ_{exp} for naphthalene with those obtained using extended corresponding states (equation 7). $\rho_{\text{c.s.}}$ = value of the density calculated using equation 7 and the parameters listed in table 7. □, Hales and Townsend;⁽²⁷⁾ ◆, Shinsaka, Gee, and Freeman;⁽⁵⁷⁾ ○, Marti;⁽⁵⁶⁾ ▲, this research; *, this research with $\rho_{\text{c.s.}}$ calculated with equation (7) and $T_c = 755 \text{ K}$, $\omega = 0.2976$ and $\rho_c = 319.6 \text{ kg}\cdot\text{m}^{-3}$.

Vapor Pressure Above the Triple Point. Numerous vapor-pressures studies on naphthalene have been reported in the literature. In this section vapor pressures in the region from the triple point to the critical point are discussed. The literature results fall into three categories; ebulliometric measurements by Ambrose et al.⁽⁴⁴⁾, other measurements in the region from the triple-point temperature to near the normal-boiling temperature,⁽⁵⁸⁻⁶²⁾ and high-temperature/high-pressure results obtained by Wilson et al.⁽⁶³⁾ from the normal-boiling temperature to the critical region. Figures 4, 5, and 6 compare results from each category with values obtained using the Wagner equation [equation (4)] and the parameters listed in table 7.

Ambrose et al.⁽⁴⁴⁾ measured vapor pressures for naphthalene using a glass ebulliometer in the temperature region 418 K to 525 K and a metal ebulliometer in the region 427 K to 613 K. They noted "slight inconsistencies" between the two sets of results. As per figure 4 (upper plot), deviations of vapor pressures reported by Ambrose et al.⁽⁴⁴⁾ from those obtained in this research range from 0.05 per cent near 400 K to approximately zero at 600 K. These deviations are virtually eliminated, if the temperatures of Ambrose et al.⁽⁴⁴⁾ are increased by 0.010 K (in addition to correction to ITS-90). All of the results (except for those above 600 K) then lie within ± 0.02 per cent of the calculated values, as shown in the lower plot of figure 4. Differences as small as 10 mK may be due to either an inconsistency in the calibration of the platinum resistance thermometers, sample purity differences, or the fact that Ambrose et al. reported boiling temperatures in their work compared with the condensation temperatures listed in this research. For the sample of naphthalene used in this work, the condensation temperatures were 5 mK less than the corresponding boiling temperatures over most of the temperature range studied (see column 6 of table 3).

The other vapor pressure studies⁽⁵⁸⁻⁶²⁾ reviewed in this section are of a much lower precision and accuracy than the study by Ambrose et al.⁽⁴⁴⁾ Note that the ordinate values increase by a factor of 100 between figures 4 and 5 or 6. Above 428 K, the ebulliometric results of Camin and Rossini are in good agreement (± 0.05 per cent in pressure) with values obtained using the Wagner equation. However, below 428 K ($p < 20$ kPa) the deviations increase significantly and reach -3 per cent at 400 K (7 kPa). Static measurements by de Kruif et al.⁽⁶²⁾ in the range 353 K to 388 K (1 kPa to 4.5 kPa) are lower on average by (2 ± 1) percent

Figure 4. Comparison of the vapor pressures for naphthalene measured by Ambrose et al.⁽⁴⁴⁾ with those obtained using the Wagner equation and the parameters listed in table 7. ●, reference 44 glass ebulliometer; △, reference 44 metal ebulliometer. In the lower plot the temperatures in reference 44 were raised by 0.010 K (see text).

Figure 5. Comparison of literature values of the vapor pressures for naphthalene with those obtained using the Wagner equation and the parameters listed in table 7. ▲, Nelson and Senseman;⁽⁵⁸⁾ ⊠, Mortimer and Murphy;⁽⁵⁹⁾ ○, Camin and Rossini;⁽⁶⁰⁾ □, Fowler et al.;⁽⁶¹⁾ X, de Kruif et al.⁽⁶²⁾

Figure 6. Comparison of values of the vapor pressures for naphthalene obtained by Wilson et al.⁽⁶³⁾ with those obtained using the Wagner equation and the parameters listed in table 7.

than values obtained using the Wagner equation and the parameters listed in table 7. Vapor pressure measurements made in the 1920s by Nelson and Senseman⁽⁵⁸⁾ and Mortimer and Murphy⁽⁵⁹⁾ are high and low, respectively, compared with the results reported in this research. The differences, except for values reported by Mortimer and Murphy⁽⁵⁹⁾ at 360 K, 371 K, and 400 K do not exceed our estimate of the probable uncertainties in the measurements. The values at 360 K, 371 K, and 400 K, reported by Mortimer and Murphy⁽⁵⁹⁾ differ from values calculated in this research by -12.6, 39.3, and 11.4 per cent, respectively.

The high-temperature measurements of Wilson et al.⁽⁶³⁾ (figure 6) lie within 3 per cent of the Wagner-equation values. Values in figure 6 outside those bounds were "suspected to be too low" by Wilson et al.⁽⁶³⁾ The uncertainty assigned by Wilson et al.⁽⁶³⁾ of 1 per cent of the measured value appears to be unduly optimistic.

Critical Properties. The d.s.c. measurements made in this research gave a critical temperature of (749 ± 1) K for naphthalene (figure 1) and a critical density of (310 ± 15) kg·m⁻³. Using the fitting procedures outlined above and the critical temperature 748.4 K measured by Ambrose et al.,⁽⁴⁴⁾ a critical pressure 4105 kPa and critical density 320 kg·m⁻³ were derived.

Ambrose, Broderick, and Townsend⁽⁴²⁾ measured $T_c = 748.4$ K, $p_c = 4051$ kPa for naphthalene. Kay and Pak⁽⁶³⁾ subsequently measured T_c and p_c using both gallium and mercury as containment fluids. Kay and Pak reported $T_c = 749.45$ K, $p_c = 4097.6$ kPa and $T_c = 748.85$ K, $p_c = 4064.5$ kPa using gallium and mercury, respectively. They also measured $T_c = 749.45$ K in a separate determination in a sealed tube. Kay and Pak⁽⁶⁴⁾ concluded that the measurements using gallium and mercury were the same within the uncertainties in their measured temperatures and pressures. Kay and Pak⁽⁶⁴⁾ used "reagent grade" naphthalene in their measurements. Ambrose, Broderick, and Townsend⁽⁴²⁾ used a sample of naphthalene which was determined by glc analysis to be 99.99 mole per cent pure. On the basis of the relative uncertainties in the measurements, and the sample purities, the critical temperature reported by Ambrose et al.^(42,44) was chosen for use in the fitting procedures outlined above in the Results section of this report.

Heat Capacities. Heat capacities for the liquid^(14, 65-68) and crystal phases^(14, 65-74) of naphthalene have been reported by many researchers. Only the studies by McCullough et al. (temperature range: 12 K to 370 K)⁽¹⁴⁾ published in 1957, and Southard and Brickwedde⁽⁷⁰⁾ (temperature range: 15 K to 295 K) published in 1933, extend to

sufficiently low temperatures to allow calculation of the entropy relative to 0 K. Differences between the results of these studies in the region of overlap are shown in figure 7. The precision of the more recent measurements is approximately a factor of 2 better than that for the earlier results. The difference between the calculated entropies near 300 K is 0.06 R (0.3 per cent), which is within the combined uncertainties of the studies.

Differences of published heat capacities for the liquid phase of naphthalene from those of this research are shown in figure 8. Values reported by McCullough et al.⁽¹⁴⁾ for the liquid phase are 0.06 to 0.18 per cent lower than those of this research. Such differences are within the combined uncertainties of the studies. Heat capacities for the liquid phase of naphthalene reported in all other studies deviate widely from the values determined in this research.

Enthalpies of Vaporization. Only one direct measurement of the enthalpy of vaporization of naphthalene was found in a search of the literature. Barrow and McClellan⁽⁷⁵⁾ made four separate determinations of the enthalpy of vaporization of naphthalene at 27.86 kPa and 440.9 K using a vapor-flow apparatus. Their result $\Delta_1^g H_m (C_{10}H_8, 440.9 \text{ K}) = (46.38 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$ is in excellent agreement with the value $(46.35 \pm 0.30) \text{ kJ} \cdot \text{mol}^{-1}$ obtained in this research.

Ideal-Gas Thermodynamic Properties. The thermodynamic properties of naphthalene in the ideal-gas state have been the subject of numerous investigations and critical reviews in the past half century. In 1981 Lielmezs et al.⁽⁷⁶⁾ listed 32 references to vibrational spectral assignments and ideal-gas property determinations for naphthalene. Several other reports have appeared since with those by Dorofeeva, Gurvich, and Cyvin⁽¹³⁾ and Sellers, Pulay, and Boggs⁽⁷⁷⁾ of most significance.

In this research most of the available literature on the assignment of the vibrational spectra of naphthalene was reviewed. Important highlights only are discussed here. Those studies not discussed explicitly yield ideal-gas properties very similar to those presented.

Barrow and McClellan⁽⁷⁵⁾ determined vapor-phase heat capacities for naphthalene at 451 K and 522.7 K using vapor-flow calorimetry. Subsequent researchers have often used those results as "anchors" in the determination of ideal-gas properties for naphthalene. McClellan and Pimentel⁽⁷⁸⁾ were the first to give a complete assignment of the 48 fundamental vibrational frequencies in naphthalene.

Figure 7. Deviation of heat capacities for the crystal phase of naphthalene reported by Southard and Brickwedde⁽⁷⁰⁾ $\{C_{\text{sat},m}(1933)\}$ from those of McCullough et al.⁽¹⁴⁾ $\{C_{\text{sat},m}(1957)\}$.

Figure 8. Deviation of heat capacities for the liquid phase of naphthalene reported in the literature from those of this research. O, McCullough et al.;⁽¹⁴⁾ Δ, Eibert;⁽⁶⁸⁾ ●, Schmidt;⁽⁶⁷⁾ ▲, Andrews et al.;⁽⁶⁵⁾ □, Spaght et al.⁽⁶⁶⁾

Barrow and McClellan⁽⁷⁵⁾ used those frequencies to calculate the ideal-gas functions to 1500 K. Figure 9 compares values for the ideal-gas entropy at 101.325 kPa for naphthalene calculated with modern values for the fundamental constants and moments of inertia $I_a = 28.99 \times 10^{-39} \text{ g}\cdot\text{cm}^2$, $I_b = 68.17 \times 10^{-39} \text{ g}\cdot\text{cm}^2$, $I_c = 95.16 \times 10^{-39} \text{ g}\cdot\text{cm}^2$ with the values determined in this research (table 10). The moment of inertia, used in the statistical calculations reported in this section, was determined using the molecular mechanics program MMP2.⁽⁷⁹⁾ In the temperature range 300 K to 700 K, the spectroscopically derived entropies are 0.2 R to 0.3 R higher than those derived from the calorimetric results reported in this research.

Of the early assignments of the fundamental vibrational frequencies of naphthalene, one of the most careful was by Krainov.⁽⁸⁰⁾ Values for the ideal-gas entropy for naphthalene derived using the calculated vibrational assignment of Krainov are compared in figure 9 with the calorimetric results reported in this research. Agreement is good, with the spectroscopically derived entropies being 0.1 R lower than the calorimetrically derived values over most of the temperature range.

Chen et al.⁽⁸¹⁾ in 1976 reviewed the available assignments and derived ideal-gas functions to 1500 K. Their results were recalculated in this research using the above product of the moments of inertia and modern fundamental constants. As per figure 9, the ideal-gas entropies derived using the assignment of Chen et al. are lower than those reported in this research. Deviations range from 0.2 R to 0.3 R.

Lielmezs et al.⁽⁷⁶⁾ in 1981 reviewed the available assignments and derived two new assignments (assignment A and assignment B). Ideal-gas entropies were recalculated in this research using both assignments. As per figure 9, the ideal-gas entropies derived using assignment A of Lielmezs et al.⁽⁷⁶⁾ are lower than the calorimetrically derived values of this research by 0.25 R at 300 K and 0.17 R at 700 K. Assignment B gave similar results.

Sellars, Pulay, and Boggs⁽⁷⁷⁾ derived a complete harmonic force field for naphthalene calculated ab initio at the 4-21 Hartree-Fock level. The diagonal force constants were then scaled with the scaling factors previously derived by fitting the similarly computed vibrational spectrum of benzene to its observed spectrum. The resulting scaled force field was then used to derive the 48 fundamental vibrational frequencies for naphthalene. Ideal-gas entropy values for naphthalene calculated using the derived vibrational wavenumbers of Sellars, Pulay, and Boggs and statistical mechanics are compared with calorimetrically derived values of this research in figure 9. Deviations range from 0.18 R at 300 K to 0.28 R at 700 K with the statistically derived value always being low.

Figure 9. Deviation of ideal-gas entropy values for naphthalene calculated from spectroscopically determined vibrational wavenumbers and statistical mechanics (spect) from the calorimetrically (calor) derived values of this research. $\blacksquare$, McClellan and Pimentel⁽⁷⁸⁾ assignment; $\circ$, Krainov⁽⁸⁰⁾ calculated assignment; $*$, Chen et al.⁽⁸¹⁾ assignment; $\blacktriangle$, Lielmezs et al.⁽⁷⁶⁾ assignment A; $\square$, Sellers, Pulay and Boggs⁽⁷⁷⁾ assignment.

Dorofeeva, Gurvich, and Cyvin⁽¹³⁾ reviewed the available literature in 1986. They concluded that the calorimetrically derived values of the ideal-gas entropy were not precise enough to allow evaluation of the various vibrational assignments. The results obtained in this research should help eliminate most of the uncertainty.

Sublimation Vapor Pressures In this section literature values^(61,62,82-91) for the sublimation pressures of naphthalene are compared with those values calculated in this research {equation (10)}. Figures 10, 11, and 12 show these comparisons.

Naphthalene has been recommended as an alternative to ice as reference material for vapor-pressure measurements below 1000 Pascals.⁽¹⁸⁾ However, the sublimation pressure of naphthalene as a function of temperature is not as reliably established as that of ice.⁽⁹²⁾ Figure 10 shows the deviations of the results from two studies,^(82,83) which recommended sublimation pressures for naphthalene in the region 250 K ($p=0.036$ Pa) to the triple-point temperature 353.40 K ($p=995$ Pa), from values calculated using equation (10). The recommended values by Ambrose et al.⁽⁸²⁾ and Sinke⁽⁸³⁾ are not consistent with each other or with equation (10). Sinke⁽⁸³⁾ based his recommended values on a measured sublimation pressure for a *single* temperature. That pressure, 0.923 Pa at 275 K, is 2 per cent higher than the value calculated in this research. Also plotted in figure 10 are the experimentally determined pressures obtained by Ambrose et al.⁽⁸²⁾ It is difficult to reconcile the good agreement (0.4 per cent) between equation (10) values and the values recommended by Ambrose et al.⁽⁸²⁾ at 250 K and 350 K with deviations of over 8 per cent within that 100 K region.

Figure 11 compares the results obtained by the research group of de Kruif^(62,84) and values obtained with equation (10). Near the triple-point temperature, the experimentally determined values have a negative bias of 2 per cent relative to the calculated values of this research (c.f. the liquid-phase measurements⁽⁶²⁾ by de Kruif and coworkers discussed earlier). However, as the temperature is decreased, that negative bias becomes a positive bias of approximately 6 per cent by 240 K.

Figure 12 compares the other results abstracted from the literature^(61,85-91) with values calculated using equation (10). In general, the results are higher than equation (10) values, but in each case the overall spread of the reported results is at least 4 per cent. In some cases the spread is much larger; 12 per cent for the results of Sonnefeld et al.⁽⁸⁶⁾ in the short temperature range of 287 K to 305 K.

Figure 10. Deviation of literature sublimation vapor pressure values for naphthalene p_{exp} from values calculated using equation (10), p_{calc} . $\square$, Ambrose et al.⁽⁸²⁾ measured values; $\blacksquare$, Ambrose et al.⁽⁸²⁾ recommended values; $*$, Sinke⁽⁸³⁾ measured value; $\oplus$, Sinke⁽⁸³⁾ recommended values.

Figure 11. Deviation of literature sublimation vapor pressure values for naphthalene, $p_{\text{exp.}}$, from values calculated using equation (10), $p_{\text{calc.}}$. $\square$, de Kruif et al.⁽⁶²⁾ $\circ$, Van Ekeren et al.⁽⁸⁴⁾.

Figure 12. Deviation of literature sublimation vapor pressure values for naphthalene, p_{exp} , from values calculated using equation (10), p_{calc} .
 $\square$, Sato et al.;⁽⁸⁵⁾ $\diamond$, Sonneteld et al.;⁽⁸⁶⁾ $\circ$, Sasse et al.;⁽⁸⁷⁾
 $\blacktriangle$, de Kruif;⁽⁸⁸⁾ $\boxplus$, Macknick and Prausnitz;⁽⁸⁹⁾ $\times$, Colomina et al.;⁽⁹⁰⁾ $\bullet$, Bradley and Cleasby;⁽⁹¹⁾ $\oplus$, Fowler et al.⁽⁶¹⁾

Enthalpies of Sublimation Numerous enthalpies of sublimation for naphthalene are reported in the literature. A representative set of values^(62,82-84,86,88,90,93-104) are listed in table 11. Values of the enthalpy of sublimation of naphthalene for each of the temperatures listed in the literature studies were calculated from equations representing the enthalpies of the solid⁽¹⁴⁾ and the ideal gas (table 10). Results are listed in table 11, column 5.

Three calorimetric measurement studies of the enthalpy of sublimation of naphthalene are reported in the literature; Morawetz⁽⁹⁷⁾, Irving⁽⁹⁸⁾, and Murata et al.⁽¹⁰¹⁾ The value obtained by Morawetz⁽⁹⁷⁾ $\Delta_c^g H_m$ (C₁₀H₈, 298.15 K) = (72.05±0.25) kJ·mol⁻¹ is 0.6 kJ·mol⁻¹ lower than the value derived in this research. Indeed, the value obtained by Morawetz⁽⁹⁷⁾ is lower than the large majority of the results listed for 298.15 K in table 11. Irving⁽⁹⁸⁾ obtained $\Delta_c^g H_m$ (C₁₀H₈, 298.15 K) = (73.00±0.25) kJ·mol⁻¹, which is 0.35 kJ·mol⁻¹ higher than the value derived in this research. The eight values determined by Murata et al.⁽¹⁰¹⁾ over the temperature range 296 K to 341.1 K are all in excellent agreement with values derived in this research (highlighted values in table 12).

Of the remaining values listed in table 11, all the results lie within the probable error bounds of the reported enthalpies of sublimation with the exceptions of the values due to Sonnefeld et al.,⁽⁸⁶⁾ Hoyer and Peperle,⁽⁹³⁾ Aihara,⁽⁹⁴⁾ Karyakin et al.,⁽⁹⁶⁾ and Sabbah et al.⁽¹⁰³⁾ In those cases deviations from values calculated in this research, and other literature values at similar temperatures, are excessively large and are assumed to represent experimental errors in the techniques used by the researchers.

2,7-DIMETHYLNAPHTHALENE

No thermochemical or thermophysical property measurements on 2,7-dimethylnaphthalene, except those reported previously by this research group,⁽¹⁵⁻¹⁷⁾ were found in a search of the literature through 1992.

Critical Properties. The d.s.c. measurements made in this research gave a critical temperature of (775±2) K for 2,7-dimethylnaphthalene (figure 2). Using the fitting procedures outlined above and the critical temperature, a critical pressure 3234 kPa and a critical density 296.5 kg·m⁻³ were derived. Estimated critical values derived using the group-contribution method of Joback⁽¹⁰⁵⁾ were $T_c = 770$ K, $p_c = 3010$ kPa, and $\rho_c = 300$ kg·m⁻³ in good agreement with the values obtained in this research.

Densities. The liquid-phase densities under saturation pressure for 2,7-dimethylnaphthalene measured in this research are compared in table 2 with values derived by extended corresponding states [equation (7)]. Agreement is excellent except at the temperature extremes. The deviation at 548 K may be due to temperature stabilization problems at the extreme of the range of operation of the temperature-control bath used in the measurements.

Sublimation Vapor Pressures. Sublimation vapor pressures for 2,7-dimethylnaphthalene obtained using equation (11) are compared in table 12 with values obtained using inclined-piston manometry by this research group in the 1970s.⁽¹⁶⁾ The deviations between the calculated and observed values of the sublimation pressure all lie within a ± 1 Pa range [five times the present $\sigma(p)$ as represented by equation (2)]. However, one Pascal probably was a better representation of the overall uncertainty interval of the measurements using the inclined-piston manometer prior to the recent modifications in its operation.⁽²⁴⁾

THERMODYNAMIC PROPERTIES OF ALKYLNAPHTHALENES

In 1956 Milligan, Becker and Pitzer⁽¹⁰⁷⁾ calculated ideal-gas thermodynamic properties for alkylnaphthalenes by the method of increments.⁽¹⁰⁸⁾ In their calculations they used the vibrational assignment for naphthalene by McClellan and Pimentel,⁽⁷⁸⁾ and experimentally determined thermodynamic results for 1-methyl and 2-methyl naphthalenes communicated by Dr. G. Waddington of this laboratory. (Those measurements were later published.⁽¹⁴⁾) In the absence of other information as to the functional form of the liquid-phase heat capacities of both methylnaphthalenes, linear equations of C_{sat} versus temperature were used in the calculations. Conclusions reached included barriers to methyl-group rotation of $15.9 \text{ kJ}\cdot\text{mol}^{-1}$ for 1-methylnaphthalene and, surprisingly, $9.6 \text{ kJ}\cdot\text{mol}^{-1}$ for 2-methylnaphthalene. The value in the 1-methyl case is "high" due to interaction between the methyl group and the hydrogen in the 8-position of the naphthalene molecule. However, in the case of 2-methylnaphthalene, the barrier to methyl-group rotation should be similar to that of toluene, which has been assessed as $58.32 \text{ J}\cdot\text{mol}^{-1}$.⁽¹⁰⁹⁾

In this research the method of increments was used to estimate ideal-gas thermodynamic properties for 2,7-dimethylnaphthalene. Ideal-gas enthalpies relative to 298.15 K and ideal-gas entropies were estimated using the equations:

$$\Delta_{298.15}^T H_m^{\circ} (2,7\text{-DMN}) = \Delta_{298.15}^T H_m^{\circ} (\text{naphthalene}) + 2\{\Delta_{298.15}^T H_m^{\circ} (\text{toluene}) - \Delta_{298.15}^T H_m^{\circ} (\text{benzene})\} \quad (12)$$

and:

$$\Delta_0^T S_m^{\circ} (2,7\text{-DMN}) = \Delta_0^T S_m^{\circ} (\text{naphthalene}) + 2\{\Delta_0^T S_m^{\circ} (\text{toluene}) - \Delta_0^T S_m^{\circ} (\text{benzene})\} - R \cdot \ln (18), \quad (13)$$

where 2,7-DMN = 2,7-dimethylnaphthalene; the $\ln$ term represents symmetry number considerations; values for naphthalene were taken from table 10 and those for benzene and toluene determined as follows. For benzene the vibrational assignment of Brodersen and Langseth⁽¹¹⁰⁾ was used in conjunction with the structure by Cabana et al.⁽¹¹¹⁾ For toluene the assignment and moments of inertia of Draeger^(112,113) were used assuming free rotation of the methyl group.

Agreement between the calculated and experimentally determined values in table 13 is excellent. From the results it can be concluded that the barriers to methyl rotation in 2,7-dimethyl-naphthalene are small (of the order of that in toluene). Previous calorimetric determinations of the methyl-group increments for naphthalenes were limited to a single temperature, 400 K.⁽¹¹⁴⁾

Using the equation:

$$\Delta_0^T S_m^{\circ} (2\text{-methylnaphthalene}) = \Delta_0^T S_m^{\circ} (\text{naphthalene}) + \{\Delta_0^T S_m^{\circ} (\text{toluene}) - \Delta_0^T S_m^{\circ} (\text{benzene})\} - R \cdot \ln(3/2), \quad (14)$$

revised ideal-gas entropies for 2-methylnaphthalene were determined, and are listed in table 14.

The revised ideal-gas entropy value at 400 K is 0.25R higher than the value determined previously⁽¹¹⁴⁾ based partially on extrapolated vapor pressures.⁽⁶⁰⁾ In the present research it was shown that vapor pressures of naphthalene published simultaneously with the 2-methylnaphthalene values are in error at the low-pressure extreme of the measurements. A similar error could account for the 0.25R discrepancy. Furthermore, none of the available vapor-pressure measurements^(60,115,116) are consistent. New measurements on 2-methylnaphthalene are planned.

The results obtained in this research show that using the method of increments,⁽¹⁰⁸⁾ accurate values for alkylnaphthalenes substituted in other than the 1-

position can be estimated. Questions remain as to the accuracy of the methods used by Milligan, Becker and Pitzer⁽¹⁰⁷⁾ to estimate ideal-gas thermodynamic properties for 1-methylnaphthalene. Future work in this research program will include vapor pressure and high-temperature liquid-phase heat-capacity measurements on 1-methylnaphthalene and subsequent calculation of its ideal-gas properties. With the completion of that work a methodology for the accurate estimation of the ideal-gas thermodynamic properties of any alkyl substituted naphthalene will be available. Exceptions will be 1,8- and ortho substitutions, which will remain special cases because of the large barriers to rotation.⁽¹⁷⁾

5. SUMMARY and HIGHLIGHTS

- Thermochemical and thermophysical properties for naphthalene and 2,7-dimethylnaphthalene are reported. Properties measured included vapor pressures, heat capacities, and densities over a range of temperatures.
- Ideal-gas thermodynamic properties for naphthalene and 2,7-dimethylnaphthalene were calculated from near 300 K to 700 K based on the accurate calorimetric measurements.
- Gibbs energies of formation were derived for naphthalene and 2,7-dimethylnaphthalene for use in equilibria calculations.
- Critical properties were determined for both compounds. The results for naphthalene confirm previous measurements, while those for 2,7-dimethylnaphthalene are the first reported in the literature.
- Vapor pressures from the triple point to the critical point are defined. For naphthalene, in the range of temperature from the triple point to the normal boiling point, the defined values agree well (± 0.010 K) with earlier precise measurements from the National Physical Laboratory at Teddington in England.
- New self-consistent sublimation vapor-pressure equations to represent the sublimation pressures of both naphthalene and 2,7-dimethylnaphthalene were derived. *The results for naphthalene will have significant technological importance in the chemical industry in general.* Naphthalene is used as a standard to calibrate apparatus used in the measurement of "low" vapor pressures of chemicals of environmental concern (e.g., dioxans).
- The ideal-gas thermodynamic properties for naphthalene are defined in this research with sufficient accuracy and precision such that the various fundamental vibrational frequency assignments for naphthalene available in the literature can now be assessed.
- A methodology for the estimation of the thermodynamic properties for alkylnaphthalenes was updated, and new values for the ideal-gas entropy of 2-methylnaphthalene in the temperature range 300 K to 700 K were derived.

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TABLE 1. Calorimeter and sample characteristics for heat capacity and enthalpy measurements by adiabatic calorimetry on naphthalene: m is the sample mass; V_i is the internal volume of the calorimeter; T_{cal} is the temperature of the calorimeter when sealed; p_{cal} is the pressure of the helium and sample when sealed; r is the ratio of the heat capacity of the full calorimeter to that of the empty; T_{max} is the highest temperature of the measurements; and $\delta C/C$ is the vaporization correction.

Naphthalene	
m/g	39.970
$V_i(298.15\text{ K})/\text{cm}^3$	59.06
T_{cal}/K	298.2
p_{cal}/kPa	6.88
$r(T_{max})$	2.9
r_{min}	2.7
$10^2(\delta C/C)_{max}$	0.105

TABLE 2. Measured densities at saturation pressure ^a

T/K	$\rho/(\text{kg}\cdot\text{m}^{-3})$	$100\cdot(\rho-\rho_{\text{cs}})/\rho$	T/K	$\rho/(\text{kg}\cdot\text{m}^{-3})$	$100\cdot(\rho-\rho_{\text{cs}})/\rho$
Naphthalene			2,7-Dimethylnaphthalene		
373.125	962.58	-0.15	373.124	935.13	0.17
398.119	942.14	-0.13	398.119	914.43	-0.03
423.114	921.04	-0.13	423.115	894.84	-0.06
448.111	899.82	-0.07	448.111	875.21	-0.03
473.110	878.15	0.03	473.111	855.30	0.03
498.110	855.66	0.14	498.112	834.37	0.07
523.111	831.94	0.22	523.111	811.91	0.02
548.111	806.11	0.19	548.105	786.42	-0.31

^a ρ_{cs} = density calculated using extended corresponding states. {See equation (7) and text.}

TABLE 3. Vapor-pressure results: IP refers to measurements performed with the inclined-piston gauge; water or decane refers to which material was used as the standard in the reference ebulliometer; T is the temperature of the experimental inclined-piston pressure gauge measurements or, for ebulliometric measurements, of the condensation temperature of the sample; the pressure p for ebulliometric measurements was calculated from the condensation temperature of the reference substance; Δp is the difference of the value of pressure calculated using the Wagner vapor pressure equation from the observed value of pressure; $\sigma(p)$ is the propagated error calculated from equations (1) and (2); ΔT is the difference between the boiling and condensation temperatures ($T_{\text{boil}} - T_{\text{cond}}$) for the sample in the ebulliometer.

Method	$\frac{T}{K}$	$\frac{p}{\text{kPa}}$	$\frac{\Delta p}{\text{kPa}}$	$\frac{\sigma(p)}{\text{kPa}}$	$\frac{\Delta T}{K}$
Naphthalene					
decane	384.439	3.9999	0.0000	0.0002	0.019
decane	391.702	5.3330	0.0001	0.0003	0.011
decane	402.519	7.9989	0.0000	0.0004	0.009
decane	410.644	10.6661	0.0000	0.0006	0.009
decane	417.221	13.332	0.000	0.001	0.008
decane	424.055	16.665	0.000	0.001	0.008
decane	429.738	19.933	0.000	0.001	0.007
decane	437.222	25.023	0.000	0.001	0.007
water	437.219	25.023	0.003	0.001	0.007
water	444.760	31.177	0.002	0.002	0.006
water	452.355	38.565	0.001	0.002	0.006
water	460.002	47.375	-0.001	0.002	0.005
water	467.702	57.817	0.000	0.003	0.006
water	475.458	70.120	-0.001	0.003	0.005
water	483.267	84.533	-0.001	0.004	0.005
water	491.130	101.325	-0.001	0.004	0.005
water	499.046	120.79	0.00	0.01	0.005
water	507.020	143.25	0.00	0.01	0.005
water	515.043	169.02	0.00	0.01	0.005
water	523.123	198.49	0.00	0.01	0.005

TABLE 3. Continued

Method	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma(p)}{kPa}$	$\frac{\Delta T}{K}$
Naphthalene (continued)					
water	531.253	232.02	0.00	0.01	0.004
water	539.434	270.02	0.00	0.01	0.004
2,7-Dimethylnaphthalene					
IP	333.124	a,b,c 0.0199	-0.0245	0.0002	
IP	338.124	a,b,c 0.0309	-0.0307	0.0002	
IP	343.124	a,b,c 0.0475	-0.0372	0.0002	
IP	348.123	a,b,c 0.0731	-0.0420	0.0002	
IP	353.123	a,b,c 0.1107	-0.0442	0.0002	
IP	358.123	a,b,c 0.1649	-0.0413	0.0002	
IP	363.123	a,b,c 0.2426	-0.0295	0.0002	
IP	368.123	a,b,c 0.3518	-0.0040	0.0003	
IP	369.124	c 0.3749	-0.0001	0.0003	
IP	373.124	c 0.4613	0.0000	0.0003	
IP	378.125	c 0.5921	-0.0011	0.0003	
IP	383.126	c 0.7570	0.0003	0.0003	
IP	388.126	c 0.9581	0.0000	0.0003	
IP	393.127	c 1.2046	0.0003	0.0004	
IP	398.129	c 1.5037	0.0003	0.0004	
decane	404.795	2.0000	0.0000	0.0001	0.042
decane	411.788	2.6660	0.0001	0.0002	0.024
decane	422.173	3.9999	0.0001	0.0002	0.019
decane	429.932	5.3330	0.0000	0.0003	0.016
decane	441.474	7.9989	0.0001	0.0004	0.013
decane	450.137	10.6661	-0.0004	0.0005	0.012
decane	457.142	13.332	-0.001	0.001	0.012
decane	464.418	16.665	-0.001	0.001	0.012
decane	470.462	19.933	0.000	0.001	0.012
decane	478.419	25.023	0.000	0.001	0.013
water	478.416	25.023	0.002	0.001	0.011

TABLE 3. Continued

Method	$\frac{T}{K}$	$\frac{p}{\text{kPa}}$	$\frac{\Delta p}{\text{kPa}}$	$\frac{\sigma(p)}{\text{kPa}}$	$\frac{\Delta T}{K}$
2,7-Dimethylnaphthalene (continued)					
water	486.427	31.177	0.002	0.002	0.012
water	494.488	38.565	0.001	0.002	0.012
water	502.599	47.375	0.000	0.002	0.012
water	510.759	57.817	0.001	0.003	0.014
water	518.972	70.120	0.001	0.003	0.013
water	527.235	84.533	0.001	0.004	0.013
water	535.548	101.325	-0.001	0.004	0.013
water	543.912	120.79	-0.01	0.004	0.012
water	552.324	143.25	0.00	0.01	0.013
water	560.782	169.02	0.00	0.01	0.012
water	569.288	198.49	0.00	0.01	0.014
water	577.840	232.02	0.01	0.01	0.015
water	586.438	270.02	0.00	0.01	0.015

- a Values at this temperature are sublimation vapor pressures.
b The value at this temperature was not included in the fit.
c Reference 16.

TABLE 4. Molar heat capacities $C_{\text{sat},m}$ for the liquid phase at vapor-saturation pressure
($R=8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

N^a	$\frac{\langle T \rangle}{\text{K}}$	$\frac{\Delta T}{\text{K}}$	$\frac{C_{\text{sat},m}^b}{R}$	N^a	$\frac{\langle T \rangle}{\text{K}}$	$\frac{\Delta T}{\text{K}}$	$\frac{C_{\text{sat},m}^b}{R}$
Naphthalene ^c							
2	357.905	6.1120	26.380	3	404.568	15.3690	28.574
3	361.992	10.1450	26.568	2	415.610	14.1950	29.093
2	366.035	10.1020	26.762	3	419.944	15.3670	29.290
3	374.249	14.3250	27.148	2	429.201	13.0170	29.720
2	376.214	10.2120	27.241	3	435.251	15.2460	30.000
3	389.148	15.4410	27.850	2	440.305	9.2190	30.237
2	401.383	14.2390	28.427				
2,7-Dimethylnaphthalene ^d							
11	372.618	4.6590	34.476	11	401.535	11.1060	36.095
11	377.537	5.1810	34.698	2	405.604	10.0260	36.331
2	378.315	5.8410	34.789	11	412.540	10.9160	36.712
11	382.978	5.7230	35.039	2	415.524	9.8440	36.899
2	385.817	9.1840	35.263	11	423.351	10.7360	37.292
11	390.932	10.1880	35.522	11	433.982	10.5370	37.924
2	395.500	10.1800	35.830				

^a Adiabatic series number.

^b Average heat capacity for a temperature increment of ΔT with a mean temperature $\langle T \rangle$.

^c These values were determined in this research with adiabatic heat-capacity calorimetry.

^d Series-2 results were published previously⁽¹⁵⁾ in terms of IPTS-68 and are updated here to ITS-90. The series-11 results were obtained as part of the same study as series 2, and are published here for the first time.

TABLE 5. Densities and temperatures for the conversion from two phases to a single phase for naphthalene and 2,7-dimethylnaphthalene

$\rho/(\text{kg}\cdot\text{m}^{-3})$	T/K
Naphthalene	
146.1	740.2
179.5	745.0
239.9	746.6
317.3	748.8
363.7	747.8
412.5	745.0
2,7-Dimethylnaphthalene	
92.0	742.5
140.8	759.0
185.5	769.0
277.3	774.5
336.1	767.0
409.6	746.0

TABLE 6. Experimental $C_{x,m}^{II}$ values ($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

mass/g	0.009731	0.013264	0.017220	0.022362
$V_{\text{cell}}/\text{cm}^3$ ^a	0.05288	0.05288	0.05292	0.05288
T/K	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$
Naphthalene				
375.0	27.13	27.31	26.85	26.96
395.0	28.27	28.12	27.79	27.90
415.0	29.22	29.24	28.74	28.98
435.0	30.21	30.27	29.66	30.00
455.0	31.74	31.37	30.76	30.89
475.0	32.74	32.37	31.84	31.93
495.0	34.13	33.34	33.03	32.82
515.0	35.18	34.62	34.08	33.94
535.0	36.72	35.83	35.23	34.79
555.0	38.23	37.16	36.75	35.71
575.0	39.64	38.47	37.79	36.84
595.0	40.93	39.77	38.89	37.42
615.0	42.42	40.99	40.12	38.57
635.0	44.15	42.19	40.54	39.20
655.0	45.47	42.58	42.04	40.26
675.0	47.55	44.08	43.25	41.32
695.0	49.28	45.70	44.53	42.49
715.0	51.69	48.31	46.51	44.14

TABLE 6. Continued

mass/g	0.007716	0.010171	0.018200
$V_{\text{cell}}/\text{cm}^3$ ^a	0.05339	0.05339	0.05272
T/K	$C_{x,m}^{\text{II}}/\text{R}$	$C_{x,m}^{\text{II}}/\text{R}$	$C_{x,m}^{\text{II}}/\text{R}$
2,7-Dimethylnaphthalene			
395.0	36.09	36.50	35.68
415.0	37.27	37.79	36.95
435.0	38.07	38.50	38.18
455.0	39.78	40.31	39.55
475.0	41.31	41.59	40.68
495.0	43.16	43.02	42.01
515.0	44.59	44.98	43.25
535.0	46.86	46.65	44.67
555.0	47.32	47.76	45.84
575.0	49.65	49.41	47.16
595.0	51.34	51.22	48.34
615.0	53.72	52.79	49.67
635.0	56.07	54.86	50.57
655.0	57.74	56.81	51.62
675.0	60.47	58.28	53.11
695.0	62.86	61.22	54.26
715.0	65.60	62.63	55.17
735.0	67.72	65.12	54.91

^a V_{cell} is the volume of the cell measured at 298.15 K.

TABLE 7. Parameters for equations (4) and (6), critical constants, and acentric factors.

Naphthalene			
A	-7.79639	b_0	-0.39907
B	2.25115	b_1	-0.60114
C	-2.70330	b_2	0.81666
D	-3.22660	b_3	-0.85620
$T_c = 748.4 \text{ K}$ $p_c = 4105 \text{ kPa}$ $\rho_c = 320.0 \text{ kg}\cdot\text{m}^{-3}$ $\omega = 0.3092$			
2,7-Dimethylnaphthalene			
A	-8.82334	b_0	-0.49656
B	3.23553	b_1	-0.96039
C	-4.03286	b_2	1.89750
D	-3.07487	b_3	-2.03849
$T_c = 775 \text{ K}$ $p_c = 3234 \text{ kPa}$ $\rho_c = 296.5 \text{ kg}\cdot\text{m}^{-3}$ $\omega = 0.4404$			

TABLE 8. Molar thermodynamic functions for the liquid phase at vapor-saturation pressure ^a
($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

$\frac{T}{\text{K}}$	$\frac{C_{\text{sat,m}}}{\text{R}}$	$\frac{\Delta_0^T S_m}{\text{R}}$	$\frac{\Delta_0^T H_m}{RT}$	$\frac{T}{\text{K}}$	$\frac{C_{\text{sat,m}}}{\text{R}}$	$\frac{\Delta_0^T S_m}{\text{R}}$	$\frac{\Delta_0^T H_m}{RT}$
Naphthalene							
260.00 ^b	21.80	23.06	16.39	480.00 ^c	32.02	39.26	21.23
280.00 ^b	22.73	24.71	16.81	500.00 ^c	32.91	40.58	21.67
298.15 ^b	23.58	26.17	17.19	520.00 ^c	33.79	41.89	22.12
300.00 ^b	23.67	26.31	17.23	540.00 ^c	34.65	43.18	22.57
320.00 ^b	24.61	27.87	17.67	560.00 ^c	35.50	44.46	23.02
340.00 ^b	25.54	29.39	18.10	580.00 ^c	36.34	45.72	23.46
360.00	26.48	30.88	18.54	600.00 ^c	37.17	46.96	23.91
380.00	27.42	32.33	18.98	620.00 ^c	38.01	48.20	24.35
400.00	28.36	33.76	19.43	640.00 ^c	38.87	49.42	24.79
420.00	29.29	35.17	19.88	660.00 ^c	39.81	50.63	25.23
440.00	30.21	36.55	20.33	680.00 ^c	40.95	51.83	25.67
460.00 ^c	31.12	37.92	20.77	700.00 ^c	42.56	53.04	26.13
2,7-Dimethylnaphthalene							
298.15 ^b	30.29	34.08	21.51	500.00 ^c	41.74	52.42	27.35
300.00 ^b	30.39	34.26	21.57	520.00 ^c	42.90	54.08	27.92
320.00 ^b	31.51	36.26	22.15	540.00 ^c	44.05	55.72	28.50
340.00 ^b	32.64	38.21	22.74	560.00 ^c	45.20	57.34	29.08
360.00 ^b	33.76	40.10	23.32	580.00 ^c	46.32	58.95	29.65
380.00	34.88	41.96	23.90	600.00 ^c	47.41	60.54	30.23
400.00	36.01	43.78	24.47	620.00 ^c	48.47	62.11	30.80
420.00	37.13	45.56	25.05	640.00 ^c	49.51	63.67	31.37
440.00	38.26	47.31	25.63	660.00 ^c	50.52	65.21	31.93
460.00 ^c	39.42	49.04	26.20	680.00 ^c	51.57	66.73	32.49
480.00 ^c	40.57	50.74	26.77	700.00 ^c	52.74	68.24	33.05

^a Values listed in this table for temperatures below the triple-point temperatures and above 450 K are reported with one digit more than is justified by the experimental uncertainty. This is to avoid round-off errors in the calculation of values listed in table 10.

^b Values at this temperature were calculated with graphically extrapolated heat capacities.

^c Values at this temperature were determined by differential-scanning calorimetry and the fitting procedures described in the text.

TABLE 9. Enthalpies of vaporization obtained from the Wagner and Clapeyron equations

T/K	$\Delta_l^g H_m/RK$	T/K	$\Delta_l^g H_m/RK$	T/K	$\Delta_l^g H_m/RK$
Naphthalene					
298.15 a,b	6596±24	440.00	5581±18	580.00 a	4460±60
300.00 a,b	6581±24	460.00	5442±19	600.00 a	4256±71
320.00 a,b	6426±22	480.00	5298±22	620.00 a	4036±83
340.00 a,b	6276±21	500.00	5149±27	640.00 a	3798±97
360.00 a	6132±19	520.00	4992±33	660.00 a	3537±112
380.00 a	5991±18	540.00 a	4826±41	680.00 a	3249±128
400.00	5854±17	560.00 a	4649±50	700.00 a	2927±146
420.00	5718±17				
2,7-Dimethylnaphthalene					
298.15 a,b	7739±33	440.00	6587±21	580.00	5406±50
300.00 a,b	7722±33	460.00	6434±21	600.00 a	5198±60
320.00 a,b	7547±31	480.00	6279±22	620.00 a	4976±73
340.00 a,b	7376±29	500.00	6120±24	640.00 a	4736±86
360.00 a,b	7211±27	520.00	5955±28	660.00 a	4475±101
380.00	7050±25	540.00	5782±33	680.00 a	4189±118
400.00	6893±23	560.00	5600±41	700.00 a	3871±137
420.00	6739±22				

a Values at this temperature were calculated with extrapolated vapor pressures determined from the fitted Wagner coefficients.

b Enthalpies of vaporization below the triple-point temperature were calculated with extrapolated vapor pressures determined from the fitted Wagner coefficients.

TABLE 10. Thermodynamic properties in the ideal-gas state
($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $p^\circ = 101.325 \text{ kPa}$)

$\frac{T}{\text{K}}$	$\frac{\Delta_f H_m^\circ}{R T}$	$\frac{\Delta_{\text{imp}} H_m^\circ}{R T}$ ^a	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_{\text{imp}} S_m^\circ}{R}$ ^b	$\frac{\Delta_f H_m^\circ}{R T}$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_f G_m^\circ}{R T}$
Naphthalene							
298.15 ^{c,d}	39.32±0.08	0.00	40.31±0.09	0.00	60.74±0.26	-29.41±0.09	90.16±0.24
300.00 ^{c,d}	39.17±0.08	0.00	40.40±0.09	0.00	60.32±0.25	-29.46±0.09	89.78±0.24
320.00 ^{c,d}	37.75±0.07	0.00	41.46±0.08	0.00	56.03±0.24	-30.00±0.08	86.03±0.23
340.00 ^{c,d}	36.57±0.06	0.00	42.53±0.07	0.00	52.27±0.22	-30.47±0.07	82.74±0.21
360.00 ^c	35.58±0.06	0.01	43.61±0.06	0.01	48.96±0.21	-30.90±0.06	79.85±0.20
380.00 ^c	34.76±0.05	0.02	44.70±0.06	0.01	46.01±0.20	-31.28±0.06	77.28±0.19
400.00	34.09±0.05	0.03	45.78±0.06	0.02	43.38±0.19	-31.62±0.06	74.99±0.18
420.00	33.53±0.05	0.04	46.87±0.06	0.03	41.01±0.18	-31.92±0.06	72.94±0.18
440.00	33.07±0.06	0.06	47.96±0.07	0.05	38.88±0.17	-32.20±0.07	71.08±0.18
460.00	32.69±0.07	0.09	49.05±0.08	0.06	36.94±0.17	-32.45±0.08	69.39±0.18
480.00	32.38±0.08	0.12	50.12±0.09	0.09	35.17±0.17	-32.68±0.09	67.86±0.18
500.00	32.13±0.09	0.16	51.19±0.10	0.12	33.56±0.17	-32.89±0.10	66.45±0.18
520.00	31.94±0.11	0.22	52.26±0.12	0.16	32.08±0.18	-33.08±0.12	65.16±0.19
540.00	31.78±0.12	0.28	53.31±0.14	0.20	30.72±0.18	-33.26±0.14	63.98±0.20
560.00 ^c	31.67±0.14	0.35	54.35±0.16	0.25	29.46±0.19	-33.42±0.16	62.88±0.21
580.00 ^c	31.58±0.16	0.43	55.38±0.17	0.31	28.29±0.20	-33.57±0.17	61.86±0.22
600.00 ^c	31.53±0.18	0.53	56.40±0.20	0.38	27.20±0.21	-33.71±0.20	60.91±0.23
620.00 ^c	31.49±0.20	0.63	57.41±0.22	0.46	26.19±0.23	-33.83±0.22	60.02±0.24
640.00 ^c	31.47±0.22	0.75	58.40±0.24	0.55	25.24±0.24	-33.95±0.24	59.20±0.25
660.00 ^c	31.47±0.24	0.88	59.38±0.26	0.65	24.36±0.26	-34.06±0.26	58.42±0.27
680.00 ^c	31.48±0.26	1.03	60.35±0.28	0.76	23.52±0.28	-34.17±0.28	57.69±0.28
700.00 ^c	31.50±0.29	1.19	61.31±0.31	0.89	22.73±0.31	-34.26±0.31	56.99±0.30

TABLE 10. continued

$\frac{T}{K}$	$\frac{\Delta_0^T H_m^\circ}{R T}$	$\frac{\Delta_{imp} H_m^\circ}{R T}$ ^a	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_{imp} S_m^\circ}{R}$ ^b	$\frac{\Delta_f H_m^\circ}{R T}$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_f G_m^\circ}{R T}$
2,7-Dimethylnaphthalene							
298.15 ^{c,d}	47.47±0.11	0.00	49.63±0.12	0.00	32.07±0.23	-52.88±0.12	84.95±0.20
300.00 ^{c,d}	47.31±0.11	0.00	49.76±0.12	0.00	31.80±0.23	-52.96±0.12	84.75±0.20
320.00 ^{c,d}	45.74±0.10	0.00	51.19±0.10	0.00	29.09±0.21	-53.70±0.10	82.79±0.19
340.00 ^{c,d}	44.43±0.09	0.00	52.62±0.09	0.00	26.72±0.20	-54.38±0.09	81.10±0.18
360.00 ^{c,d}	43.35±0.08	0.00	54.04±0.08	0.00	24.64±0.18	-55.00±0.08	79.63±0.17
380.00	42.46±0.07	0.01	55.47±0.08	0.01	22.79±0.17	-55.56±0.08	78.35±0.16
400.00	41.72±0.06	0.01	56.89±0.07	0.01	21.15±0.16	-56.07±0.07	77.22±0.16
420.00	41.11±0.06	0.02	58.31±0.07	0.02	19.69±0.15	-56.53±0.07	76.23±0.15
440.00	40.63±0.05	0.03	59.72±0.07	0.02	18.39±0.15	-56.96±0.07	75.34±0.15
460.00	40.23±0.05	0.05	61.12±0.07	0.04	17.21±0.14	-57.34±0.07	74.55±0.14
480.00	39.93±0.06	0.07	62.52±0.07	0.05	16.15±0.14	-57.69±0.07	73.84±0.14
500.00	39.69±0.07	0.10	63.91±0.08	0.08	15.19±0.14	-58.01±0.08	73.20±0.15
520.00	39.52±0.09	0.14	65.29±0.10	0.10	14.32±0.14	-58.30±0.10	72.62±0.16
540.00	39.40±0.10	0.19	66.66±0.12	0.14	13.53±0.15	-58.56±0.12	72.09±0.17
560.00	39.32±0.12	0.25	68.02±0.13	0.18	12.81±0.16	-58.80±0.13	71.61±0.18
580.00	39.29±0.14	0.32	69.37±0.15	0.23	12.15±0.17	-59.02±0.15	71.17±0.19
600.00 ^c	39.29±0.16	0.40	70.71±0.18	0.29	11.55±0.19	-59.21±0.18	70.76±0.21
620.00 ^c	39.32±0.18	0.49	72.03±0.20	0.36	11.00±0.20	-59.39±0.20	70.39±0.23
640.00 ^c	39.37±0.20	0.60	73.34±0.22	0.45	10.49±0.22	-59.55±0.22	70.04±0.24
660.00 ^c	39.44±0.23	0.72	74.63±0.25	0.54	10.01±0.24	-59.70±0.25	69.72±0.26
680.00 ^c	39.52±0.25	0.86	75.90±0.27	0.65	9.57±0.27	-59.84±0.27	69.41±0.28
700.00 ^c	39.61±0.28	1.02	77.16±0.30	0.77	9.15±0.29	-59.97±0.30	69.12±0.30

^a Gas-imperfection correction included in the ideal-gas enthalpy.

^b Gas-imperfection correction included in the ideal-gas entropy.

^c Values at this temperature were calculated with extrapolated vapor pressures calculated from the fitted Wagner-equation parameters.

^d Values at this temperature were calculated with extrapolated liquid-phase heat capacities.

TABLE 11. Comparison of literature values for the enthalpy of sublimation of naphthalene with values obtained in this research. ^a
($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

Year	Reference No.	T/K	$\Delta_{\text{l}}^{\text{g}}\text{H}_{\text{m}}$ (lit.) kJ·mol ⁻¹	This research kJ·mol ⁻¹	Δ^{b} kJ·mol ⁻¹
1953	91	286.85	72.38	73.01	-0.63
1958	93	268.15	67.36	73.57	-6.21
1959	94	280	66.27±2.26	73.22	-6.95
1963	95	298.15	72.68±0.33	72.65	0.03
1968	96	303.15	66.53±1.67	72.48	-5.95
1972	97	298.15	72.05±0.25	72.65	-0.60
1972	98	298.15	73.00±0.25	72.65	0.35
1974	83	298.15	72.50	72.65	-0.15
1974	99	289.65	72.72±1.67	72.92	-0.21
1975	92	298.15	72.50±0.25	72.65	-0.15
1977	100	263.15	74.77±0.42	73.72	1.05
1977	100	263.15	73.89±0.21	73.72	0.17
1980	88	267.85	74.80±0.50	73.58	1.22
1980	88	298.15	72.60±0.60	72.65	-0.05
1981	62	298.15	72.51±0.14	72.65	-0.13
1982	90	278	73.93±0.29	73.28	0.65
1982	90	298.15	72.80±0.30	72.65	0.15
1982	101	297.3	72.47±0.60	72.67	-0.20
1982	101	306.5	71.87±0.10	72.36	-0.49
1982	101	311.3	72.08±0.22	72.19	-0.11
1982	101	321.3	71.89±0.66	71.81	0.08
1982	101	331.1	71.17±0.34	71.42	-0.25
1982	101	341.1	70.65±0.62	70.98	-0.33
1982	101	297	72.51±0.26	72.68	-0.17
1982	101	296	72.77±0.34	72.72	0.05
1982	102	315	72.28±0.28	72.05	0.23
1983	86	303.15	75.80±1.10	72.48	3.32
1983	84	248.51	72.92±0.37	74.12	-1.20
1983	84	298.15	72.92±0.37	72.65	0.27
1987	103	298.15	70.73	72.65	-1.91
1988	104	323	70.85±0.78	71.74	-0.89

^a Values listed for reference 101 are experimental results. The authors also listed four values for 298.15 K, which were derived from the results listed here.

^b $\Delta = [\Delta_{\text{l}}^{\text{g}}\text{H}_{\text{m}} (\text{lit.}) - \Delta_{\text{l}}^{\text{g}}\text{H}_{\text{m}} (\text{this research})]$.

TABLE 12. Comparison of experimental and calculated sublimation pressures

$\frac{T}{K}$	$\frac{p(cr)}{Pa}$ ^a	$\frac{p(liquid)}{Pa}$ ^b	$\frac{p(calc)}{Pa}$ ^c	$\frac{\Delta(p)}{Pa}$ ^d
2,7-Dimethylnaphthalene				
333.124	19.9	44.4	20.1	-0.2
338.124	30.9	61.6	31.4	-0.5
343.124	47.5	84.7	48.4	-0.9
348.123	73.1	115.1	73.7	-0.6
353.123	110.7	154.8	110.9	-0.2
353.123	164.9	206.2	164.7	0.2
363.123	242.6	272.1	241.8	0.8
368.123	351.8	355.8	350.9	0.9

^a Sublimation pressure measured in inclined piston, see reference 16.

^b Vapor pressure for supercooled liquid calculated using the Wagner-equation parameters listed in table 7.

^c Sublimation pressure calculated using equation (11).

^d $\Delta(p) = \{p(cr) - p(calc)\}$ is the difference between measured and calculated values of the sublimation pressure.

TABLE 13. Comparison of ideal-gas enthalpies and entropies for 2,7-dimethylnaphthalene a,b,c,d,e,f

T/K	$\Delta_{298.15}^T H_m^0 / RT$					Delta
	Benzene	Toluene	Naph.	2,7-DMN calc.	2,7-DMN calor.	
300	0.06	0.08	0.09	0.12	0.13	-0.01
400	3.00	3.74	4.78	6.26	6.34	-0.07
500	5.44	6.74	8.68	11.29	11.38	-0.09
600	7.53	9.30	11.99	15.54	15.70	-0.16
700	9.34	11.53	14.75	19.13	19.39	-0.26

T/K	$\Delta_0^T S_m^0 / R$					Delta	$\pm$
	Benzene	Toluene	Naph.	2,7-DMN calc.	2,7-DMN calor.		
300	32.45	38.67	40.41	49.96	49.76	0.20	0.15
400	35.83	42.88	45.78	57.00	56.89	0.11	0.09
500	39.20	47.04	51.19	63.98	63.91	0.07	0.13
600	42.47	51.07	56.40	70.71	70.71	0.00	0.27
700	45.58	54.90	61.31	77.06	77.16	-0.10	0.42

a Value for toluene calculated assuming free rotation of the methyl group.

b Naph. = naphthalene; 2,7-DMN = 2,7-dimethylnaphthalene.

c Values listed under 2,7-DMN calc. were determined using equations (12) and (13).

d Values listed under 2,7-DMN calc. are those listed in table 10.

e Delta = (2,7-DMN calc. - 2,7-DMN calor.).

f $\pm$ = Overall single standard deviation calculated from the values given in table 10 assuming zero error in the values for toluene and benzene.

TABLE 14. Estimated ideal-gas entropies for 2-methylnaphthalene

T/K	$\Delta_0^T S_m^\circ / R$
300	46.22
400	52.43
500	58.62
600	64.59
700	70.22

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