Thermodynamic properties of 1-phenylnaphthalene and 2-phenylnaphthalene

Robert D. Chirico [a,*], William V. Steele [b], Andrei F. Kazakov [a]

[a] *Applied Chemicals and Materials Division, National Institute of Standards and Technology, Boulder, CO 80305-3337, USA*
[b] *Physical Properties Research Facility, Chemical and Biomolecular Engineering Department, University of Tennessee, Knoxville, TN 37996-2200, USA*

ABSTRACT

Measurements leading to the calculation of thermodynamic properties in the ideal-gas state for 1-phenylnaphthalene (Chemical Abstracts registry number [605-02-7]) and 2-phenylnaphthalene (Chemical Abstracts registry number [612-94-2]) are reported. Experimental methods for 1-phenylnaphthalene were adiabatic heat-capacity calorimetry, differential scanning calorimetry, inclined-piston manometry, comparative ebulliometry, vibrating-tube densitometry, and combustion calorimetry. For 2-phenylnaphthalene, the experimental methods were adiabatic heat-capacity calorimetry, differential scanning calorimetry, and comparative ebulliometry. Critical properties were estimated for both compounds. Molar thermodynamic functions (enthalpies, entropies, and Gibbs free energies) for the condensed and ideal-gas states were derived from the experimental studies at selected temperatures. Statistical calculations were performed based on molecular geometry optimization and vibrational frequencies calculated at the B3LYP/6-31+G(d,p) and B3LYP/cc-pVTZ levels of theory. Ideal-gas entropies derived with two the independent methods are shown to be in good accord for 1-phenylnaphthalene, but significant differences are apparent for 2-phenylnaphthalene. These differences are likely due to a disorder of unknown type in the crystals of 2-phenylnaphthalene at low temperatures, as evidenced by the presence of a glass-like transition in the measured heat capacities for the solid state. All experimental results are compared with property values reported in the literature.

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1. Introduction

Phenylnaphthalenes are of interest in a variety of research areas, including modeling of solubilities for polycyclic aromatic hydrocarbons in water [1], development of high-temperature heat transfer fluids [2], as well as in fundamental studies of aromatic conjugation [3].This work is a continuation of our investigations (cf., [4–7]) into the quantification of uncertainties for thermodynamic properties derived with computational chemistry with particular focus on entropies for the ideal-gas state. Entropies for the ideal-gas state can be calculated with structural information and the methods of computational chemistry, as well as through appropriate combination of experimentally determined thermodynamic properties. These two methods are completely independent and their study provides the means for their mutual validation through analysis of observed consistencies and deviations. Reliable ideal-gas properties have key roles in property predictions, thermodynamic-consistency analyses, constrained property
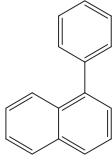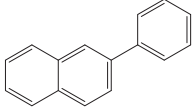
extrapolations, and they form the basis of important equation-of-state formulations, which are expressed as deviations from the ideal-gas state [8,9]. As noted previously [5], the ability to derive ideal-gas properties solely from computational methods with reliable uncertainties would provide key values that are difficult or impossible to obtain experimentally for numerous materials, such as those of high expense, high toxicity, or low stability.

This article describes thermodynamic property measurements for 1-phenylnaphthalene (Chemical Abstracts registry number [605-02-7]) and 2-phenylnaphthalene [612-94-2]. A summary of the new experimental property measurements reported here is provided in table 1. Entropies for the ideal-gas state are derived from the thermophysical property measurements for both compounds, and these are compared with independently derived values calculated with the methods of computational chemistry. It will be shown that very good accord is achieved for 1-phenylnaphthalene, while significant deviations are seen for 2-phenylnaphthalene. The deviations likely arise from a "frozen-in" disorder in the crystals of 2-phenylnaphthalene, as evidenced by the presence of a glass-like transition in the solid-state.

* Corresponding author. Tel.: +1 303 497 4126; fax: +1 303 497 5044.
E-mail address: chirico@boulder.nist.gov (R.D. Chirico).

TABLE 1

Summary of experimental results reported here for 1-phenylnaphthalene and 2-phenylnaphthalene.

Property	Method	Temperature range/K
1-phenylnaphthalene		

Property	Method	Temperature range/K
Heat capacity	Adiabatic calorimetry	5 to 442
Triple-point temperature		
Enthalpy of fusion		
Heat capacity	Differential scanning calorimetry	400 to 650
Vapor pressure	Inclined-piston manometry	375 to 480
	Comparative ebulliometry	466 to 630
Density	Vibrating-tube densimetry	323 to 523
Enthalpy of combustion	Oxygen-bomb calorimetry	298.15
Mole fraction purity (this study) = 0.9993		
2-phenylnaphthalene		

Property	Method	Temperature range/K
Heat capacity	Adiabatic calorimetry	5 to 442
Triple-point temperature		
Enthalpy of fusion		
Heat capacity	Differential scanning calorimetry	400 to 650
Vapor pressure	Comparative ebulliometry	483 to 604
Mole fraction purity (this study) = 0.9998_5		

2. Experimental

2.1. Materials

The research group of Professor E.J. "Pete" Eisenbraun (retired) of Oklahoma State University synthesized and purified the samples of 1-phenylnaphthalene (1-PhN) and 2-phenylnaphthalene (2-PhN). Final purification was by high-performance liquid chromatography for 1-PhN and by fractional sublimation for 2-PhN. Sample purities were established in fractional-melting studies determined as part of the adiabatic heat-capacity calorimetric results reported here. The mole-fraction purities x were $x = 0.9993$ for 1-PhN and $x = 0.9998_5$ for 2-PhN. The purified samples were transferred under nitrogen or helium or by vacuum distillation prior to the property measurements. Purification of the water and decane used as reference materials in the ebulliometric vapor-pressure measurements reported here has been described [10].

2.2. Physical constants and standards

Property values are reported in terms of molar mass $M = 204.256$ [11] based on the formula $C_{16}H_{12}$ for the compounds and the gas constant $R = 8.3144621 \, J \cdot K^{-1} \cdot mol^{-1}$ adopted in 2010 by CODATA [12]. Platinum resistance thermometers used in these studies were calibrated by comparison with standard thermometers whose constants were determined at the National Bureau of Standards (NBS), now the National Institute of Standards and Technology (NIST). All temperatures were measured in terms of IPTS-68 [13] and were converted to ITS-90 with published temperature increments [14]. The platinum resistance thermometer used in the adiabatic heat-capacity study was calibrated below $T/K = 13.81$ with the method of McCrackin and Chang [15]. Mass, time, electrical resistance, and potential difference were measured in terms of standards traceable to calibrations at NIST.

2.3. Apparatus and procedures

New experimental measurements reported here, including temperature ranges and methods used, are summarized in table 1. All derived properties are based on these measurements with the addition of the enthalpy of combustion for 2-PhN reported by Lima et al. [3] and unpublished vapor pressures for 1-PhN measured with the vapor-saturation method for the temperature range ($313 < T/K < 371$) by Verevkin [16]. The enthalpy of combustion for 2-PhN was not measured in this research, but is necessary to calculate the Gibbs free energies of formation, and the vapor pressure measurements by Verevkin complement those measured here for the temperature range ($375 < T/K < 630$).

Heat-capacities and enthalpy increments for 1-PhN and 2-PhN were measured with an adiabatic calorimetric system that has been described [17]. The calorimeter characteristics and sealing conditions are given in table 2. Energies were measured with a repeatability of 0.01%, and temperatures were measured with a repeatability of 0.0001 K. The energy increments to the filled platinum calorimeter were corrected for enthalpy changes in the empty calorimeter, for the helium exchange gas, and for vaporization of the sample into the free space of the sealed vessel. The maximum sizes of these corrections are indicated in table 2.

Densities for the liquid phase along the liquid–gas saturation line ρ_{sat} were measured with a vibrating-tube densimeter in this research for 1-PhN. The instrument and its operation have been described [18], as have test measurements on the density of benzene for the temperature range ($310 < T/K < 523$) [19]. Results for benzene agree within $5 \cdot 10^{-4} \rho_{sat}$ with the critical evaluation in the NIST REFPROP Database [20].

Heat capacities at vapor-saturation pressure $C_{sat,m}$ for the liquid phase over the temperature range ($400 < T/K < 650$) were determined with a differential scanning calorimeter (dsc) for both compounds. An intermittent heating method, as first described by Mraw and Naas [21], was used with sequential measurements