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Thermodynamic properties of 9-fluorenone: Mutual validation of experimental and computational results

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

[a] *Thermophysical Properties 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*

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ABSTRACT

Measurements leading to the calculation of thermodynamic properties for 9-fluorenone (IUPAC name 9*H*-fluoren-9-one and Chemical Abstracts registry number [486-25-9]) in the ideal-gas state are reported. Experimental methods were adiabatic heat-capacity calorimetry, inclined-piston manometry, comparative ebulliometry, and combustion calorimetry. Critical properties were estimated. Molar entropies for the ideal-gas state were derived from the experimental studies at selected temperatures T between $T = 298.15$ K and $T = 600$ K, and independent statistical calculations were performed based on molecular geometry optimization and vibrational frequencies calculated at the B3LYP/6 − 31 + G(d,p) level of theory. Values derived with the independent methods are shown to be in excellent accord with a scaling factor of 0.975 applied to the calculated frequencies. This same scaling factor was successfully applied in the analysis of results for other polycyclic molecules, as described in recent articles by this research group. All experimental results are compared with property values reported in the literature. Thermodynamic consistency between properties is used to show that several studies in the literature are erroneous.

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1. Introduction

The rigid nature of fused-ring systems, together with the absence of internal rotations, makes such molecules good candidates for accurate calculation of entropies for the ideal-gas state with computational methods. In the present paper, entropies for the ideal-gas state are derived from the reported thermodynamic property measurements and are compared with independently calculated values derived with the methods of computational chemistry. The accord achieved provides a mutual validation of the two methods, and demonstrates an important path to the quantification of uncertainties for the computational methods. Reliable ideal-gas properties have numerous applications in thermodynamics, including key roles in property predictions, consistency analyses, constrained property extrapolations, and equation of state formulations. The ability to derive ideal-gas properties from computational methods with reliable uncertainties would provide essential data that are, otherwise, impractical or impossible to obtain, such as those for materials of high expense, high toxicity, low chemical stability, or materials that cannot be synthesized in adequate quantity or purity for experimental investigation.

Previously, we reported on combined studies of computed and experimental thermodynamic properties for a series of aza-aromatics: 2-methylquinoline [1], 8-methylquinoline [1], 2,6-dimethylquinoline [1], phenazine [2], acridine [2], phenanthridine [3], 1,10-phenanthroline [3], and 7,8-benzoquinoline [3]. For these studies, calculations were performed at the B3LYP/6 − 31 + G(d,p) model chemistry with a consistent scaling factor (0.975), and excellent accord was demonstrated between computed entropies for the ideal gas and those based on the experimental property measurements. In the present work, this analysis is applied for the first time to a three-ring aromatic oxygen-containing compound, 9-fluorenone (IUPAC name 9*H*-fluoren-9-one and Chemical Abstracts Service Registry Number [486-25-9]).

The thermodynamic properties of 9-fluorenone were measured by oxygen bomb calorimetry, adiabatic heat-capacity calorimetry, comparative ebulliometry, and inclined-piston gauge manometry. Standard molar enthalpies, entropies, enthalpies of formation, entropies of formation, and molar Gibbs free energies of formation in the ideal gas state were derived. Comparisons of computed and experimentally derived entropies for the ideal gas are discussed in detail. Measured or derived thermodynamic property values are compared with those reported in the literature. A summary of the new experimental thermodynamic property measurements reported is given in table 1.

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* Corresponding author.
E-mail address: chirico@boulder.nist.gov (R.D. Chirico).

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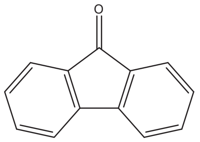
TABLE 1
Summary of experimental results reported in this research for 9-fluorenone.[a]

Property	Method	Temperature range/K
		
Heat capacity and derived properties	Adiabatic calorimetry	5 to 525
Vapor pressure	Inclined-piston manometry	368 to 483
	comparative ebulliometry	465 to 668[a]
Enthalpy of combustion	Oxygen-bomb calorimetry	298.15

[a] Evidence of sample decomposition was observed for temperatures T greater than $T = 650$ K.

TABLE 2
Calorimeter and sample characteristics for adiabatic calorimetric studies on 9-fluorenone.[a]

m/g	53.540
V_i(298.15 K)/cm^3	61.78
T_{cal}/K	297.0
p_{cal}/kPa	8.05
$r(T_{max})$	3.4
r_{min}	1.8
$10^2 \cdot (\delta C/C)_{max}$	0.026
x_{pre}	0.0000_4

[a] m is the sample mass; V_i is the internal volume of the calorimeter vessel; T_{cal} is the temperature of the calorimeter when sealed; p_{cal} is the pressure of the helium and sample when sealed; $r(T_{max})$ is the ratio of the heat capacity of the full calorimeter to that of the empty at the highest temperature $T_{max} \approx 525$ K of these measurements; r_{min} is the minimum value of r observed in this study; $(\delta C/C)_{max}$ is the vaporization correction at the highest temperature measured (*i.e.*, $T_{max} \approx 525$ K); and x_{pre} is the mole-fraction impurity used for pre-melting corrections.

2. Experimental

2.1. Materials

The research group of Professor E.J. "Pete" Eisenbraun (retired) of Oklahoma State University purified the sample used in this research. A commercial sample of 9-fluorenone was recrystallized from hexane. The mole fraction purity x of the sample used in all of the experimental studies ($x = 0.9998_2$) was determined by fractional melting as part of the adiabatic calorimetric studies. Sample handling during purification and transfer was done under an argon, nitrogen, or helium atmosphere or by vacuum distillation. Purification of the water and decane used as reference materials in the ebulliometric vapor–pressure measurements reported here has been described [4].

2.2. Physical constants and standards

Property values are reported in terms of molar mass $M = 180.201$ [5] based on the formula $C_{13}H_8O$ for 9-fluorenone and the gas constant $R = 8.3144621\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ adopted in 2010 by CODATA [6]. The platinum resistance thermometers used in these measurements 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 [7] and were converted to ITS-90 with published temperature scale differences [8]. The platinum resistance thermometer used in the adiabatic heat-capacity study was calibrated below $T = 13.81$ K with the method of McCrackin and Chang [9]. Mass, time, electrical resistance, and potential difference were measured in terms of standards traceable to calibrations at NIST.

2.3. Apparatus and procedures

Heat-capacities, enthalpy increments, and the triple-point temperature for 9-fluorenone were measured with an adiabatic calorimetric system described previously [10]. Characteristics of the sample container and sealing conditions are given in table 2. Energies were measured with a standard uncertainty of 0.01%, and temperatures were measured with a repeatability of 0.0001 K and standard uncertainty of 0.005 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 correction to the measured energy for the helium exchange gas was 0.4% near $T = 4.6$ K, and the sizes of the other two corrections are given in table 2.

The essential features of the ebulliometric equipment and procedures for the precise determination of vapor pressures have been described [11]. The ebulliometers were used to reflux the 9-fluorenone with a standard of known vapor pressure under a common atmosphere of He(g). The boiling and condensation temperatures of the two substances were determined, and the vapor pressure of the sample was derived from the condensation temperature of the standard. In the pressure region 25 kPa to 270 kPa, water was used as the standard, and the pressures were derived from the international equation of state for ordinary water [12]. In the pressure region 2 kPa to 25 kPa, decane was used as the standard. The vapor pressures for decane that were used can be calculated with equation (1) of reference [4].

The standard uncertainty for the temperature measurements in the ebulliometric vapor–pressure studies was 0.002 K. Standard uncertainties in the pressures are adequately described by

$$u(p) = (0.002\ \mathrm{K})\left\{(\mathrm{d}p_{ref}/\mathrm{d}T)^2 + (\mathrm{d}p_x/\mathrm{d}T)^2\right\}^{1/2}, \tag{1}$$

where p_{ref} is the vapor pressure of the reference substance and p_x is the vapor pressure of the sample under study. The repeatability of the temperature measurements was $5 \cdot 10^{-4}$ K.

Vapor pressures for 9-fluorenone were measured with an inclined-piston apparatus described initially by Douslin and McCullough [13] and Douslin and Osborn [14]. Changes to the equipment and procedures have been reported [4]. Standard uncertainties for the measured values $u(p)$, based on estimated uncertainties in measuring the mass, area, and angle of inclination of the piston, are described by the expression:

$$u(p) = (1.5 \cdot 10^{-4} p \pm 0.2)\ \mathrm{Pa}. \tag{2}$$

The standard uncertainties for the temperatures $u(T)$ are 0.002 K. Contributions of the temperature uncertainties to $u(p)$ are not significant in the reported results.

The experimental procedures used in the combustion calorimetry reported here have been described [10,15–17]. The enthalpy of combustion for crystalline 9-fluorenone was determined in this research. A rotating-bomb calorimeter (laboratory designation BMR II) [16] and platinum-lined bomb (laboratory designation Pt-3b) [18] with an internal volume of 0.393_4 dm^3 were used without rotation. The calorimetric sample of 9-fluorenone was burned in pellet form [19]. For each experiment, a volume of 0.0010 dm^3 of water was added to the bomb, and the bomb was charged to a