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Thermodynamic properties of xanthone: Heat capacities, phase-transition properties, and thermodynamic-consistency analyses using computational results ☆

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ABSTRACT

Heat capacities and phase-transition properties for xanthone (IUPAC name 9*H*-xanthen-9-one and Chemical Abstracts registry number [90-47-1]) are reported for the temperature range $5 < T/\mathrm{K} < 524$. Statistical calculations were performed and thermodynamic properties for the ideal gas were derived based on molecular geometry optimization and vibrational frequencies calculated at the B3LYP/6-31+G(d,p) level of theory. These results are combined with sublimation pressures from the literature to allow critical evaluation of inconsistent enthalpies of sublimation for xanthone, also reported in the literature. Literature values for the enthalpy of combustion of xanthone are re-assessed, a revision is recommended for one result, and a new value for the enthalpy of formation of the ideal gas is derived. Comparisons with thermophysical properties reported in the literature are made for all other reported and derived properties, where possible.

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1. Introduction

This article is part of a series in which we have reported studies of experimental and computed thermodynamic properties for aromatic ring systems, including an extensive series of azaaromatics (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]), some hydroaromatics (1-phenyl and 2-phenylnaphthalene [4]), and oxygen-containing compounds (9-fluorenone [5], and 1-naphthol [6]). For this series, computations were performed at the B3LYP/6-31+G(d,p) model chemistry with excellent accord demonstrated between computed entropies for the ideal gas and those based on the experimental property measurements. In the present work, this approach is applied to xanthone (IUPAC name 9*H*-xanthen-9-one and Chemical Abstracts registry number [90-47-1]).

Results of our previous work [1–6] have demonstrated that for rigid fused-ring systems thermodynamic properties for the ideal-gas state can be computed with relative standard uncertainties near 0.1%. In the present work, we use this finding together with new condensed-phase thermodynamic properties determined with adiabatic calorimetry to assess and resolve inconsistencies between enthalpies of sublimation reported in the literature for xanthone [7–9]. These results allow evaluation of the enthalpy of formation of xanthone in the ideal gas state with high confidence, based on enthalpies of combustion reported in the literature [7,8,10]. As part of this assessment, an apparent error in one report [10] was detected and corrected.

Here, we report results of measurements of heat capacities and phase-transition properties for xanthone for the temperature range $5 < T/\mathrm{K} < 524$. The (crystal + liquid + gas) triple-point temperature and enthalpy of fusion were determined, together with properties associated with a small lambda-like transition in the solid state. Measured and derived thermodynamic property values are compared with those reported in the literature, where possible.

2. Experimental

2.1. Materials

The research group of Professor E.J. "Pete" Eisenbraun (retired) of Oklahoma State University purified the sample of xanthone used in this research. A commercial sample was recrystallized twice

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from ethanol (95%) and twice from a 1:1 by volume mixture of (hexane + ethyl acetate). The resulting crystals were filtered and dried by evacuation at room temperature. The mole fraction purity x of the sample ($x = 0.9999$) was determined by fractional melting as part of the adiabatic calorimetric studies. Sample handling during purification and transfer was done under a dry atmosphere of argon, nitrogen, or helium.

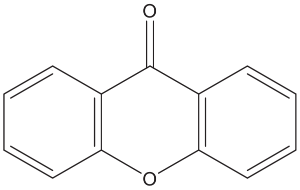
2.2. Physical constants and standards

Property values for xanthone are reported in terms of molar mass $M = 196.19\ \mathrm{g \cdot mol^{-1}}$ [11] based on the formula $C_{13}H_8O_2$ and the gas constant $R = 8.3144621\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ adopted in 2010 by CODATA [12]. The platinum resistance thermometer used here was calibrated by comparison with a standard thermometer calibrated at the National Bureau of Standards (NBS), now the National Institute of Standards and Technology (NIST). Temperatures were measured in terms of IPTS-68 [13] and were converted to ITS-90 with published differences [14]. The thermometer was calibrated below $T/\mathrm{K} = 13.81$ 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. Adiabatic calorimetry

Heat-capacities, enthalpy increments, and the triple-point temperature for xanthone were measured with an adiabatic calorimetric system described previously [16]. Sample-container characteristics and sealing conditions are given in table 1. Energies were measured with a relative standard uncertainty of 0.01%. Temperatures were measured with a repeatability of 0.0001 K, which represents the lower limit in the standard uncertainty for measured temperature increments. The standard uncertainty for a single temperature measurement was 0.005 K, due to uncertainties associated with the thermometer calibration, and represents the lower limit for the standard uncertainty in reported absolute temperatures, including phase-transition temperatures. The energy increments to the filled platinum calorimeter were corrected for enthalpy changes in the empty calorimeter and for the helium exchange gas. Corrections for vaporization of the sample into the free space of the sealed vessel were estimated to be insignificant, so none were applied. The maximum correction to the measured energy for the helium exchange gas was 0.4% near $T/\mathrm{K} = 5$. The approximate size of the correction for the enthalpy changes in the empty calorimeter is given in table 1.

TABLE 1
Calorimeter and sample characteristics for adiabatic calorimetric studies on xanthone.[a]



m/g	47.893
V_i(298.15 K)/cm^3	61.78
T_{cal}/K	298.2
p_{cal}/kPa	4.53
$r(T_{max})$	3.1
r_{min}	1.6
x_{pre}	0.0001

[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 $T_{max} \approx 524$ K of these measurements; r_{min} is the minimum value of r observed in this study; and x_{pre} is the mole-fraction impurity used for pre-melting corrections.

3. Experimental results

3.1. Heat capacities, phase-transition properties, and derived thermodynamic functions for the condensed phases

Measurements were made for the temperature range ($5 < T/\mathrm{K} < 524$), and included determination of heat capacities for the solid and liquid phases, the triple-point temperature T_{tp}, the molar enthalpy of fusion $\Delta_{cr}^{l}H_m$, and the temperature of a lambda-like transition T_{tr} in the solid state. The density of liquid xanthone under saturation pressure at temperature $T/\mathrm{K} = 473$ $\{\rho_{sat} = 1090 \pm 20\ \mathrm{kg \cdot m^{-3}}\}$ was determined from the sample mass and volume measured as part of the filling procedure for the calorimetric vessel.

Crystallization of xanthone in the calorimeter was initiated by slow cooling (approximately $7\ \mathrm{mK \cdot s^{-1}}$) the liquid sample to approximately 10 K below T_{tp}. Complete crystallization was obtained by maintaining the sample under adiabatic conditions in the partially melted state (10% to 20% liquid) until ordering of the crystals was complete, as evidenced by the absence of spontaneous warming of the sample. In these experiments, no spontaneous warming was observed, indicating rapid and complete crystallization of the sample. The sample was then cooled at an effective rate of $7\ \mathrm{mK \cdot s^{-1}}$ to crystallize the remaining liquid and was thermally cycled from approximately 100 K to within 3 K of the triple-point temperature ($T_{tp} = 448.79_5$ K), where it was held for a minimum of 16 h to provide further tempering. All of the solid-phase measurements were performed upon crystals pre-treated in this way. Excellent repeatability (within 0.01%) was observed for three separate $\Delta_{cr}^{l}H_m$ determinations, which further indicates complete conversion to the crystalline state.

The triple-point temperature T_{tp} and mole fraction purity x for xanthone were determined by measurement of the equilibrium melting temperatures $T(F)$ as a function of fraction F of the sample in the liquid state [17]. Equilibrium melting temperatures were determined by measuring temperatures for ~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 the end of the equilibration period were within 2 mK of the calculated equilibrium temperatures for F values listed in table 2 and used in the determination of T_{tp}. Results showed no evidence for the presence of solid-soluble impurities. The calculated triple-point temperature and sample purity are included in table 2.

The experimental heat capacities under vapor saturation pressure $C_{sat,m}$ determined by adiabatic calorimetry for xanthone are listed in table 3 and shown in figure 1. The values listed in table 3 were corrected for pre-melting with the mole fraction impurity

TABLE 2
Melting-study summary for xanthone.[a]

F	T/K
0.2046	448.755_0
0.4047	448.774_5
0.5547	448.780_1
0.7048	448.783_3
0.8548	448.785_0
$T_{tp} = (448.79_5 \pm 0.02)$ K[b]	
$x = 0.9999$	

[a] F is the fraction melted at observed temperature T, T_{tp} is the triple-point temperature, x is the derived mole-fraction purity of the sample.

[b] The uncertainty is the expanded uncertainty with 0.95 level of confidence.