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The Thermodynamic Properties of Thianthrene and Phenoxathiin

Topical Report

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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, $\rho/(\mathrm{kg\cdot m^{-3}})$ rather than " ρ $(\mathrm{kg/m^3})$" or " ρ $\mathrm{kg/m^3}$". Molar values, i.e., intensive functions, are denoted by the subscript "m", e.g., $C_{\mathrm{sat,m}}$, 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 $\mathrm{g\cdot mol^{-1}}$

T = temperature in Kelvin

p = pressure in Pascals (Pa)

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

$\Delta_c U^\circ_m$ = molar energy of combustion

$\Delta_c U^\circ_m/M$ = energy of combustion per gram

$\Delta_c H^\circ_m$ = molar enthalpy of combustion

$\Delta_f H^\circ_m$ = 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

$C_{\mathrm{sat,m}}$ = 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

$C_v^{II}(\rho = \rho_{\mathrm{sat}})$ = 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 K)

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

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

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

$T \to 0$ = 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·T. Units of time are s (seconds), d (days), and h (hours).

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, reduced T90, 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 representative diheteroatom-containing compounds. Type Two Reports apply the experimental information detailed in Type One Reports to thermodynamic analyses of key reaction networks involving the diheteroatom-containing compounds [e.g., derivation of the optimum conditions for formation of hydroaromatics (naphthenes) and hydrogen sulfide, ammonia or water]. 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 heteroatom removal.

The results reported here derive from the portion of the program providing accurate experimental thermochemical and thermophysical properties for "key" diheteroatom-containing aromatic and hydroaromatic compounds present in heavier feedstocks. This report details the thermochemical and thermophysical properties, measured at NIPER, for thianthrene and phenoxathiin. Compounds of this type are significant constituents of the heavier ends of feedstocks with low API gravity. However, few thermodynamic property measurements on such compounds exist in the literature.

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 would be reproduced in the pilot plant.

A Type Two Report, using the thermodynamic property measurements reported here in conjunction with upcoming measurements on diphenyl sulfide, is planned. That report will give an overall picture of the thermodynamics of hydrodesulfurization of the heavier ends of feedstocks with low API gravity. Initial calculations point to thermodynamic equilibria restrictions in the removal of dibenzothiophenes using existing HDS technology, and hence, possible non-attainment of the EPA-mandated sulfur levels for certain crude oil feeds.

ABSTRACT

Measurements leading to the calculation of the ideal-gas thermodynamic properties are reported for thianthrene (Chemical Abstracts registry number [92-85-3]) and phenoxathiin (registry number [262-20-4]). Experimental methods included combustion calorimetry, adiabatic heat-capacity calorimetry, vibrating-tube densitometry, comparative ebulliometry, inclined-piston gauge manometry, and differential-scanning calorimetry (d.s.c.). Critical properties were estimated for both materials based on the measurement results. Entropies, enthalpies, and Gibbs energies of formation were derived for the ideal gas for both compounds for selected temperatures between 298.15 K and 700 K. The property-measurement results reported here for thianthrene and phenoxathiin provide the first experimental gas-phase Gibbs energies of formation for tricyclic diheteroatom-containing molecules.

ACKNOWLEDGMENTS

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The authors acknowledge Professor E. J. "Pete" Eisenbraun and his research group at Oklahoma State University for preparation of the samples, and the assistance of I. Alex Hossenlopp in vapor-transfer of the materials prior to the calorimetric measurements. The authors thank Dr. J. M. "Mike" Simonson for permission to inspect his densitometry apparatus and for copies of sections of his apparatus design prior to publication by his research group.

1. INTRODUCTION

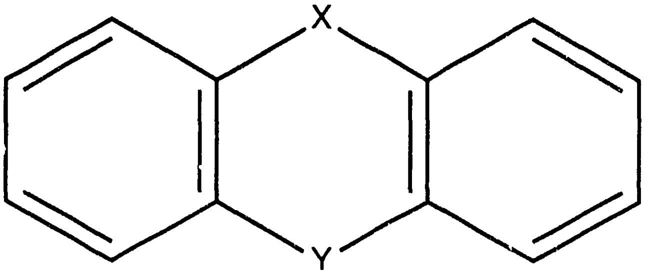
The world supply of petroleum crude and light petroleum crude in particular, continues to decline. It is a fact that the density and, hence, complexity of refinery feedstocks have increased markedly in the last decade. The average API gravity of the crude oil run to stills in the United States decreased by about 0.21° per year in the period 1980 through 1990.(1) That drop in gravity has been accompanied by an equivalent increase in the amount of petroleum coke produced. Refiners have moved more towards carbon rejection methods of processing rather than hydrogen addition (hydroprocessing) methods. U.S.A. petroleum coke production has increased 64 per cent during the ten year period 1980 - 1990.(1) Over the same period crude oil runs dropped significantly in the early 1980's and by 1990 had just returned to the 1980 level. Such a large amount of coke production is a waste of a valuable commodity.

Hydrodesulfurization (HDS) is one aspect of the hydroprocessing of petroleum crudes. HDS has long been one of the major catalytic operations in the petroleum industry.(2-7) In HDS, sulfur-containing compounds are generally converted to hydrocarbons and hydrogen sulfide (H_2S). In the past, the major reason for this conversion was to prevent the poisoning of the sulfur-sensitive catalysts used in subsequent operations in the refinery (e.g., platinum-containing catalysts used in reforming). A secondary reason was to avoid major atmospheric pollution. Most fuels leaving the refinery still contained appreciable amounts of sulfur. For example, diesel fuel in the U.S.A. contained up to 0.5 weight per cent (0.5 wt. %) sulfur.(1) This sulfur was bound in structures resistant to the conditions operating in the refinery for HDS reactions -- 550° F to 750° F and 75 to 150 atm. hydrogen pressure -- and did not poison the platinum catalysts. The resilient structural types were all aromatic thiophenic compounds including benzothiophene, dibenzothiophene, thianthrene, phenoxathiin, etc.

High-sulfur coke has little salable value. Hence, economic restraints have focused attention on the HDS of refractory sulfur-containing compounds. In addition, environmental constraints are growing world wide. In the U.S.A. the 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.(8) To compound refiners' problems, the level of aromatics in diesel fuel has been the topic of several regulatory efforts in California and by the U.S.A. government in the 1990 Clean Air Act Amendments.(9) [Increasing the severity of HDS (as a means of removing the more refractory sulfur-containing compounds) without a corresponding increase in hydrogen pressure will produce more aromatics.]

A 0.05 wt. % sulfur content is very small. To put it in perspective, it corresponds to 0.053 moles of dibenzothiophene in a gallon (3.8 dm^3) of a typical highway diesel fuel. Thermodynamic equilibria may restrict the attainment of such low levels. For example, using the thermodynamic properties for dibenzothiophene recently published by this research group,(10) under thermodynamic equilibrium control, attainment of a level of 0.05 wt. % dibenzothiophene would require approximately 100 atm. hydrogen pressure at 650° F.

At 0.05 wt. % sulfur content, other sulfur-containing aromatic structural types which were not of serious contention for the lighter crudes of the past become important species in the refining process. These include compounds of the type:



Two of these compounds are the subject of this report. They are thianthrene, where X and Y are both sulfur atoms; and phenoxathiin, where X is a sulfur atom and Y is an oxygen atom. HDS studies reported in the literature(7,11-21) for both of these compounds note strong resistance to sulfur and/or oxygen removal. For thianthrene, dibenzothiophene formation was reported under certain conditions.(15,21) For phenoxathiin, both dibenzothiophene and dibenzofuran formation were reported.(15,21) Prior to this research thermodynamic analyses of the HDS [and hydrodeoxygenation (HDO)] reaction pathways for these compounds were based on crude extrapolations from the properties of pyran and thiacyclohexane.

The thermodynamic properties of thianthrene and phenoxathiin were measured by adiabatic heat-capacity calorimetry, comparative ebulliometry, inclined-piston gauge manometry, vibrating tube densitometry, and differential-scanning calorimetry. For phenoxathiin, the energy of combustion -- and hence, the enthalpy of formation -- was determined by rotating-bomb calorimetry. For thianthrene, which has been recommended as a secondary standard for combustion bomb calorimetry of sulfur-containing compounds,(22) the energy-of-combustion literature(23-30) was reviewed recently(29) and an enthalpy-of-formation value selected. The density measurements were shown to provide key information for the accurate estimation of critical properties for these materials, which decompose far below their critical temperatures. Critical temperatures for thianthrene and phenoxathiin were estimated with an uncertainty of only ±10 K, even though the compounds decomposed nearly 200 K lower. 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.

A future paper is planned using the thermodynamic-property measurements reported here in conjunction with upcoming measurements on diphenyl sulfide. That paper will give an overall picture of the thermodynamics of hydrodesulfurization of the heavier ends of feedstocks with low API gravity. As stated above, initial calculations indicate thermodynamic equilibria restrictions using existing HDS technology in the removal of dibenzothiophene, thianthrene, or phenoxathiin, which implies that EPA-mandated sulfur levels for certain crude oil feeds may not be attained.

2. EXPERIMENTAL

MATERIALS

Samples for thermodynamic-property measurements were prepared by Professor E. J. Eisenbraun and his research group at Oklahoma State University. The thianthrene used in the heat-capacity studies was a purified commercial material. Commercial thianthrene (150 g) was eluted through acidic, basic, and neutral alumina using diethyl ether under argon. The eluate was concentrated to 0.8 dm^3 and was filtered. The crystals were dried under vacuum and were outgassed thoroughly by freeze-pump-thaw cycles prior to loading the sample into the calorimeters. All sample handling was done in vacuo or under nitrogen.

The thianthrene used for density and vapor pressure measurements was U.S. Department of Interior, Bureau of Mines standard material for enthalpy-of-combustion determinations of sulfur compounds (designation: USBM-P2a).

The phenoxathiin used in this research was synthesized as follows. Diphenyl ether $C_{12}H_{10}O$ (6.5 mol), sulfur (4 mol), and anhydrous $AlCl_3$ (1.9 mol) were combined and heated at reflux for 4 h. Hydrogen sulfide was trapped in an alkaline solution as it emerged. The cooled reaction mixture was poured onto a (water + ice) mixture and extracted with diethyl ether. The extract was washed with water and brine, dried ($MgSO_4$), filtered, concentrated by rotary evaporation, and distilled to give recovered diphenyl ether (3.2 mol) and crude phenoxathiin (0.95 mol). The phenoxathiin was recrystallized from methanol. The crystals were dried under vacuum and were outgassed thoroughly by freeze-pump-thaw cycles prior to loading the sample into the calorimeters. To ensure removal of all methanol, the phenoxathiin was cycled six times between 80 K and 350 K (T_{tp} = 328.8 K) under vacuum. All sample handling was done in vacuo or under nitrogen.

Mole-fraction impurities for each sample were determined by fractional melting as part of the adiabatic heat-capacity calorimetric studies. The mole-fraction impurities were 0.00003 and 0.00013 for thianthrene and phenoxathiin, respectively. 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 $M = 216.316\ g{\cdot}mol^{-1}$ and $200.255\ g{\cdot}mol^{-1}$ for thianthrene and phenoxathiin, respectively, based on the relative atomic masses of 1981(31)† and the gas constant $R = 8.31451\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ adopted by CODATA.(32) 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), formerly the National Bureau of Standards (NBS). All temperatures reported are in terms of the IPTS-68.(33) The platinum resistance thermometer used in the adiabatic heat-capacity studies was calibrated below 13.81 K with the method of McCrackin and Chang.(34) 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,(35) which had an upper temperature limit of approximately 430 K. Studies on high-molecular-weight compounds (three aromatic rings and greater) required that this upper temperature limit be raised substantially. As a result, a new

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† The 1981 relative atomic masses were used because the CODATA Recommended Key Values for Thermodynamics (reference 57) are based on them.

densitometer was constructed with an upper temperature limit near 520 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.(36)

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.(37) Results agreed with the values published by Hales and Townsend(38) within ±0.1 per cent. The precision of the measurements was approximately 0.05 per cent.

Combustion Calorimetry. In this research the energy of combustion of phenoxathiin was determined. Numerous determinations of the energy of combustion of thianthrene exist already in the literature.(23-28,30) The experimental procedures used in the combustion calorimetry of organic sulfur-containing compounds at the National Institute for Petroleum and Energy Research have been described.(39,40) A rotating-bomb calorimeter (laboratory designation BMR II)(41) and platinum-lined bomb (laboratory designation Pt-3b)(42) with an internal volume of 0.3934 dm^3 were used with rotation. For each experiment, 1.0×10^{-2} dm^3 of water was added to the bomb, and the bomb was charged to 3.04 MPa with pure oxygen without flushing. In addition, rotation of the bomb was started at the "midtime of the combustion"(40) and continued until the finish of the combustion measurements. This ensured a homogeneous solution of aqueous sulfuric acid in the bomb at the conclusion of the measurements. In the benzoic acid calibration measurements accompanying the phenoxathiin combustions, rotation was also instituted to ensure exact consistency between the measurements. Judicious choice of sample mass allowed the temperature rise in the combustion series and its corresponding calibration series to be the same within 0.1 per cent. All experiments were completed within 0.01 K of 298.15 K.

Temperatures were measured by quartz-crystal thermometry.(43,44) A computer was used to control the combustion experiments and record the results. The quartz-crystal thermometer was calibrated by comparison with a platinum resistance thermometer. Counts of the crystal oscillation were taken over periods of 100 s throughout the experiments. Integration of the time-temperature curve is inherent in the quartz-crystal thermometer readings.(45)

Ebulliometric Vapor-Pressure Measurements. The essential features of the ebulliometric equipment and procedures are described in the literature.(46,47) 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.(48)

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

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

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(49) to vapor pressures of the reference materials (decane and water) reported in reference 48.

Inclined-Piston Vapor-Pressure Measurements. The equipment for the inclined-piston vapor-pressure measurements has been described by Douslin and McCullough(50) and Douslin and Osborn.(51) Recent revisions to the equipment and procedures have been reported.(35) 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:

$$\sigma(p) = 1.5\times10^{-4}p + 0.2\ \mathrm{Pa}. \qquad (2)$$

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 with a calorimetric system described previously.(35) The calorimeter characteristics and sealing conditions are given in table 1.¶ Energy measurement procedures were the same as those described for studies on quinoline.(35) Thermometer resistances were measured with self-balancing, alternating-current 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 platinum calorimeter were

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

corrected for enthalpy changes in the empty calorimeter, for the helium exchange gas, and for vaporization of the sample. The maximum correction to the measured energy for the helium exchange gas was 0.1 per cent near 5 K. 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.(52-54)

3. RESULTS

DENSITY MEASUREMENTS

Measured densities for thianthrene and phenoxathiin in the liquid phase are listed in table 2.

COMBUSTION CALORIMETRY

NIST Standard Reference Material benzoic acid (sample 39i) was used for calibration of the combustion calorimeter; its specific energy of combustion is $-(26434.0\pm3.0)$ $J \cdot g^{-1}$ under certificate conditions. Conversion to standard states(55) gives $-(26413.7\pm3.0)$ $J \cdot g^{-1}$ for $\Delta_c U^{\circ}_m/M$, the specific energy of the idealized combustion reaction. Calibration experiments were interspersed with the phenoxathiin measurements. Nitrogen oxides were not formed in the calibration experiments due to the high purity of the oxygen used and preliminary bomb flushing. The energy equivalent of the calorimeter obtained for the calibration series, ε(calor), was (16779.4 ± 0.8) $J \cdot K^{-1}$ (mean and standard deviation of the mean). For the cotton fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta_c U^{\circ}_m/M$ was -16945 $J \cdot g^{-1}$.

In the phenoxathiin combustions, the final bomb solutions were analyzed for nitric acid, nitrous acid, and total acids.(39,40) The amount of sulfuric acid was obtained by difference. No evidence of thermally significant amounts of SO_2, or of sulfuric acid attack on the bomb was found. No nitrous acid was obtained in the combustions. Due to the relatively large amount of water used to ensure a homogeneous solution of sulfuric acid in the phenoxathiin combustions, no CO_2 analyses were made. The combustion products were checked for unburned carbon and other products of incomplete combustion, but none was detected.

Auxiliary information, necessary for reducing apparent mass to mass, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states,(55) included a density at 298.15 K of 1342 $kg \cdot m^{-3}$ for crystalline phenoxathiin. An estimated value of 5×10^{-7} $m^3 \cdot K^{-1}$ for $(\partial V_m/\partial T)_p$ was used in the reduction to standard states. Phenoxathiin was burned in the form of pellets. The density was obtained by weighing a pellet of known volume. The molar heat capacity at 298.15 K for phenoxathiin used in the corrections to standard states is given later as part of the heat-capacity study results.

A typical combustion experiment for phenoxathiin is summarized in table 3. It is impractical to list summaries for each combustion, but values of $\Delta_c U^\circ_m/M$ for all the experiments are reported in table 4. All values of $\Delta_c U^\circ_m/M$ in table 4 refer to the reaction:

$$C_{12}H_8SO(cr) + 15\ O_2(g) + 112\ H_2O(l) = 12\ CO_2(g) + H_2SO_4 \cdot 115H_2O(aq). \qquad (\mathbf{3})$$

Table 4 also gives derived values of the standard molar energy of combustion $\Delta_c U^\circ_m$, the standard molar enthalpy of combustion $\Delta_c H^\circ_m$, and the standard molar enthalpy of formation $\Delta_f H^\circ_m$ for phenoxathiin. Values of $\Delta_c U^\circ_m$ and $\Delta_c H^\circ_m$ refer to reaction (**3**). Two values of $\Delta_f H^\circ_m$ are listed which refer to the reactions:

$$12\ C(cr, graphite) + 4\ H_2(g) + 1/2\ O_2(g) + S\ (cr, rhombic) = C_{12}H_8SO(cr), \qquad (\mathbf{4})$$

and:

$$12\ C(cr, graphite) + 4\ H_2(g) + 1/2\ O_2(g) + 1/2\ S_2(g) = C_{12}H_8SO(cr). \qquad (\mathbf{5})$$

"Selected" values of $\Delta_f H^\circ_m$ for thianthrene from reference 29 are also listed in Table 4. For thianthrene the $\Delta_f H^\circ_m$ values refer to the reactions:

$$12\ C(cr, graphite) + 4\ H_2(g) + 2\ S\ (cr, rhombic) = C_{12}H_8S_2(cr), \qquad (\mathbf{6})$$

and:

$$12\ C(cr, graphite) + 4\ H_2(g) + S_2(g) = C_{12}H_8S_2(cr). \qquad (\mathbf{7})$$

Uncertainties given in table 4 are the "uncertainty interval" defined in reference 56. The enthalpies of formation of $CO_2(g)$, $H_2O(l)$, and $S_2(g)$ were taken to be $-(393.51 \pm 0.13)$ $kJ \cdot mol^{-1}$, $-(285.830 \pm 0.042)$ $kJ \cdot mol^{-1}$, and (128.50 ± 0.30) $kJ \cdot mol^{-1}$, respectively, as assigned by CODATA.(57) The values of the enthalpy of dilution of $H_2SO_4 \cdot nH_2O$ were interpolated from the table in reference 58 adjusted to the CODATA(57) assigned value for $SO_4^{2-}(aq)$. The enthalpy of formation of $H_2SO_4 \cdot 115H_2O$ was taken to be $-(887.811 \pm 0.200)$ $kJ \cdot mol^{-1}$.(58)

VAPOR-PRESSURE MEASUREMENTS

Vapor pressures for thianthrene and phenoxathiin are reported in table 5. Following previous practice,(47) 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 temperatures (column 6 table 5) indicated correct operation of the equipment and the high purity of the samples. At the highest temperature measured for thianthrene (639 K), the larger value of ΔT relative to the previous temperatures is indicative of sample decomposition.

ADIABATIC HEAT-CAPACITY CALORIMETRY

Crystallization and Melting Studies. Crystallizations of thianthrene and phenoxathiin were initiated by slowly cooling the liquid samples at rates of approximately 4.0 $\mathrm{mK \cdot s^{-1}}$ and 1.7 $\mathrm{mK \cdot s^{-1}}$, respectively. Nucleation occurred approximately 8 K below the triple-point temperature for thianthrene and 25 K below the triple-point temperature for phenoxathiin. Complete crystallization was ensured by maintaining the samples under adiabatic conditions in the partially melted state (10 per cent to 20 per cent liquid). Both samples warmed spontaneously for approximately 1 d, while under adiabatic conditions. After cessation of warming, the samples were cooled at effective rates of 4 $\mathrm{mK \cdot s^{-1}}$ (thianthrene) and 1.5 $\mathrm{mK \cdot s^{-1}}$ (phenoxathiin) to crystallize the remaining liquid. Finally, the samples were thermally cycled from approximately 280 K to within 2 K of the triple-point temperatures, where they were held for a minimum of 8 h to provide further tempering. All of the solid-phase measurements were performed upon crystals pre-treated in this manner. The extensive supercooling of the phenoxathiin sample allowed the measurement of several heat capacities for the liquid phase below the triple-point temperature.

The triple-point temperatures T_{tp} and sample purities were determined by measurement of the equilibrium melting temperatures $T(F)$ as a function of fraction F of the sample in the liquid state.(59) Equilibrium melting temperatures were determined by measuring temperatures at approximately 300-s intervals for 1 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 3 mK of the calculated equilibrium temperatures for F values listed in table 6. No evidence for the presence of solid-soluble impurities was found for either sample. Published procedures(59) were used to derive the apparent mole fraction of impurities and triple-point temperatures. The results are summarized in table 6.

Phase Transformations and Enthalpy Measurements. Experimental molar enthalpy results are summarized in table 7. The table includes both enthalpies of fusion and single-phase measurements, which serve as checks on the integration of the heat-capacity results. Corrections for pre-melting caused by impurities were made in these evaluations. Results with the same series number in tables 7 and 8 were taken without interruption of adiabatic conditions.

Excellent reproducibility (within ±0.01 per cent) was obtained in the enthalpy-of-fusion results for each compound. This implies that the crystalline phase was formed reproducibly by means of the tempering methods described above. No phase transitions in the solid state were observed for either compound. The complete heat-capacity curves are shown in figures 1 and 2.

Equilibrium was reached in less than 1 h for heat-capacity measurements in the liquid phase for both compounds. Equilibration times for thianthrene in the crystalline phase were less than 1 h for temperatures below 370 K, and increased to 2 h at 380 K, 5 h at 400 K, and 12 h at 420 K. Equilibration times for phenoxathiin in the crystalline phase were less than 1 h for temperatures below 305 K, and increased to 2 h at 315 K, and 6 h at 325 K.

The experimental molar heat capacities under vapor saturation pressure $C_{\mathrm{sat,m}}$ determined by adiabatic calorimetry are listed in table 8. Values in table 8 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 $C_{\mathrm{sat,m}}$ with temperature. The precision of the heat-capacity measurements ranged from approximately 5 per cent at 5 K, to 2 per cent at 10 K, 0.2 per cent near 20 K, and improved gradually to less than 0.1 per cent above 100 K, except in the solid phases near the triple-point temperatures where equilibration times were long. The heat capacities for the crystalline phases in table 8 have not been corrected for pre-melting. Pre-melting corrections(59) can be calculated with the temperature increments provided. Extrapolation of the heat-capacity results to $T \rightarrow 0$ for each compound was made by linear extrapolation of a plot of $C_{\mathrm{sat,m}}/T$ against T^2 for results below 10 K.

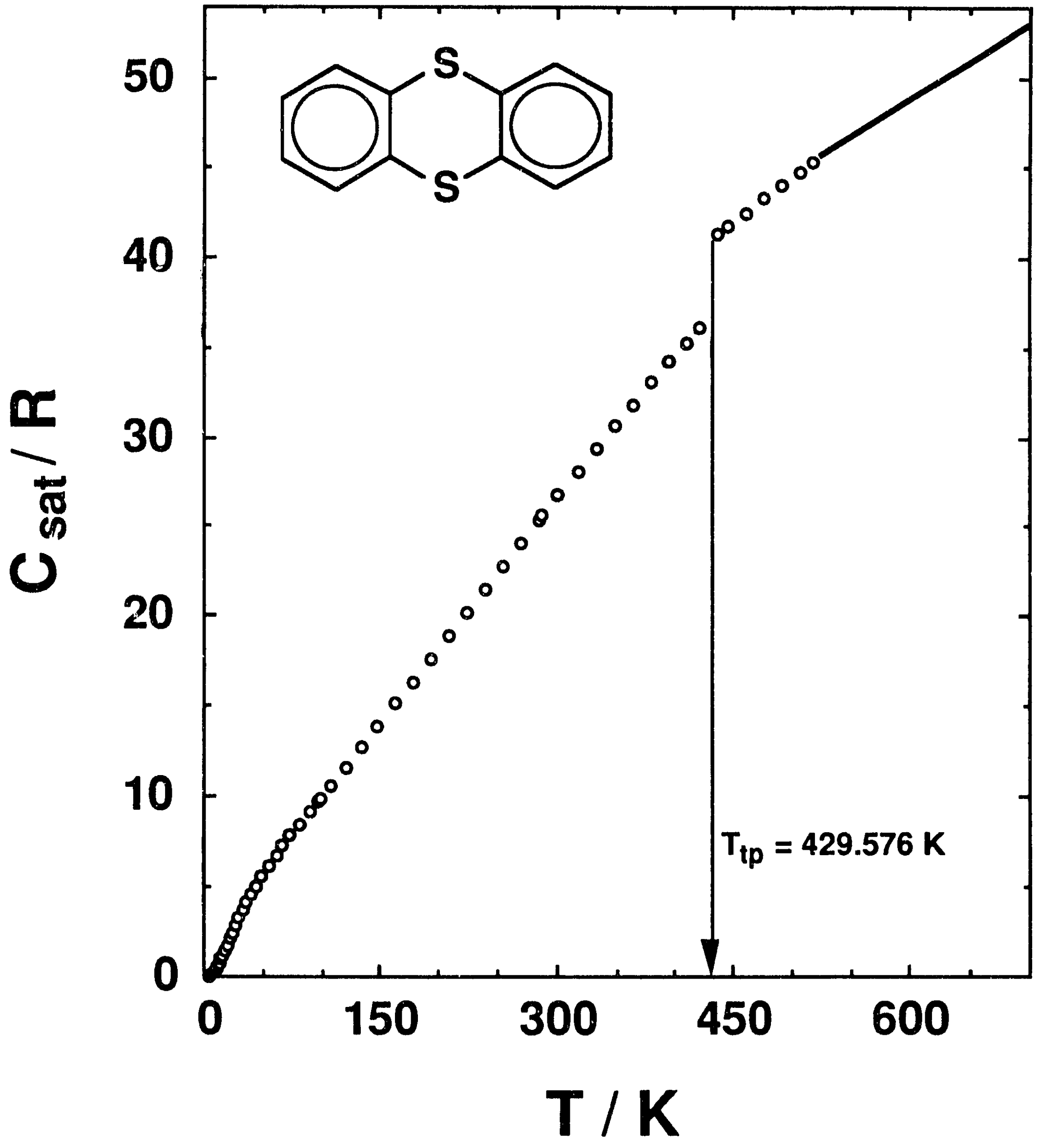

FIGURE 1. Curve of heat capacity against temperature for thianthrene. The vertical line indicates the triple-point temperature. Results above 520 K were obtained by differential-scanning calorimetry and the fitting procedures described in the text.

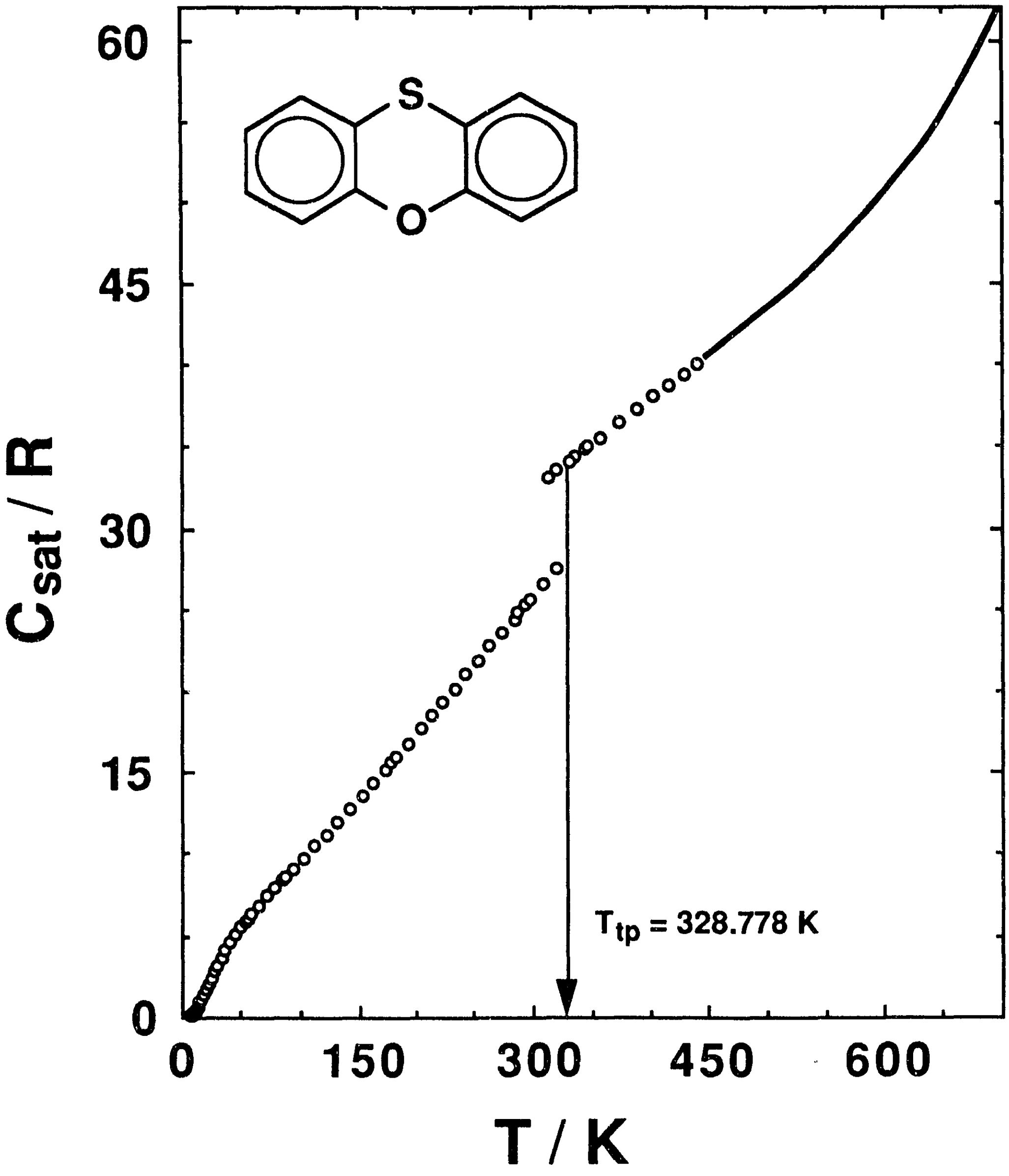

FIGURE 2. Curve of heat capacity against temperature for phenoxathiin. The vertical line indicates the triple-point temperature. Results above 445 K were obtained by differential-scanning calorimetry and the fitting procedures described in the text.

DIFFERENTIAL-SCANNING CALORIMETRY

Theoretical Background. The theoretical background for the determination of heat capacities for the liquid phase at vapor-saturation pressure $C_{\mathrm{sat,m}}$ with results obtained with a d.s.c. has been described.(53,60) 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 9 lists the experimental two-phase heat capacities $C_{x,m}^{II}$ for thianthrene and phenoxathiin obtained for three cell fillings for each compound. Heat capacities were determined at 20-K intervals with a heating rate of 0.083 $\mathrm{K{\cdot}s^{-1}}$ and a 120-s equilibration period between heats. Sample decomposition precluded heat-capacity measurements above 665 K for both materials.

For other compounds, e.g., dibenzothiophene(10) and 2-aminobiphenyl,(61) a rapid heating method was used for critical temperature and critical density determinations. By employing a single continuous heat at a rate of 0.333 $\mathrm{K{\cdot}s^{-1}}$, sample decomposition was greatly reduced, and the abrupt decrease in heat capacity associated with the conversion from two phases to one phase was observed. However, this method failed in the present research as there was extensive sample decomposition above the range of the heat-capacity measurements.

SIMULTANEOUS FITS TO VAPOR PRESSURES AND TWO-PHASE HEAT CAPACITIES

A simultaneous non-linear least-squares fit to the vapor pressures listed in table 5 and the $C_{x,m}^{II}$ values given in table 9 was completed. The fitting procedure has been described.(53,60)

The Wagner equation,(62) as formulated by Ambrose,(63) was used to represent the vapor pressures:

$$\ln(p/p_c) = (1/T_r)[A(1-T_r) + B(1-T_r)^{1.5} + C(1-T_r)^{2.5} + D(1-T_r)^5], \qquad (8)$$

where $T_r = T/T_c$. Experimental $C_{x,m}^{II}$ values were converted to $C_{V,m}^{II}$ by means of equation (9) with the equation for the cell expansion(60) and the vapor-pressure fit for $(\partial p/\partial T)_{\mathrm{sat}}$.

$$C_{V,m}^{II} = C_{x,m}^{II} - T/n\,\{(\partial V_x/\partial T)_x\,(\partial p/\partial T)_{\mathrm{sat}}\}. \qquad (9)$$

The values of $C^{II}_{V,m}$ were used to derive functions for $(\partial^2 p/\partial T^2)_{sat}$ and $(\partial^2\mu/\partial T^2)_{sat}$, as described previously.(60) The functional form chosen for variation of the second derivative of the chemical potential with temperature was:

$$(\partial^2\mu/\partial T^2)_{sat} / (\mathrm{J{\cdot}K^{-2}{\cdot}mol^{-1}}) = \sum_{i=0}^{n} b_i(1 - T/T_c)^i. \qquad (10)$$

{For compounds where sufficient information was available to evaluate reliably $(\partial^2\mu/\partial T^2)_{sat}$ [e.g., benzene(64), toluene(65)], four terms (i.e., expansion to n=3) were required to represent the function. Three terms were used in this research.}

Estimation of Critical Temperatures. The fits were repeated for a range of fixed T_c values with the critical pressure included as a variable. The T_c values listed in table 10 for thianthrene and phenoxathiin were selected to optimize agreement between the measured densities listed in table 2 and values calculated with the extended corresponding-states equation of Riedel,(66) as formulated by Hales and Townsend:(38)

$$(\rho/\rho_c) = 1.0 + 0.85\{1.0 - (T/T_c)\} + (1.692 + 0.986\omega)\{1.0 - (T/T_c)\}^{1/3}. \qquad (11)$$

The acentric factor, ω, is defined as $\{-\lg(p/p_c)-1\}$, where p is the vapor pressure at $T_r = 0.7$ and p_c is the critical pressure. The Wagner-equation parameters given in table 10 were used to calculate p. Agreement between the measured and calculated values of the density is indicated by a near-zero slope on a plot of their fractional differences with temperature. The critical density ρ_c was subsequently adjusted to minimize absolute differences. Figures 3 and 4 are plots of fractional differences against temperature for each compound for several values of T_c. The uncertainty in the selected critical temperature for each compound was estimated to be ±10 K based on figures 3 and 4. All of the measured densities (except the value at 548 K for phenoxathiin) are within 0.1 per cent of values calculated with equation (**11**) and the selected critical properties, as shown in table 2 and figures 3 and 4. Temperature fluctuations in the temperature-controlled bath at 548 K precluded accurate density measurements at this temperature.

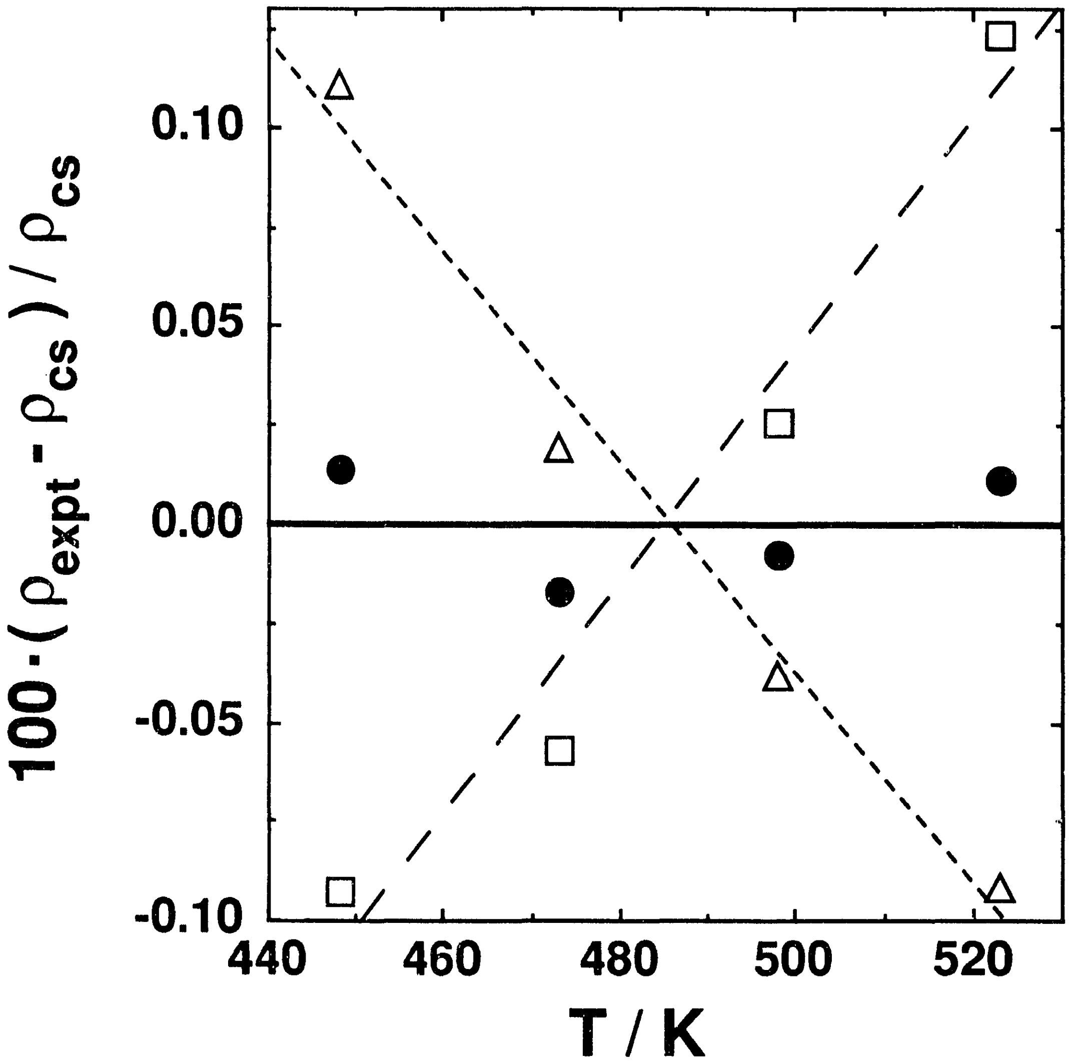

FIGURE 3. Deviation of measured densities ρ_{expt} for thianthrene from values calculated with corresponding states ρ_{cs} {equation (11)} for several values of the critical temperature T_c. ●, T_c = 920 K; △, T_c = 940 K; □, T_c = 900 K. The short dashes represent a straight-line fit to the results for T_c = 940 K; long dasnes, T_c = 900 K; and uninterrupted line, T_c = 920 K. The estimated uncertainties in the measured densities are 0.1 per cent.

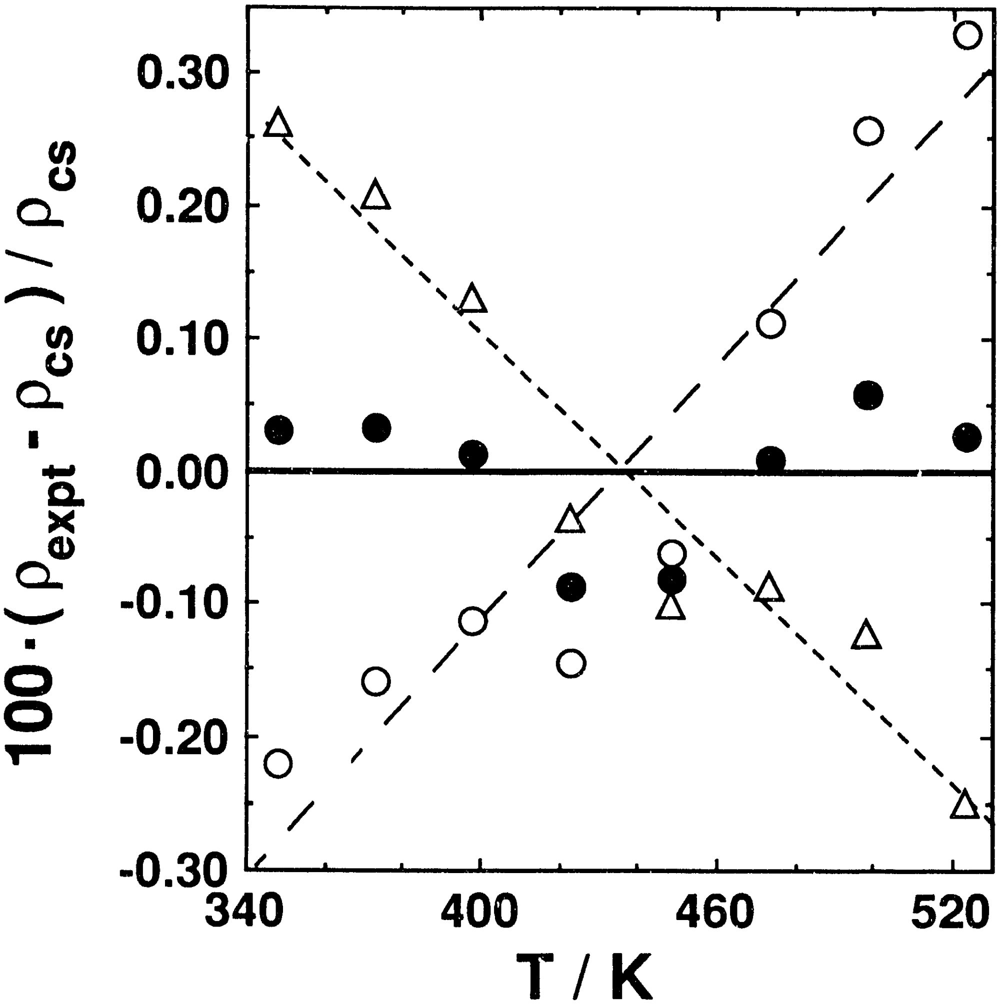

FIGURE 4. Deviation of measured densities ρ_{expt} for phenoxathiin from values calculated with corresponding states ρ_{cs} {equation (**11**)} for several values of the critical temperature T_c. ●, T_c = 863 K; △, T_c = 883 K; ○, T_c = 843 K. The short dashes represent a straight-line fit to the results for T_c = 883 K; long dashes, T_c = 843 K; and uninterrupted line, T_c = 863 K. The estimated uncertainties in the measured densities are 0.1 per cent.

Table 10 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 5. Values of $C_{\mathrm{sat,m}}$ for thianthrene and phenoxathiin were derived from $C^{\mathrm{II}}_{\mathrm{V,m}}(\rho=\rho_{\mathrm{sat}})$ values and densities obtained with equation (**11**), as described previously.(60) The results for $C_{\mathrm{sat,m}}/R$ are reported in table 11. The estimated uncertainty in these values is 1 per cent. Differences between $C^{\mathrm{II}}_{\mathrm{V,m}}(\rho=\rho_{\mathrm{sat}})/R$ and $C_{\mathrm{sat,m}}/R$ are not significant in the temperature range of the measurements reported here. Differences in these quantities can be large as the critical temperature is approached.(41)

Derived Enthalpies of Vaporization. Enthalpies of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ were derived from the Wagner-equation fits by means of the Clapeyron equation:

$$\mathrm{d}p/\mathrm{d}T = \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}} \,/\, (T\,\Delta_{\mathrm{l}}^{\mathrm{g}}V_{\mathrm{m}})\,. \qquad (\mathbf{12})$$

$\Delta_{\mathrm{l}}^{\mathrm{g}}V_{\mathrm{m}}$ 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 (**11**) and the critical constants listed in table 10. The uncertainty in the liquid-phase volumes was estimated to be 1 per cent. The Wagner-equation parameters given in table 10 were used to calculate p.

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,(67) and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera.(68) This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene, toluene, and decane.(69) 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 12. For p>1 bar the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived enthalpies of vaporization. The effect of the ±10 K uncertainty in the critical temperatures was included in the uncertainty calculations. The effect is negligible below 500 K, but increases to approximately 45 per cent of the total uncertainty in the enthalpy of vaporization near 700 K.

THERMODYNAMIC PROPERTIES IN THE CONDENSED STATE

Entropies and enthalpies under vapor saturation pressure relative to that of the crystals at $T \rightarrow 0$ for the solid and liquid phases of thianthrene and phenoxathiin are listed in table 13. The tabulated values were derived by integration of the smoothed heat capacities corrected for pre-melting, together with the entropies and enthalpies of fusion. 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 8 and 11 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. Pre-melting corrections were made by means of standard methods(59) for solid-insoluble impurities and the mole-fraction impurities values shown in table 1.

THERMODYNAMIC PROPERTIES IN THE IDEAL-GAS STATE

Enthalpies and entropies at selected temperatures for the ideal gas were calculated using values in tables 12 and 13 and are listed in columns 2 and 4 of table 14. Entropies and enthalpies of compression to 101.325 kPa were calculated based on the virial equation truncated after the third virial coefficient:

$$pV_m = RT + Bp + C'p^2 . \qquad (13)$$

Formulations used to calculate the entropy and enthalpy of compression, which include the "gas-imperfection corrections," are available in the literature.(70,36) Required temperature derivatives of virial coefficients were calculated by numerical differentiation of values estimated by the methods of Pitzer and Curl(67) and Orbey and Vera.(68) The gas-imperfection corrections are listed in table 14. Uncertainties in these 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 thianthrene and phenoxathiin were combined with the condensed-phase enthalpies of formation given in table 4 to calculate the enthalpies, entropies, and Gibbs energies of formation listed in columns 6, 7, and 8, respectively, of table 14.

Enthalpies and entropies for $O_2(g)$, $S_2(g)$, and equilibrium hydrogen were determined from JANAF tables.(71) Values for graphite were determined with the polynomial(72) used to calculate the values from 298.15 K to 6000 K listed in the JANAF tables. All uncertainties in table 14 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 thianthrene from 350 K to the triple-point temperature. The "third-law" values were calculated from the tabulated thermodynamic functions of the ideal gas (table 14) and the crystalline solid (table 13). The method applied here was the same as that used previously for biphenyl.(60) The sublimation vapor pressures for thianthrene were represented by the equation:

$$\ln(p/p^{\circ})=29.3663-7641.7(T/K)^{-1}-1.5411\times10^{6}(T/K)^{-2}+1.6388\times10^{8}(T/K)^{-3}, \quad \textbf{(14)}$$

in the temperature region 350 K to 429.576 K with $p^{\circ} = 1$ Pa.

4. DISCUSSION

THIANTHRENE

THE ENERGY OF COMBUSTION AND ENTHALPY OF FORMATION

Literature values(23-28,30) for the energy of combustion of thianthrene are in excellent accord. Hence, thianthrene is an excellent candidate for use as a secondary standard for the combustion calorimetry of sulfur-containing organic compounds. The U.S. Bureau of Mines sample USBM-P2a was prepared as such a standard, and continues to be available on request to the NIPER Thermodynamics Group.

Pedley et al.(29) reviewed the literature on the energy of combustion of thianthrene. Their "assessed" value was adopted in this research, and was used to derive the enthalpies of formation listed in table 4. Since that assessment, Sabbah and El Watik(30) published the results of another study of the energy of combustion of thianthrene. Their results do not change the "assessed" value mainly because of the relatively large uncertainty on their measured energy of combustion.

COMPARISON OF MEASURED AND CALCULATED SUBLIMATION PRESSURES

Sublimation pressures for thianthrene were obtained as part of the inclined-piston vapor-pressure measurements. The measured values are reported in table 5 and are marked by footnotes. Table 15 lists the measured sublimation pressures, liquid vapor pressures calculated with the Wagner equation parameters listed in table 10, and sublimation pressures calculated by means of the "third law" method {equation (**14**)}.

The differences between the measured and calculated sublimation pressures (column 5 of table 15) are slightly outside the expected uncertainty (0.2 Pa) for the inclined-piston measurements. The deviation probably arises from incomplete outgassing of the system during the inclined-piston measurements. This illustrates the difficulty in making low-pressure measurements in a static system, even when special outgassing techniques are used.

Two studies of the sublimation vapor pressure of thianthrene were found in the literature. Figure 5 is a deviation plot for sublimation pressures reported by Edwards and Prausnitz(73) for temperatures between 358.05 K (0.8 Pa) and 426.65 K (149.3 Pa). Deviations are plotted as both absolute and per centage differences. Except for the sublimation pressure at 426.65 K, which is 15 Pa lower than that of this research, the agreement is well within the combined uncertainties of the two methods.

Sublimation pressures reported graphically by Sandman et al.(74) are approximately a factor of 10 larger than those of this research. However, the enthalpy of sublimation reported by Sandman et al. (97.5±6.3) $kJ \cdot mol^{-1}$ is in accord with the value calculated in this research (103.6±0.4) $kJ \cdot mol^{-1}$ for 350 K, the mid-temperature of the measurements by Sandman et al.(74)

Sabbah and El Watik(30) in the same paper as their energy of combustion study reported an enthalpy of sublimation for thianthrene of (98.59±0.54) $kJ \cdot mol^{-1}$ at 353 K. This value is 5 $kJ \cdot mol^{-1}$ lower than that determined here. The deviation is ten times larger than the uncertainty claimed by Sabbah and El Watik. The source of the discrepancy is not apparent.

COMPARISON OF RESULTS WITH LITERATURE LIQUID-PHASE VAPOR PRESSURES

Liquid-phase vapor-pressure measurements for thianthrene have been reported by Edwards and Prausnitz(73) and by Sivaraman and Kobayashi.(75) Figure 6 is a deviation plot for the measurements above the triple-point temperature relative to those of this research. Relative to values calculated with the fitted Wagner parameters (table 10), values listed by Edwards and Prausnitz(73) range from 1 per cent high to 5 per cent low, which is in accord with their claimed accuracy.

Sivaraman and Kobayashi(75) reported vapor pressures and derived enthalpies of vaporization for thianthrene for the temperature range 431 K to 593 K. Their results range from 8 per cent low to 6 per cent high relative to the values of this research.

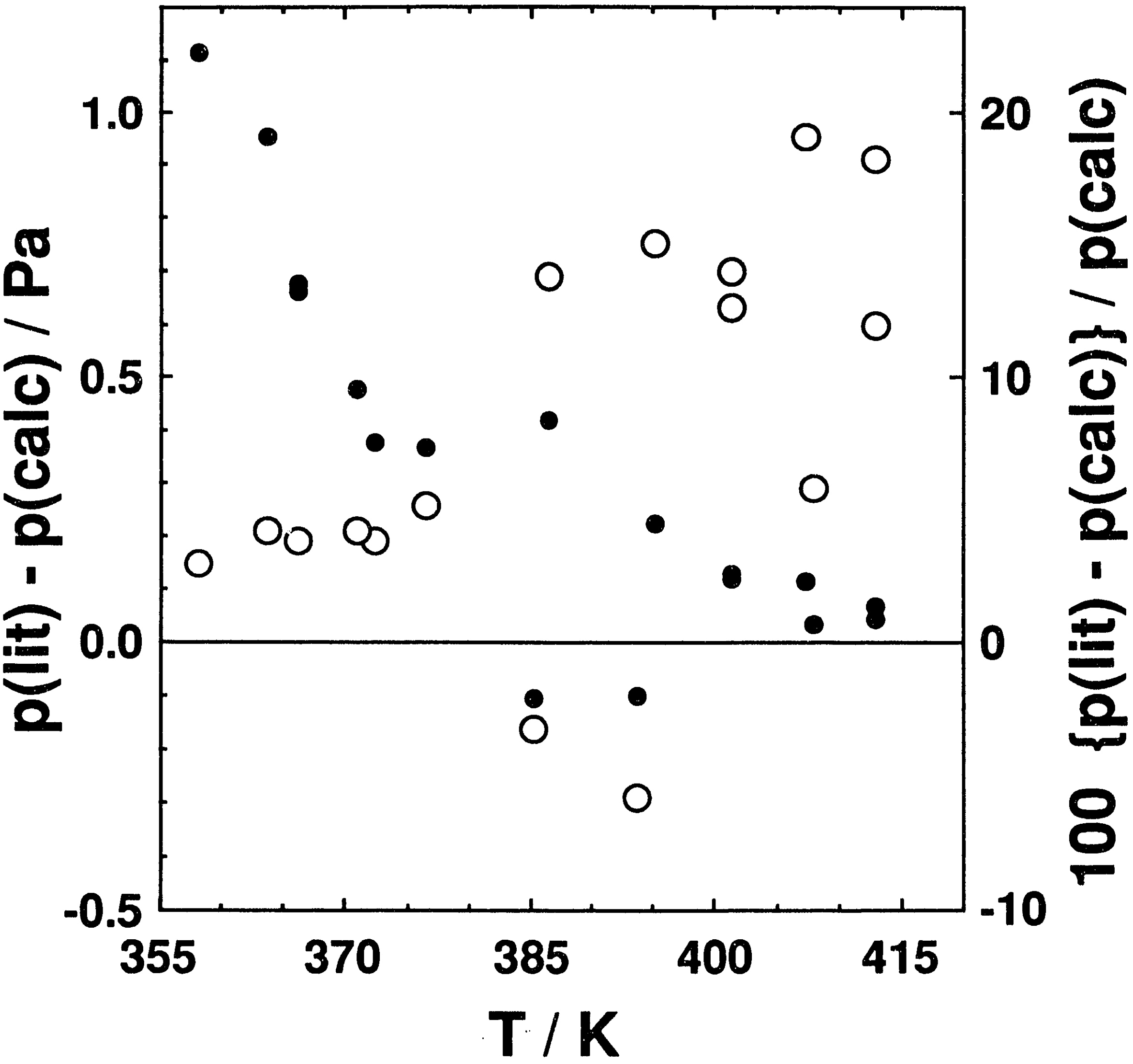

FIGURE 5. Deviation plot for sublimation pressures for thianthrene measured by Edwards and Prausnitz(73) relative to those of this research. ○, Absolute deviation (left axis); ●, per centage deviation (right axis).

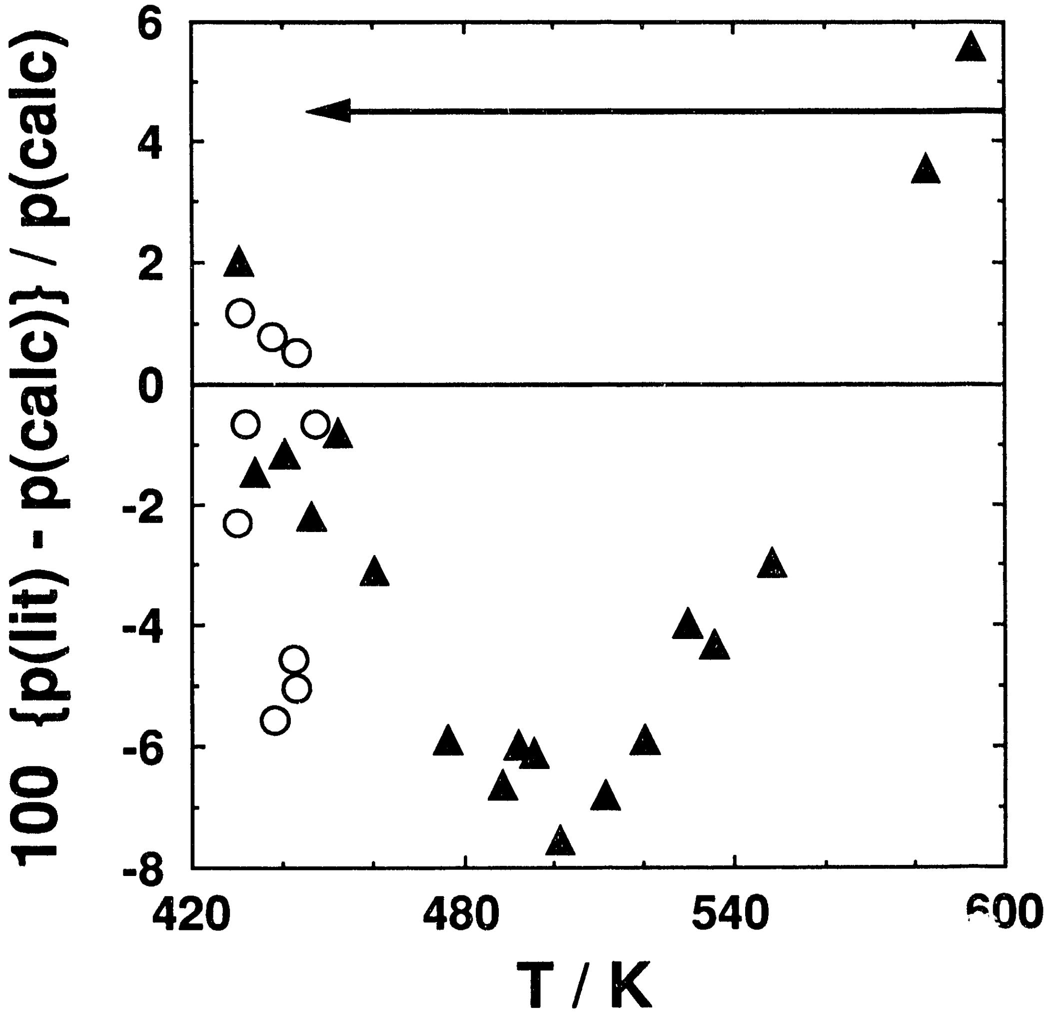

FIGURE 6. Deviation plot for literature vapor pressures of thianthrene relative to those of this research. The arrow indicates the range of the experimental measurements of this research, as listed in table 5. ○, Edwards and Prausnitz; (73) ▲, Sivaraman and Kobayashi.(75)

Similar large deviations were reported previously for vapor pressures of acridine,(76) which were published by Sivaraman and Kobayashi(75) with their results for thianthrene. Furthermore, the enthalpies of vaporization calculated by Sivaraman and Kobayashi show a local minimum near 500 K. This unprecedented behavior is not confirmed in our research.

PHENOXATHIIN

The property measurements reported here for phenoxathiin are the first for this material. A search of the literature (Chemical Abstracts; 1907 through 1991) failed to locate any previous thermodynamic-property measurements.

5. SUMMARY and HIGHLIGHTS

- Thermochemical and thermophysical properties for thianthrene and phenoxathiin are reported. Properties measured included vapor pressures, heat capacities, and densities over a range of temperatures, and the energy of combustion.

- Ideal-gas thermodynamic properties for thianthrene and phenoxathiin were calculated based on the accurate calorimetric measurements.

- Gibbs energies of formation were derived for thianthrene and phenoxathiin for use in equilibria calculations. These are the first such values reported for three-ring diheteroatom-containing compounds.

- The first results of measurements on heteroatom-containing aromatics with a new high-temperature densitometer were reported.

- The new density measurements were shown to provide key information for the accurate estimation of critical properties for materials, which decompose far below their critical temperatures. Critical temperatures for thianthrene and phenoxathiin were estimated to be 920 K and 863 K, respectively, with an uncertainty of only ±10 K, even though the compounds decomposed approximately 200 K lower.

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TABLE 1. Calorimeter and sample characteristics for adiabatic heat-capacity calorimetry studies: 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; x_{pre} is the mole-fraction impurity used for pre-melting corrections

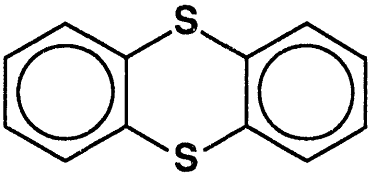
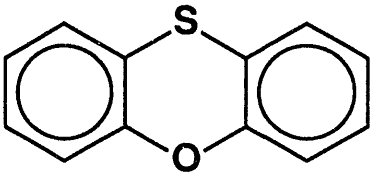
	Thianthrene	Phenoxathiin
		
m/g	47.792	61.975
$V_i(298.15\ \mathrm{K})/\mathrm{cm}^3$	61.0	62.47
T_{cal}/K	297.2	299.0
p_{cal}/kPa	4.35	5.92
$r(T_{max})$	2.9	3.5
r_{min}	1.6	1.7
$10^2 \cdot (\delta C/C)_{max}$	0.035	0.008
x_{pre}	0.00003	0.0

TABLE 2. Measured densities at saturation pressure [a]

T/K	$\rho/(\mathrm{kg \cdot m^{-3}})$	$100 \cdot (\rho - \rho_{cs})/\rho$	T/K	$\rho/(\mathrm{kg \cdot m^{-3}})$	$100 \cdot (\rho - \rho_{cs})/\rho$
	Thianthrene			Phenoxathiin	
448.150	1169.0	0.03	348.150	1206.9	0.02
473.150	1148.6	−0.01	373.149	1187.1	0.02
498.150	1128.2	0.00	398.148	1166.8	−0.01
523.150	1107.5	0.02	423.150	1145.0	−0.10
548.150 [b]	1085.1	−0.07	448.150	1124.1	−0.09
			473.151	1103.6	0.00
			498.151	1082.0	0.05
			523.150	1059.0	0.02
			548.150 [b]	1032.7	−0.26

[a] ρ_{cs} = density calculated using extended corresponding states. {See equation (11) and text.}

[b] The value at this temperature was not included in the fit. See text.

TABLE 3. Typical combustion experiment at 298.15 K [a] (p° = 101.325 kPa)

	Phenoxathiin
m'(compound)/g	1.037187
m'''(fuse)/g	0.001585
$n_i(H_2O)$/mol	0.52425
m(Pt)/g	19.692
$\Delta T/K = (T_i - T_f + \Delta T_{corr})/K$	2.00225
ε(calor)(ΔT)/J	−33596.6
ε(cont)(ΔT)/J [b]	−111.5
ΔU_{ign}/J	0.8
$\Delta U_{dec}(HNO_3)$/J	23.3
$\Delta U_{dil}(H_2SO_4)$/J	−0.3
ΔU(corr. to std. states)/J [c]	32.8
$-m'''(\Delta_c U^o_m/M)$(fuse)/J	26.9
$m'(\Delta_c U^o_m/M)$(compound)/J	−33624.6
$(\Delta_c U^o_m/M)$(compound)/J·g^{-1}	−32419.1

---

[a] The symbols and abbreviations of this Table are those of reference 55 except as noted.

[b] $\varepsilon_i(\text{cont})(T_i - 298.15\text{ K}) + \varepsilon_f(\text{cont})(298.15\text{ K} - T_f + \Delta T_{corr})$

[c] Items 81 to 85, 87 to 90, 93, and 94 of the computational form of reference 55.

TABLE 4. Summary of experimental energy of combustion results and molar thermodynamic functions. $T = 298.15$ K, and $p^{\circ} = 101.325$ kPa

Phenoxathiin

$\{(\Delta_c U^{\circ}_m/M)(\text{Phenoxathiin})\}/(\text{J}\cdot\text{g}^{-1})$			
−32419.1	−32417.2	−32415.1	−32407.9
−32427.1	−32414.3	−32404.1	−32409.2

$<\{(\Delta_c U^{\circ}_m/M)(\text{Phenoxathiin})\}/(\text{J}\cdot\text{g}^{-1})>$	-32414.3 ± 2.6 [a]
$(\Delta_c U^{\circ}_m)(\text{Phenoxathiin})/(\text{kJ}\cdot\text{mol}^{-1})$	-6491.25 ± 1.42 [a]
$(\Delta_c H^{\circ}_m)(\text{Phenoxathiin})/(\text{kJ}\cdot\text{mol}^{-1})$	-6498.69 ± 1.41 [a]
$(\Delta_f H^{\circ}_m)(\text{Phenoxathiin})/(\text{kJ}\cdot\text{mol}^{-1})$	31.27 ± 1.74 [b]
$(\Delta_f H^{\circ}_m)(\text{Phenoxathiin})/(\text{kJ}\cdot\text{mol}^{-1})$	-32.98 ± 1.84 [c]

Thianthrene

$(\Delta_f H^{\circ}_m)(\text{Thianthrene})/(\text{kJ}\cdot\text{mol}^{-1})$	182.0 ± 1.8 [d,e]
$(\Delta_f H^{\circ}_m)(\text{Thianthrene})/(\text{kJ}\cdot\text{mol}^{-1})$	53.5 ± 2.0 [d,f]

---

[a] Value for the following reaction (see text):
$C_{12}H_8SO(cr) + 15O_2(g) + 112H_2O(l) = 12CO_2(g) + H_2SO_4\cdot 115H_2O$.

[b] Value for the following reaction (see text):
$12C(\text{cr, graphite}) + 4H_2(g) + 1/2O_2(g) + S(\text{cr, rhombic}) = C_{12}H_8SO(cr)$.

[c] Value for the following reaction (see text):
$12C(\text{cr, graphite}) + 4H_2(g) + 1/2O_2(g) + 1/2S_2(g) = C_{12}H_8SO(cr)$.

[d] "Selected" value from reference 29 (see text).

[e] Value for the following reaction (see text):
$12C(\text{cr, graphite}) + 4H_2(g) + 2S(\text{cr, rhombic}) = C_{12}H_8S_2(cr)$.

[f] Value for the following reaction (see text):
$12C(\text{cr, graphite}) + 4H_2(g) + S_2(g) = C_{12}H_8S_2(cr)$.

TABLE 5. 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; σ(p) is the propagated error calculated from equations (**1**) and (**2**); ΔT is the difference between the boiling and condensation temperatures $(T_{boil}-T_{cond})$ for the sample in the ebulliometer

Method	T/K	p/kPa	Δp/kPa	$\sigma(p)$/kPa	ΔT/K
Thianthrene					
IP	395.000 [a,b]	0.0172	-0.0147	0.0002	
IP	410.001 [a,b]	0.0522	-0.0217	0.0002	
IP	420.002 [a,b]	0.1049	-0.0193	0.0002	
IP	425.008 [a,b]	0.1474	-0.0120	0.0002	
IP	444.998	0.4041	0.0004	0.0003	
IP	455.002	0.6198	0.0005	0.0003	
IP	465.009	0.9303	0.0007	0.0003	
IP	475.009	1.3668	0.0006	0.0004	
IP	485.005	1.9698	0.0005	0.0005	
decane	485.442	2.0000	-0.0002	0.0001	0.041
IP	495.009	2.7894	0.0006	0.0006	
decane	505.927	3.9999	0.0000	0.0002	0.031
decane	515.070	5.3330	-0.0004	0.0003	0.030
decane	528.663	7.9989	0.0001	0.0004	0.026
decane	538.862	10.666	0.000	0.001	0.024
decane	547.107	13.332	0.001	0.001	0.023
decane	555.674	16.665	0.000	0.001	0.023
decane	562.787	19.933	0.000	0.001	0.019
decane	572.150	25.023	0.001	0.001	0.016
water	572.149 [b]	25.023	0.002	0.001	0.017

TABLE 5. Continued

Method	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma(p)}{kPa}$	$\frac{\Delta T}{K}$
		Thianthrene (continued)			
water	581.573	31.177	0.002	0.002	0.016
water	591.057	38.565	−0.001	0.002	0.015
water	600.599	47.375	−0.004	0.002	0.015
water	610.199	57.817	−0.008	0.003	0.014
water	619.850	70.120	−0.003	0.003	0.018
water	629.554	84.533	0.011	0.004	0.023
water	639.256 [b]	101.325	0.135	0.004	0.062
		Phenoxathiin			
IP	365.000	0.0216	0.0001	0.0002	
IP	375.004	0.0402	0.0000	0.0002	
IP	385.002	0.0721	0.0000	0.0002	
IP	394.998	0.1250	0.0001	0.0002	
IP	405.002	0.2096	0.0001	0.0002	
IP	415.000	0.3412	0.0002	0.0003	
IP	425.002	0.5402	0.0000	0.0003	
IP	434.999	0.8343	0.0001	0.0003	
IP	445.001	1.2584	−0.0001	0.0004	
IP	455.001	1.8577	0.0001	0.0005	
decane	456.957	2.0000	0.0001	0.0001	0.090
IP	460.004	2.2400	0.0001	0.0005	
decane	464.784	2.6660	−0.0002	0.0002	0.076
IP	465.006	2.6878	0.0001	0.0006	
IP	470.001	3.2092	0.0002	0.0007	
decane	485.068	5.3330	−0.0004	0.0003	0.036
decane	497.963	7.9989	0.0003	0.0004	0.025
decane	507.641	10.666	0.000	0.001	0.021
decane	515.465	13.332	0.000	0.001	0.018
decane	523.592	16.665	0.001	0.001	0.016
decane	530.343	19.933	0.001	0.001	0.016

TABLE 5. Continued

Method	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma(p)}{kPa}$	$\frac{\Delta T}{K}$
Phenoxathiin (continued)					
decane	539.232	25.023	0.000	0.001	0.013
water	539.227 [b]	25.023	0.003	0.001	0.013
water	548.176	31.177	0.000	0.002	0.012
water	557.178	38.565	−0.001	0.002	0.011
water	566.237	47.375	−0.003	0.002	0.010
water	575.351	57.817	−0.003	0.003	0.012
water	584.523	70.120	−0.003	0.003	0.012
water	593.749	84.533	0.002	0.004	0.013
water	603.034	101.325	0.002	0.004	0.013
water	612.375	120.79	0.00	0.01	0.012
water	621.775	143.25	0.00	0.01	0.013
water	631.225	169.02	0.00	0.01	0.011
water	640.736	198.49	−0.01	0.01	0.009

[a] Phase cr(I).

[b] The value at this temperature was not included in the fit.

TABLE 6. Melting-study summaries: F is the fraction melted at observed temperature $T(F)$; T_{tp} is the triple-point temperature; x is the mole-fraction impurity

F	T(F)/K	F	T(F)/K
Thianthrene		Phenoxathiin	
0.1500	429.5655	0.1518	328.7380
0.2998	429.5710	0.3029	328.7580
0.4497	429.5725	0.4540	328.7645
0.5995	429.5735	0.6051	328.7675
0.7992	429.5740	0.8066	328.7700
T_{tp} = 429.576 K x = 0.00003		T_{tp} = 328.778 K x = 0.00013	

TABLE 7. Molar enthalpy measurements ($R=8.31451$ $J{\cdot}K^{-1}{\cdot}mol^{-1}$)

N[a]	h[b]	T_i/K	T_f/K	T_{trs}/K	$\Delta_{tot}U_m/R{\cdot}K$[c]	$\Delta_{trs}H_m/R{\cdot}K$[d]
Thianthrene						
single-phase measurements in cr						
13	1	290.634	404.937		3485.3	1.4
17	1	87.109	214.841		1811.9	0.0
17	1	214.801	304.802		2093.4	−0.3
18	1	300.749	424.881		3930.5	1.8
cr to liquid						
12	2	426.482	431.777	429.576	3517.5	3314.2
18	3	424.784	432.410		3605.0	3314.0
					Average:	3314.1
Phenoxathiin						
single-phase measurements in cr						
2	1	286.325	324.756		1012.8	0.1
4	1	184.168	215.874		551.4	−0.2
8	1	49.986	155.444		1032.5	0.1
8	1	155.463	265.739		2017.9	−0.7
8	1	265.729	319.965		1369.2	−0.7
cr to liquid						
1	2	324.524	332.029	328.778	2668.8	2437.7
2	6	324.771	331.835		2654.8	2437.3
8	2	319.856	331.503		2780.5	2437.5
					Average:	2437.5
liquid						
10	1	338.193	402.801		2345.1	0.0
10	1	402.756	442.959		1571.3	−0.4

[a] Adiabatic series number.

[b] Number of heating increments.

[c] $\Delta_{tot}U_m$ is the molar energy input from the initial temperature T_i to the final temperature T_f.

[d] $\Delta_{trs}H_m$ is the net molar enthalpy of transition at the transition temperature T_{trs} or the excess enthalpy relative to the heat-capacity curve described in the text for single-phase measurements.

TABLE 8. Molar heat capacities at vapor-saturation pressure ($R = 8.31451\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)

N^a	$\langle T\rangle/\mathrm{K}$	$\Delta T/\mathrm{K}$	$C_{\mathrm{sat,m}}{}^b/R$	N^a	$\langle T\rangle/\mathrm{K}$	$\Delta T/\mathrm{K}$	$C_{\mathrm{sat,m}}{}^b/R$
Thianthrene							
cr							
16	5.122	1.1710	0.055	15	89.079	8.4716	9.136
16	6.222	0.8789	0.093	14	96.252	9.4773	9.722
16	7.168	0.9346	0.148	15	97.860	8.9795	9.853
16	8.154	1.0104	0.220	14	107.047	12.0840	10.599
16	9.184	1.0661	0.310	15	107.351	9.8971	10.626
16	10.267	1.1220	0.427	14	119.999	13.8061	11.649
16	11.467	1.2685	0.565	14	133.819	13.8004	12.769
16	12.774	1.3463	0.751	14	148.067	14.6401	13.927
16	14.190	1.4761	0.953	14	162.775	14.7583	15.129
16	15.737	1.6139	1.190	14	177.628	14.9179	16.352
16	17.419	1.7634	1.451	14	192.641	15.1097	17.604
16	19.278	1.9633	1.751	14	207.851	15.3199	18.871
16	21.355	2.2039	2.083	14	223.129	15.4287	20.174
16	23.652	2.3871	2.445	14	238.292	15.4129	21.448
16	26.182	2.6826	2.830	14	253.678	15.4115	22.753
16	29.039	3.0274	3.242	14	268.961	15.3965	24.043
16	32.214	3.2987	3.673	14	284.318	15.4006	25.334
16	35.761	3.7861	4.126	12	287.139	12.9319	25.575
16	39.727	4.1434	4.596	12	301.674	16.1267	26.771
16	44.133	4.6689	5.081	12	317.768	16.0625	28.108
16	49.082	5.2302	5.600	12	333.629	15.6704	29.395
16	54.585	5.7753	6.139	12	349.205	15.6608	30.639
15	55.107	5.1003	6.189	12	364.673	15.3239	31.863
15	60.529	5.6554	6.700	12	380.137	15.3502	33.050
15	66.587	6.3151	7.241	12	395.776	15.3845	34.232
15	73.321	6.9745	7.825	12	410.242	13.1008	35.317
15	80.882	7.8046	8.458	12	421.672	9.3292	36.253
liquid							
12	435.712	7.8283	41.188	11	490.473	18.4606	43.929
18	437.389	9.9797	41.280	10	490.883	15.3786	43.953
12	445.713	12.1579	41.702	10	506.156	15.2378	44.697
10	446.128	12.4060	41.727	11	506.788	14.2183	44.721
10	460.150	15.6795	42.433	10	518.278	9.0816	45.256
10	475.730	15.5222	43.217	11	518.415	9.0806	45.265

TABLE 8. Continued

N[a]	$\langle T \rangle$ / K	ΔT / K	$C_{\mathrm{sat,m}}$ / R [b]	N[a]	$\langle T \rangle$ / K	ΔT / K	$C_{\mathrm{sat,m}}$ / R [b]
			Phenoxathiin cr				
6	6.364	0.8280	0.087	3	85.273	7.0663	8.508
6	7.301	0.9275	0.135	5	86.041	8.3554	8.564
6	8.265	0.9887	0.200	3	93.222	8.7070	9.098
6	9.293	1.0347	0.288	3	102.328	9.3838	9.773
6	10.346	1.0724	0.396	3	111.906	9.6196	10.482
6	11.488	1.2058	0.526	3	121.765	9.9965	11.216
6	12.745	1.3088	0.692	3	131.775	9.9220	11.974
7	13.946	1.4510	0.864	3	142.248	9.9719	12.772
6	14.134	1.4643	0.892	3	152.315	10.0613	13.551
7	15.486	1.6317	1.100	3	162.425	10.0853	14.347
6	15.674	1.6142	1.129	3	172.519	10.0223	15.152
7	17.219	1.8321	1.377	4	178.785	10.7436	15.649
7	19.147	2.0223	1.693	3	182.662	10.1744	15.966
7	21.263	2.2099	2.041	3	192.869	10.1571	16.807
7	23.591	2.4395	2.421	3	203.395	10.1629	17.679
7	26.206	2.7864	2.829	3	213.793	10.1088	18.538
7	29.140	3.0789	3.258	4	221.879	11.9245	19.208
7	32.413	3.4626	3.709	4	232.843	9.9978	20.140
7	36.062	3.8373	4.176	4	242.889	10.0908	20.996
7	40.092	4.2190	4.639	4	253.029	10.1884	21.861
7	44.533	4.6634	5.116	4	263.229	10.2206	22.730
7	49.432	5.1334	5.596	4	273.474	10.2808	23.603
5	53.386	4.6502	5.968	4	283.583	10.1699	24.452
7	54.868	5.7412	6.098	1	287.731	9.7506	24.811
5	58.537	5.5862	6.417	4	293.737	10.1721	25.323
5	64.420	6.1159	6.902	1	297.720	10.1953	25.675
5	70.876	6.7271	7.412	1	309.073	12.4772	26.645
5	78.050	7.5852	7.963	1	319.948	9.1523	27.609

TABLE 8. Continued

N[a]	$\langle T \rangle$/K	ΔT/K	$C_{\mathrm{sat,m}}/R$[b]	N[a]	$\langle T \rangle$/K	ΔT/K	$C_{\mathrm{sat,m}}/R$[b]
Phenoxathiin (continued)							
liquid							
9	313.332	5.6195	33.209	9	357.923	14.9402	35.618
9	320.847	9.6835	33.616	9	373.665	16.5602	36.473
9	331.448	11.4965	34.186	9	389.309	14.5149	37.308
2	335.638	7.6303	34.421	9	403.291	13.4395	38.063
8	336.177	9.3428	34.444	9	416.655	13.2877	38.765
1	336.595	9.1455	34.487	9	428.996	11.3971	39.418
9	343.828	13.2500	34.858	9	439.806	10.2171	39.990
1	345.879	9.4418	34.985				

---

[a] Adiabatic series number.

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

TABLE 9. Experimental $C^{II}_{x,m}$ values ($R = 8.31451\ J{\cdot}K^{-1}{\cdot}mol^{-1}$)

mass/g	0.009359	0.015369	0.023298	0.010628	0.016205	0.024182
V_{cell}/cm^3 [a]	0.05576	0.05409	0.05387	0.05288	0.05292	0.05288
T/K	$C^{II}_{x,m}/R$	$C^{II}_{x,m}/R$	$C^{II}_{x,m}/R$	$C^{II}_{x,m}/R$	$C^{II}_{x,m}/R$	$C^{II}_{x,m}/R$
	Thianthrene			Phenoxathiin		
355.0				35.6	35.6	35.6
375.0				36.7	36.6	36.6
395.0				37.6	37.6	37.6
415.0				38.7	38.7	38.6
435.0				39.7	39.8	39.8
455.0				41.0	40.8	40.8
475.0	43.4	43.2	43.3	42.0	41.9	42.2
495.0	44.8	44.3	44.0	43.4	43.1	42.8
515.0	44.9	45.2	44.9	44.6	44.3	44.2
535.0	46.5	45.9	45.8	45.9	45.7	45.0
555.0	47.8	47.1	46.5	47.5	47.1	46.9
575.0	48.7	47.7	47.5	49.1	48.6	48.3
595.0	49.9	48.1	48.3	50.9	50.4	49.9
615.0	51.7	49.7	48.8	53.0	52.2	51.7
635.0	52.3	50.6	49.6	53.9	53.1	52.6
655.0	54.4	51.5	50.7	55.3	55.2	53.9

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

TABLE 10. Parameters for equations (**8**) and (**10**), estimated critical constants and acentric factors. [a]

		Thianthrene	
A	−9.86858	b_0	−0.54477
B	5.12487	b_1	−0.19380
C	−5.67192	b_2	−0.50109
D	−2.57500		
T_c = 920 K	p_c = 3420 kPa	ρ_c = 367.7 $kg \cdot m^{-3}$	ω = 0.4917
		Phenoxathiin	
A	−9.45840	b_0	−0.84178
B	4.41384	b_1	0.96394
C	−5.34840	b_2	−1.60724
D	−2.28833		
T_c = 863 K	p_c = 3105 kPa	ρ_c = 362.6 $kg \cdot m^{-3}$	ω = 0.4775

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[a] Values for the critical constants and acentric factor are estimates derived from the fitting procedures. See text.

TABLE 11. Values of $C_{sat,m}/R$ derived from differential-scanning calorimetric measurements ($R = 8.31451\ J{\cdot}K^{-1}{\cdot}mol^{-1}$)

T/K	$C_{sat,m}/R$	T/K	$C_{sat,m}/R$	T/K	$C_{sat,m}/R$
		Thianthrene			
440.0	41.4	540.0	46.2	640.0	50.5
460.0	42.4	560.0	47.1	660.0	51.4
480.0	43.4	580.0	48.0	680.0	52.2
500.0	44.4	600.0	48.8	700.0	53.2
520.0	45.3	620.0	49.7		
		Phenoxathiin			
360.0	35.8	480.0	42.2	600.0	50.8
380.0	36.8	500.0	43.4	620.0	52.6
400.0	37.9	520.0	44.7	640.0	54.7
420.0	38.9	540.0	46.0	660.0	56.9
440.0	40.0	560.0	47.5	680.0	59.3
460.0	41.1	580.0	49.1	700.0	61.9

TABLE 12. 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	$\Delta_l^g H_m/RK$
		Thianthrene			
298.15 [a]	10020±68	440.00	8741±33	580.00	7589±35
300.00 [a]	10002±67	460.00	8573±31	600.00	7420±41
320.00 [a]	9816±56	480.00	8407±30	620.00	7248±49
340.00 [a]	9631±48	500.00	8243±29	640.00	7071±59
360.00 [a]	9448±43	520.00	8080±30	660.00	6888±74
380.00 [a]	9266±40	540.00	7918±30	680.00 [a]	6699±91
400.00 [a]	9088±37	560.00	7754±32	700.00 [a]	6502±111
420.00 [a]	8913±35				
		Phenoxathiin			
290.00 [a]	9193±45	420.00	8102±30	580.00	6808±42
298.15 [a]	9122±44	440.00	7943±28	600.00	6628±53
300.00 [a]	9107±44	460.00	7786±27	620.00	6441±65
320.00 [a]	8934±41	480.00	7628±27	640.00	6246±81
340.00 [a]	8763±38	500.00	7471±27	660.00 [a]	6041±100
360.00 [a]	8594±36	520.00	7311±29	680.00 [a]	5825±122
380.00	8428±33	540.00	7148±31	700.00 [a]	5597±148
400.00	8264±32	560.00	6981±36		

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

TABLE 13. Molar thermodynamic functions at vapor-saturation pressure [a]
(R = 8.31451 $J \cdot K^{-1} \cdot mol^{-1}$)

$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m}{R}$	$\frac{\Delta_0^T H_m}{RT}$	$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m}{R}$	$\frac{\Delta_0^T H_m}{RT}$
Thianthrene							
cr							
5.00	0.05	0.02	0.01	200.00	18.21	18.96	9.68
10.00	0.40	0.13	0.10	220.00	19.91	20.77	10.54
20.00	1.87	0.83	0.60	240.00	21.59	22.58	11.39
30.00	3.38	1.88	1.28	260.00	23.29	24.37	12.24
40.00	4.63	3.03	1.96	280.00	24.97	26.16	13.09
50.00	5.69	4.18	2.60	298.15	26.48	27.77	13.86
60.00	6.65	5.31	3.20	300.00	26.63	27.94	13.94
70.00	7.54	6.40	3.76	320.00	28.29	29.71	14.78
80.00	8.39	7.46	4.28	340.00	29.90	31.47	15.62
90.00	9.21	8.50	4.79	360.00	31.49	33.23	16.46
100.00	10.03	9.51	5.27	380.00	33.04	34.97	17.29
120.00	11.65	11.48	6.20	400.00	34.54	36.71	18.12
140.00	13.27	13.40	7.09	420.00	36.00	38.43	18.94
160.00	14.90	15.28	7.97	429.576 [b]	36.68	39.25	19.32
180.00	16.55	17.13	8.83				
liquid							
298.15 [b]	34.07	33.36	22.44	500.00	44.40	53.43	29.24
300.00 [b]	34.17	33.57	22.52	520.00	45.33	55.19	29.84
320.00 [b]	35.18	35.80	23.27	540.00	46.22	56.92	30.43
340.00 [b]	36.21	37.97	24.00	560.00	47.10	58.61	31.01
360.00 [b]	37.25	40.07	24.71	580.00	47.96	60.28	31.58
380.00 [b]	38.30	42.11	25.40	600.00	48.82	61.92	32.14
400.00 [b]	39.34	44.10	26.07	620.00	49.66	63.54	32.69
420.00 [b]	40.38	46.04	26.73	640.00	50.51	65.13	33.23
429.576 [b]	40.88	46.96	27.04	660.00	51.37	66.69	33.77
440.00	41.41	47.95	27.37	680.00	52.25	68.24	34.30
460.00	42.43	49.81	28.00	700.00	53.15	69.77	34.83
480.00	43.43	51.64	28.63				

TABLE 13. continued

$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m}{R}$	$\frac{\Delta_0^T H_m}{RT}$	$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m}{R}$	$\frac{\Delta_0^T H_m}{RT}$
Phenoxathiin							
cr							
5.00	0.04	0.01	0.01	140.00	12.60	13.01	6.84
10.00	0.36	0.12	0.09	160.00	14.16	14.79	7.66
20.00	1.83	0.78	0.57	180.00	15.75	16.55	8.47
30.00	3.38	1.83	1.26	200.00	17.40	18.30	9.28
40.00	4.63	2.98	1.95	220.00	19.05	20.03	10.09
50.00	5.65	4.13	2.59	240.00	20.75	21.77	10.91
60.00	6.54	5.24	3.18	260.00	22.46	23.49	11.73
70.00	7.34	6.31	3.72	280.00	24.15	25.22	12.56
80.00	8.11	7.34	4.22	298.15	25.71	26.78	13.31
90.00	8.86	8.34	4.69	300.00	25.87	26.94	13.39
100.00	9.60	9.31	5.15	320.00	27.61	28.67	14.22
120.00	11.08	11.19	6.01	328.778 [b]	28.45	29.43	14.59
liquid							
298.15 [b]	32.38	33.59	20.85	500.00	43.42	52.91	27.71
300.00 [b]	32.48	33.79	20.92	520.00	44.68	54.64	28.34
320.00	33.57	35.93	21.68	540.00	46.03	56.35	28.97
328.778	34.04	36.84	22.00	560.00	47.49	58.05	29.60
340.00	34.65	37.99	22.41	580.00	49.07	59.75	30.25
360.00	35.73	40.00	23.12	600.00	50.77	61.44	30.90
380.00	36.81	41.96	23.81	620.00	52.63	63.13	31.57
400.00	37.88	43.88	24.49	640.00	54.65	64.83	32.26
420.00	38.94	45.75	25.15	660.00	56.86	66.55	32.97
440.00	40.01	47.59	25.81	680.00	59.28	68.28	33.71
460.00	41.08	49.39	26.44	700.00	61.93	70.04	34.48
480.00	42.22	51.17	27.08				

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[a] Values listed in this table 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 14.

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

TABLE 14. Thermodynamic properties in the ideal-gas state
($R = 8.31451\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and $p^\circ = 101.325$ kPa)

$\frac{T}{K}$	$\frac{\Delta_0^T H_m^\circ}{RT}$	$\frac{\Delta_{imp} H_m^\circ}{RT}$ [a]	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_{imp} S_m^\circ}{R}$ [b]	$\frac{\Delta_f H_m^\circ}{RT}$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_f G_m^\circ}{RT}$
			Thianthrene				
298.15 [c,d]	56.05±0.23	0.00	50.99±0.23	0.00	63.77±0.46	−47.54±0.23	111.32±0.41
300.00 [c,d]	55.85±0.22	0.00	51.14±0.23	0.00	63.35±0.46	−47.57±0.23	110.92±0.40
320.00 [c,d]	53.95±0.18	0.00	52.78±0.18	0.00	59.05±0.41	−47.92±0.18	106.97±0.38
340.00 [c,d]	52.33±0.14	0.00	54.38±0.15	0.00	55.27±0.38	−48.24±0.15	103.51±0.36
360.00 [c,d]	50.96±0.12	0.00	55.96±0.13	0.00	51.91±0.36	−48.54±0.13	100.45±0.34
380.00 [c,d]	49.78±0.11	0.00	57.51±0.11	0.00	48.91±0.33	−48.81±0.11	97.72±0.32
400.00 [c,d]	48.79±0.10	0.00	59.04±0.10	0.00	46.22±0.31	−49.06±0.10	95.28±0.30
420.00 [c,d]	47.95±0.09	0.00	60.56±0.09	0.00	43.81±0.30	−49.28±0.09	93.09±0.29
440.00 [c]	47.24±0.08	0.00	62.07±0.09	0.00	41.62±0.28	−49.48±0.09	91.10±0.28
460.00	46.65±0.07	0.01	63.56±0.08	0.01	39.65±0.27	−49.65±0.08	89.30±0.27
480.00	46.15±0.07	0.01	65.04±0.08	0.01	37.85±0.26	−49.80±0.08	87.65±0.26
500.00	45.74±0.06	0.02	66.50±0.08	0.01	36.21±0.25	−49.92±0.08	86.13±0.25
520.00	45.40±0.07	0.03	67.95±0.08	0.02	34.71±0.24	−50.03±0.08	84.74±0.24
540.00	45.13±0.06	0.04	69.39±0.08	0.03	33.33±0.23	−50.13±0.08	83.46±0.23
560.00	44.91±0.07	0.06	70.81±0.09	0.04	32.06±0.23	−50.21±0.09	82.27±0.23
580.00	44.74±0.08	0.08	72.21±0.10	0.06	30.89±0.22	−50.27±0.10	81.17±0.23
600.00	44.61±0.10	0.10	73.59±0.11	0.08	29.81±0.22	−50.33±0.11	80.14±0.23
620.00	44.51±0.11	0.13	74.96±0.13	0.10	28.81±0.22	−50.37±0.13	79.17±0.23
640.00	44.46±0.13	0.17	76.31±0.15	0.13	27.88±0.23	−50.40±0.15	78.27±0.24
660.00 [c,d]	44.43±0.16	0.22	77.65±0.17	0.16	27.01±0.24	−50.41±0.17	77.43±0.25
680.00 [c,d]	44.43±0.18	0.27	78.98±0.20	0.20	26.21±0.25	−50.42±0.20	76.63±0.26
700.00 [c,d]	44.45±0.21	0.33	80.30±0.22	0.25	25.47±0.27	−50.41±0.22	75.88±0.27

TABLE 14. continued

$\frac{T}{K}$	$\frac{\Delta_0^T H_m^\circ}{RT}$	$\frac{\Delta_{imp} H_m^\circ}{RT}$ [a]	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_{imp} S_m^\circ}{R}$ [b]	$\frac{\Delta_f H_m^\circ}{RT}$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_f G_m^\circ}{RT}$
			Phenoxathiin				
290.00 [c,d]	52.24±0.16	0.00	49.65±0.16	0.00	25.71±0.41	−46.68±0.16	72.38±0.38
298.15 [c,d]	51.45±0.15	0.00	50.30±0.15	0.00	24.83±0.40	−46.85±0.15	71.68±0.37
300.00 [c,d]	51.28±0.15	0.00	50.45±0.15	0.00	24.65±0.40	−46.88±0.15	71.53±0.37
320.00 [c]	49.60±0.13	0.00	52.02±0.13	0.00	22.72±0.37	−47.28±0.13	70.00±0.35
340.00 [c]	48.19±0.11	0.00	53.57±0.12	0.00	21.03±0.34	−47.64±0.12	68.67±0.33
360.00 [c]	47.00±0.10	0.00	55.10±0.11	0.00	19.54±0.32	−47.97±0.11	67.52±0.31
380.00	45.99±0.09	0.00	56.61±0.10	0.00	18.22±0.30	−48.28±0.10	66.50±0.29
400.00	45.15±0.08	0.00	58.11±0.09	0.00	17.04±0.29	−48.55±0.09	65.59±0.28
420.00	44.45±0.08	0.00	59.59±0.08	0.00	15.99±0.27	−48.79±0.08	64.78±0.27
440.00	43.87±0.07	0.01	61.06±0.08	0.01	15.05±0.26	−49.01±0.08	64.06±0.26
460.00	43.39±0.07	0.01	62.52±0.08	0.01	14.21±0.25	−49.21±0.08	63.41±0.25
480.00	42.99±0.07	0.02	63.96±0.08	0.02	13.45±0.24	−49.38±0.08	62.82±0.24
500.00	42.69±0.08	0.03	65.40±0.09	0.03	12.77±0.23	−49.52±0.09	62.29±0.24
520.00	42.45±0.09	0.05	66.83±0.10	0.04	12.16±0.23	−49.64±0.10	61.80±0.24
540.00	42.28±0.10	0.07	68.26±0.12	0.05	11.62±0.23	−49.73±0.12	61.35±0.24
560.00	42.17±0.12	0.10	69.69±0.13	0.07	11.15±0.23	−49.79±0.13	60.94±0.25
580.00	42.12±0.13	0.13	71.12±0.15	0.10	10.73±0.23	−49.82±0.15	60.55±0.26
600.00	42.12±0.15	0.18	72.55±0.17	0.13	10.38±0.24	−49.82±0.17	60.19±0.26
620.00	42.19±0.17	0.23	74.00±0.19	0.17	10.08±0.25	−49.77±0.19	59.86±0.28
640.00	42.30±0.20	0.28	75.46±0.22	0.21	9.85±0.26	−49.69±0.22	59.54±0.29
660.00 [c,d]	42.48±0.22	0.35	76.95±0.25	0.26	9.68±0.28	−49.56±0.25	59.23±0.30
680.00 [c,d]	42.71±0.25	0.43	78.45±0.28	0.32	9.57±0.30	−49.37±0.28	58.94±0.32
700.00 [c,d]	43.00±0.28	0.52	79.99±0.31	0.39	9.52±0.33	−49.14±0.31	58.66±0.34

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[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 15. Comparison of experimental and calculated sublimation pressures

T K	p{cr(l)}[a] Pa	p(liquid)[b] Pa	p(calc)[c] Pa	Δ(p)[d] Pa
		Thianthrene		
395.000	17.2	31.9	16.5	0.7
410.001	52.2	73.8	51.3	0.9
420.002	104.9	124.2	104.3	0.6
425.008	147.4	159.4	146.8	0.6

[a] Sublimation pressure measured in inclined piston.

[b] Vapor pressure for supercooled liquid calculated using the Wagner-equation parameters listed in table 5.

[c] Sublimation pressure calculated using equation (**14**).

[d] Δ(p) = p{cr(l)} − p(calc)} is the difference between measured and calculated values of the sublimation pressure.

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