J. Chem. Eng. Data **2005,** *50,* 697−708

Thermodynamic Properties of 2-Methylquinoline and 8-Methylquinoline

R. D. Chirico*

Thermodynamics Research Center (TRC), Physical and Chemical Properties Division, National Institute of Standards and Technology (NIST), Boulder, Colorado 80305-3328

W. V. Steele†

Physical Properties Research Facility, Chemical Engineering Department, 327 Dougherty Engineering Building, 1512 Middle Drive, University of Tennessee, Knoxville, Tennessee 37996-2200, and Nuclear Science and Technology Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee 37831-6273

Measurements leading to the calculation of the standard thermodynamic properties for gaseous 2-methylquinoline (Chemical Abstracts registry number [91-63-4]) and 8-methylquinoline (Chemical Abstracts registry number [611-32-5]) are reported. Experimental methods include oxygen bomb calorimetry, adiabatic heat capacity calorimetry, vibrating-tube densitometry, comparative ebulliometry, inclined-piston gauge manometry, and differential scanning calorimetry (dsc). The critical temperature was measured with a differential scanning calorimeter. The critical pressure and critical density were estimated. Standard molar entropies, standard molar enthalpies, and standard molar Gibbs free energies of formation were derived at selected temperatures between 298.15 K and 700 K. All results are compared with experimental values reported in the literature.

Introduction

This work is a product of research funded by the U.S. Department of Energy Office of Fossil Energy, Advanced Oil Recovery (AOR) program. Within a portion of this research program, the thermochemical and thermophysical properties are determined for key aromatics and hydroaromatics present in the spectrum of fossil fuel materials. The results of the thermodynamic property measurements are used to provide insights into the reaction networks and relative reactivities of polycyclic aromatics and hydroaromatics within the complex processes operating in hydroprocessing. The high-precision measurements reported here also provide the basis for improved and extended methods for estimations and correlations necessary to provide reliable property values for cyclic aromatics, which are key in the analysis of technological problems in a wide variety of fields from pharmaceuticals to "science-based" environmental regulations and ecosystem restoration, as well as to the processing of fossil fuels.

The methylquinolines were chosen for study following completion of work on the parent compound quinoline.[1] Results of that study showed the possible existence of a glassy crystalline phase at low temperatures. Agreement between statistical and experimental determinations of ideal-gas entropies was good (within 0.1 to 0.2%) but was not as good as numerous similar comparisons for other aromatics studied by this research group. Agreement in each of those cases was well within 0.1%. An extensive list of citations to more than 15 compounds, including pyridine, the xylenes, methylpyridines, and dimethylpyridines, was given recently.[2] Contributions of methyl groups to the ideal-gas properties of aromatics can often be estimated with the free-rotor approximation. The expected difference between ideal-gas properties for a parent compound and its unhindered methyl derivatives can be calculated with high accuracy. In this way, measurements for methyl derivatives provide results that can be used to substantiate those for the parent compound. This research group has also completed experimental research on the thermodynamic properties of 2,6-dimethylquinoline. That work has not been published. Complete discussion of the topic of property consistency within the family of quinolines will be provided with the publication of that work.

The thermodynamic properties of 2- and 8-methylquinoline reported here were measured with oxygen bomb calorimetry, adiabatic heat capacity calorimetry, comparative ebulliometry, inclined-piston gauge manometry, vibrating tube densimetry, and differential-scanning calorimetry (dsc). Standard molar formation properties (Gibbs free energies, enthalpies, and entropies) in the ideal gaseous state were derived. All measured or derived thermodynamic property values are compared with those reported in the literature.

Experimental Procedure

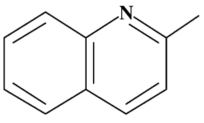
Materials. The research group of Professor E. J. "Pete" Eisenbraun (retired) of Oklahoma State University purified the calorimetric samples of 2-methylquinoline and 8-methylquinoline. Both materials were purified through conversion to an oxalate by reaction of the methylquinoline with oxalic acid in propan-2-ol. The oxalates were purified by multiple recrystallizations from 2-propanol/water (9:1) (2-methylquinoline) and from 2-propanol (8-methylquinoline). The oxalates were cleaved with aqueous KOH, extracted with diethyl ether, dried (Na_2CO_3 or $MgSO_4$), and triply distilled. Initial analyses with gas−liquid chromatography

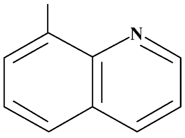
---

* Corresponding author. E-mail: chirico@boulder.nist.gov.
† E-mail: steelewv@ornl.gov.

10.1021/je049595u CCC: $30.25

Table 1. Calorimeter and Sample Characteristics for Adiabatic Heat Capacity Calorimetric Studies[a]





	2-methylquinoline	8-methylquinoline
m/g	36.307	45.398
V_i(298.15 K)/cm^3	59.06	62.47
T_{cal}/K	296.2	296.7
p_{cal}/kPa	5.57	6.47
$\rho(T_{max})$	2.7	3.2
ρ_{min}	1.7	1.8
$10^2(\delta C/C)_{max}$	0.083	0.046
x_{pre}	0.00008[b]	0.0012

[a] 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 the calorimeter is sealed, r is the ratio of the heat capacity of the full calorimeter to that of the empty; $(\delta C/C)_{max}$ is the vaporization correction at the highest temperature measured (i.e., $T_{max} \approx 444$ K), and x_{pre} is the mole-fraction impurity used for premelting corrections. [b] Because of the presence of solid-soluble impurities, this value was used as a parameter in the premelting calculations only and does not represent the purity of the sample of 2-methylquinoline. See the text.

(GLC) indicated purities greater than 0.999 mole fraction. The mole fraction purities of the samples used in this research (2-methylquinoline, 0.9996 and 8-methylquinoline, 0.9988) were determined by fractional melting as part of the adiabatic heat capacity calorimetric studies reported here. The purity levels were further corroborated in ebulliometric vapor-pressure studies reported here by the small differences observed between the boiling and condensation temperatures of the samples. All transfers of the purified samples were done under nitrogen or helium or by vacuum distillation.

The water used as a reference material in the ebulliometric vapor-pressure measurements was deionized and distilled from potassium permanganate. The decane also used as a reference material for the ebulliometric measurements was purified by urea complexation, two recrystallizations of the complex, decomposition of the complex with water, extraction with ether, drying with $MgSO_4$, and distillation at 337 K and 1 kPa pressure. GLC analysis of the decane sample failed to show any impurity peaks.

Molar values for 2- and 8-methylquinoline are reported in terms of M = 143.185 g·mol^{-1} for $C_{10}H_9N$[3] and the gas constant R = 8.314472 J·K^{-1}·mol^{-1} adopted in 1998 by CODATA.[4] 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[5] and were converted approximately to ITS-90 with published temperature increments.[6] The platinum resistance thermometer used in the adiabatic heat capacity studies was calibrated below 13.81 K with the method of McCrackin and Chang.[7] Measurements of mass, time, electrical resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

Apparatus. Adiabatic heat capacity and enthalpy measurements were made with a calorimetric system that has been described previously.[1] The calorimeter characteristics and sealing conditions are given in Table 1. Energy measurement procedures were the same as those described for studies on quinoline.[1] Thermometer resistances were measured with self-balancing alternating-current resistance bridges (H. Tinsley & Co. Ltd.; models 5840C and 5840D) that were calibrated with standard resistors specifically designed for use with alternating current. Energies were measured to a precision of 0.01%, and temperatures were measured to a precision of 0.0001 K. The energy increments to the filled platinum calorimeter were corrected for enthalpy changes in the empty calorimeter, for the helium exchange gas, and for vaporization of the sample into the free space of the sealed vessel. The maximum correction to the measured energy for the helium exchange gas was 0.3% near T = 5 K for both methylquinolines. The sizes of the other two corrections are indicated in Table 1.

Densities along the liquid-phase saturation line ρ_{sat} for a range of temperatures were obtained in this research for both compounds with a vibrating-tube densitometer. The instrument and its operation have been described.[8] Test measurements of the density of benzene between T = 310 K and T = 523 K have been reported.[9] Results agreed with the values published by Hales and Townsend[10] within $1 \times 10^{-3}\rho_{sat}$. The precision of the measurements was approximately $5 \times 10^{-4}\rho_{sat}$.

The experimental procedures, used in the combustion calorimetry of organic nitrogen-containing compounds, have been described.[11,12] A rotating-bomb calorimeter (laboratory designation BMR II)[13] and platinum-lined bomb (laboratory designation Pt-3b)[14] with an internal volume of 0.393_4 dm^3 were used without rotation. The calorimetric samples of 2-methylquinoline and 8-methylquinoline were confined in flexible borosilicate-glass ampules.[12,15] For each experiment, a volume of 0.0010 dm^3 of water was added to the bomb, and the bomb was charged to a pressure of 3.04 MPa with pure oxygen with flushing.[11,12] Judicious choice of sample and auxiliary masses allowed the temperature rise in the combustion series and its corresponding calibration series to be the same within 0.1%. All experiments were completed within 0.01 K of T = 298.15 K.

Temperatures were measured by quartz-crystal thermometry.[16,17] 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-against-temperature curve is inherent in the quartz-crystal thermometer readings.[18]

NIST Standard Reference Material benzoic acid (sample 39i) was used to calibrate the combustion calorimeter; its massic energy of combustion is −(26434.0 ± 3.0) J·g^{-1} under certificate conditions. Conversion to standard states[19] gives −(26413.7 ± 3.0) J·g^{-1} for $\Delta_c U°$/M, the massic energy of the idealized combustion reaction. Calibration experiments were interspersed with both sets of methylquinoline measurements. Because of the high purity of the oxygen used and preliminary bomb flushing, nitrogen oxides were not formed in the calibration experiments. The energy equivalent of the calorimeter obtained for the calibration series, ϵ(calor), was (16776.2 ± 0.9) J·K^{-1} (mean and standard deviation of the mean). The auxiliary oil (laboratory designation TKL66) had the empirical formula $CH_{1.913}$. For this material $\Delta_c U°$/M was −(46042.5 ± 1.8) J·g^{-1}. For the cotton fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta_c U°$/M was −16945 J·g^{-1}.

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,[19] included a density at T = 298.15 K of

1055 kg·m^{-3} for liquid 2-methylquinoline and a value of 1.05×10^{-7} m^3·K^{-1} for $(\partial V_m/\partial T)_p$. For liquid 8-methylquinoline the corresponding values used were a density at T = 298.15 K of 1069 kg·m^{-3} and a value of 1.08×10^{-7} m^3·K^{-1} for $(\partial V_m/\partial T)_p$. These values were estimated by extrapolation of the density values reported later in this paper. The molar heat capacity at T = 298.15 K for each methylquinoline used in the corrections to standard states is given later in this paper as part of the results of heat capacity measurements.

Nitric acid, formed during combustions of both methylquinolines was determined by titration with standardized sodium hydroxide.[11] Carbon dioxide was also recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as adsorbent for the CO_2 recoveries.[20] The combustion products were checked for unburned carbon and other products of incomplete combustion, but none was detected. For the benzoic acid calibrations the carbon dioxide recovery percentage was (100.012 ± 0.004) mean and standard deviation of the mean. The percentage recoveries for the methylquinolines were (100.005 ± 0.010) for 2-methylquinoline and (100.003 ± 0.015) for 8-methylquinoline.

The essential features of the ebulliometric equipment and procedures have been described.[21,22] The ebulliometers were used to reflux the methylquinolines 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 respective methylquinoline 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 internationally accepted equation of state for ordinary water.[23] In the pressure region 2 kPa to 25 kPa, decane was used as the standard. Pressures were calculated on ITS-90 for measurements with decane as the reference material with eq 1 of ref 2.

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

$$\sigma(p) = (0.002\ \text{K})\left\{\left(\frac{d p_{\text{ref}}}{\text{d}T}\right)^2 + \left(\frac{\text{d}p_{\text{x}}}{\text{d}T}\right)^2\right\}^{1/2} \qquad (1)$$

where p_{ref} is the vapor pressure of the reference substance and p_{x} is the vapor pressure of the sample under study. The precision of the temperature measurements was near 5×10^{-4} K. Values of $\text{d}p_{\text{ref}}/\text{d}T$ for the reference substances were calculated from vapor pressures of the reference materials (decane and water).

Douslin and McCullough[24] and Douslin and Osborn[25] have described the equipment for the inclined-piston vapor-pressure measurements. Revisions to both the equipment and procedures have been reported.[1] Standard uncertainties in the pressures determined with the inclined-piston apparatus, on the basis of estimated uncertainties of measuring the mass, area, and angle of inclination of the piston, are adequately described by the expression

$$\sigma(p) = 1.5 \times 10^{-4} p + 0.2 \qquad (2)$$

The pressure p in eq 2 is expressed in Pa. The uncertainties in the temperatures are 0.002 K. The contributions of the temperature uncertainties to $\sigma(p)$ are insignificant in the range of the measurements.

Table 2. Measured Values of Density ρ at Saturation Pressure[a]

T/K	ρ/kg·m^{-3}	$100(\rho - \rho_{cs})/\rho$	T/K	ρ/kg·m^{-3}	$100(\rho - \rho_{cs})/\rho$
2-Methylquinoline			8-Methylquinoline		
323.14	1035.2	0.16	323.14	1049.3	0.14
348.14	1015.9	0.14	348.13	1029.0	0.02
373.12	996.1	0.11	373.12	1009.5	0.01
398.12	973.9	−0.12	398.12	988.5	−0.11
423.11	952.8	−0.19	423.11	967.8	−0.15
448.11	931.9	−0.18	448.11	947.5	−0.09
473.11	910.8	−0.12	473.11	926.6	−0.03
498.11	888.8	−0.08	498.11	904.0	−0.08
523.11	865.1	−0.14			

[a] Values of ρ_{cs} were calculated with the corresponding-states correlation shown as eq 6.

Table 3. Typical Details of a Combustion Experiment at T = 298.15 K (p° = 101.325 kPa)[a]

	2-methylquinoline	8-methylquinoline
m'(compound)/g	0.857995	0.812892
m''(oil)/g	0.061445	0.068231
m'''(fuse)/g	0.001034	0.001336
$n_i(H_2O)$/mol	0.055345	0.055345
m(Pt)/g	19.543	19.543
$\Delta T/\text{K} = (T_i - T_f + \Delta T_{corr})/\text{K}$	2.06943	1.99078
ϵ(calor)(ΔT)/J	−34709.8	−33390.8
ϵ(cont)(ΔT)/J[b]	−42.3	−40.4
ΔU_{ign}/J	0.8	0.8
$\Delta U_{dec}(HNO_3)$/J	51.3	44.2
ΔU(corr. to std states)/J[c]	19.6	18.8
$-m''(\Delta_c U^\circ/M)$(oil)/J	2829.1	3141.5
$-m'''(\Delta_c U^\circ/M)$(fuse)/J	17.5	22.6
$m'(\Delta_c U^\circ/M)$ (compound)/J	−31833.8	−30203.5
$(\Delta_c U^\circ/M)$ (compound)/J·g^{-1}	−37102.5	−37155.4

[a] The symbols and abbreviations are those used in ref 19, except as noted. [b] $\epsilon_i(\text{cont})(T_i - 298.15\ \text{K}) + \epsilon_f(\text{cont})(298.15\ \text{K} - T_f + \Delta T_{corr})$. [c] Items 81−85, 87−90, 93, and 94 of the computational form of ref 19.

Table 4. Summary of the Experimental Energy of Combustion Results and Molar Thermodynamic Functions at T = 298.15 K and p° = 101.325 kPa

$\{(\Delta_c U^\circ/M)$(2-methylquinoline)$\}$/J·g^{-1}					
−37102.5	−37098.9	−37095.6	−37098.0	−37099.7	
$\langle\{(\Delta_c U^\circ/M)$(2-methylquinoline)$\}$/J·g$^{-1}\rangle$				−37099.0 ± 1.1[a]	
$\Delta_c U^\circ_m$(2-methylquinoline)/kJ·mol^{-1}				−5312.15 ± 0.76[a]	
$\Delta_c H^\circ_m$(2-methylquinoline)/kJ·mol^{-1}				−5316.49 ± 0.76[a]	
$\Delta_f H^\circ_m$(2-methylquinoline)/kJ·mol^{-1}				95.15 ± 0.90[b]	
$\{(\Delta_c U^\circ/M)$(8-methylquinoline)$\}$/J·g^{-1}					
−37155.4	−37144.0	−37161.6	−37172.8	−37156.6	−37141.8
$\langle\{(\Delta_c U^\circ/M)$(8-methylquinoline)$\}$/J·g$^{-1}\rangle$				−37155.4 ± 4.7[a]	
$\Delta_c U^\circ_m$(8-methylquinoline)/kJ·mol^{-1}				−5320.23 ± 1.52[a]	
$\Delta_c H^\circ_m$(8-methylquinoline)/kJ·mol^{-1}				−5324.57 ± 1.52[a]	
$\Delta_f H^\circ_m$(8-methylquinoline)/kJ·mol^{-1}				103.23 ± 1.58[b]	

[a] Value for the following reaction (see the text): $C_{10}H_9N(l) + 12.25O_2(g) = 10CO_2(g) + 0.5N_2(g) + 4.5H_2O$. [b] Value for the following reaction (see the text): $10C(\text{cr, graphite}) + 4.5H_2(g) + 0.5N_2(g) = C_{10}H_9N(l)$.

Differential scanning calorimetry measurements were made with a Perkin-Elmer DSC-7. Experimental methods were described previously.[26,27]

Results

Measured densities for 2- and 8-methylquinoline in the liquid phase at saturation pressure are listed in Table 2.

Results of a typical combustion experiment for each methylquinoline are summarized in Table 3. It is impractical to list summaries for each combustion, but values of $\Delta_c U^\circ/M$ for all the experiments are reported in Table 4. All

Table 5. Summary of Vapor-Pressure Results[a]

method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K	method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
					2-Methylquinoline						
IP	319.989	0.0315	0.0000	0.0002		decane	457.677	19.933	0.001	0.002	0.009
IP	329.984	0.0630	0.0002	0.0002		decane	465.364	25.023	0.001	0.002	0.008
IP	339.987	0.1198	0.0004	0.0002		water	465.361	25.023	0.003	0.003	0.006
IP	349.980	0.2174	0.0002	0.0002		water	473.099	31.177	0.002	0.003	0.007
IP	364.979	0.4962	0.0002	0.0003		water	480.886	38.565	0.002	0.004	0.007
IP	374.984	0.8233	0.0002	0.0003		water	488.723	47.375	0.000	0.005	0.007
IP	384.974	1.3227	0.0000	0.0004		water	496.610	57.817	−0.002	0.005	0.005
decane	394.236	2.0000	−0.0006	0.0003	0.044	water	504.548	70.120	−0.005	0.006	0.005
IP	394.971	2.0656	0.0003	0.0005		water	512.535	84.533	−0.005	0.007	0.006
IP	404.970	3.1406	0.0001	0.0007		water	520.572	101.325	−0.007	0.009	0.005
decane	411.020	3.9999	0.0011	0.0005	0.037	water	528.659	120.79	−0.01	0.01	0.005
decane	418.528	5.3330	−0.0008	0.0006	0.021	water	536.797	143.25	0.00	0.01	0.005
decane	429.677	7.9989	−0.0003	0.0009	0.015	water	544.981	169.02	0.00	0.01	0.006
decane	438.045	10.6661	−0.0004	0.0011	0.011	water	553.218	198.49	0.01	0.01	0.007
decane	444.810	13.332	0.000	0.001	0.011	water	561.500[b]	232.02	0.04	0.02	0.008
decane	451.838	16.665	0.001	0.002	0.011	water	569.828[b]	270.02	0.07	0.02	0.010
					8-Methylquinoline						
IP	315.614[b]	0.0242	0.0003	0.0002		decane	457.459	19.934	0.002	0.002	0.009
IP	324.984	0.0466	0.0001	0.0002		decane	465.161	25.018	0.002	0.002	0.008
IP	334.987	0.0905	0.0002	0.0002		water	465.162[b]	25.019	0.002	0.003	0.007
IP	344.982	0.1674	0.0002	0.0002		water	465.167[b]	25.024	0.003	0.003	0.007
IP	354.978	0.2975	0.0003	0.0002		water	472.938	31.185	0.003	0.003	0.007
IP	364.976	0.5091	0.0004	0.0003		water	480.744	38.566	0.001	0.004	0.007
IP	374.976	0.8418	0.0002	0.0003		water	488.597	47.364	−0.001	0.005	0.006
IP	384.976	1.3496	0.0003	0.0004		water	496.506	57.798	−0.002	0.005	0.006
decane	393.840	2.0014	−0.0002	0.0003	0.054	water	504.487	70.123	−0.007	0.006	0.006
IP	394.974	2.1024	0.0004	0.0005		water	512.497	84.527	−0.008	0.007	0.006
decane	400.595	2.6651	−0.0003	0.0003	0.043	water	520.559	101.310	−0.009	0.009	0.005
IP	404.974	3.1902	0.0007	0.0007		water	528.685	120.80	−0.01	0.01	0.005
decane	410.696	4.0039	−0.0006	0.0005	0.029	water	536.845	143.23	−0.01	0.01	0.005
decane	418.203	5.3361	−0.0004	0.0006	0.023	water	545.061	169.00	0.00	0.01	0.005
decane	429.382	8.0019	−0.0001	0.0009	0.015	water	553.324	198.45	0.01	0.01	0.006
decane	437.771	10.6685	0.0000	0.0011	0.013	water	553.325	198.45	0.02	0.01	0.006
decane	444.500	13.310	0.001	0.001	0.011	water	561.646[b]	232.00	0.04	0.02	0.007
decane	451.611	16.671	0.001	0.002	0.010	water	570.010[b]	270.00	0.08	0.02	0.008

[a] IP denotes inclined piston, water or decane refers to the material used as the standard in the reference ebulliometer, and T is 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 with eq 5 and the parameters listed in Table 11, from the observed value of pressure. σ is the propagated standard uncertainty calculated from eqs 1 and 2. ΔT is the difference between the boiling and condensation temperatures ($T_{\text{boil}} - T_{\text{cond}}$) for the sample. [b] Values at this temperature were not included in the fit of the Wagner equation.

Table 6. Melting-Study Summaries[a]

F	$T(F)$/K	F	$T(F)$/K
2-methylquinoline		8-methylquinoline	
0.144	270.398	0.214	246.682
0.243	270.425	0.409	246.803
0.390_5	270.441	0.652	246.853
0.587	270.452		
0.784	270.459		
$T_{\text{tp}} = 270.48$ K		$T_{\text{tp}} = 246.94$ K	
$x = 0.0004$		$x = 0.0012$	

[a] F is the fraction melted at observed temperature $T(F)$, T_{tp} is the triple-point temperature, and x is the mole-fraction impurity.

values of $\Delta_cU°/M$ in Table 4 refer to the reaction

$$C_{10}H_9N(l) + {}^{49}/_4O_2(g) = 10CO_2(g) + {}^{1}/_2N_2(g) + {}^{9}/_2H_2O(l) \quad (3)$$

Table 4 also gives derived values of the standard molar energy of combustion $\Delta_cU^0_m$, the standard molar enthalpy of combustion $\Delta_cH^o_m$, and the standard molar enthalpy of formation $\Delta_fH^0_m$ for 2-methylquinoline and 8-methylquinoline. Values of $\Delta_cU^0_m$ and $\Delta_cH^0_m$ refer to reaction 3. Values of $\Delta_fH^0_m$ refer to the reaction

$$10C(cr, graphite) + {}^{9}/_2H_2(g) + {}^{1}/_2N_2(g) = C_{10}H_9N(l) \quad (4)$$

Uncertainties given in Table 4 are expressed as the "uncertainty interval" defined in reference.[28] The standard molar enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ were taken to be −(393.51 ± 0.13) kJ·mol^{-1} and −(285.830 ± 0.042) kJ·mol^{-1}, respectively, as assigned by CODATA.[29]

Vapor pressures for 2- and 8-methylquinoline are reported in Table 5. The pressures, the condensation temperatures, and the difference between condensation and boiling temperatures for the sample are reported. The small differences obtained between the boiling and condensation temperatures indicated correct operation of the equipment and the high purity of the samples.

Summaries of melting studies for 2- and 8-methylquinoline obtained with adiabatic calorimetry are reported in Table 6. Crystallization of 2-methylquinoline was initiated by slow cooling (approximately 1 mK·s^{-1}) of the liquid sample. The sample supercooled approximately 25 K before nucleation. Following nucleation, complete crystallization of 2-methylquinoline occurred rapidly. After partially remelting the sample (10% to 20% liquid) and maintaining adiabatic conditions, there was no evidence of spontaneous warming. Spontaneous warming would indicate continued slow ordering of the crystals.

The sample of 8-methylquinoline did not crystallize on cooling. To achieve nucleation, the sample was cooled below the glass transition $\{T_\mathrm{g} = (170 \pm 3)\ \mathrm{K}\}$, and reheated to near 190 K, where crystallization commenced. The partially crystallized sample was heated to within 3 K of the triple-point temperature ($T_\mathrm{tp} = 246.94$ K), where slow crystallization continued for roughly 4 days.

After the initial tempering in the partially melted state, both samples were then cooled at an effective rate of 1.5 $\mathrm{mK{\cdot}s^{-1}}$ to crystallize the remaining liquid. Finally, the samples were thermally cycled from approximately 100 K to within 3 K of the respective triple-point temperatures, where they were held for a minimum of 24 h to provide further tempering. No additional spontaneous warming was observed. All of the solid-phase measurements were performed upon crystals pretreated in a similar manner. As shown later, good repeatability was observed for separate enthalpy-of-fusion determinations, which also is indicative of complete conversion to the crystalline state.

The triple-point temperatures T_tp and the mole fraction purities x were determined by measurement of the equilibrium melting temperatures $T(F)$ as a function of fraction F of the sample in the liquid state.[30] Equilibrium melting temperatures were determined by measuring temperatures at intervals of approximately 240 s for 1 h to 1.5 h after an energy input and extrapolating to infinite time by assuming an exponential decay toward the equilibrium value. The observed temperatures at the end of the equilibration period were within 2 mK of the calculated equilibrium temperatures for F values listed in Table 6 and used in the determination of T_tp. No evidence for the presence of solid-soluble impurities was found for 8-methylquinoline, and published procedures[31] were used to derive the mole fraction purity x and T_tp. For 2-methylquinoline, the presence of solid soluble impurities was evident, and the method of Mastrangelo and Dornte[32] was used to determine the mole fraction purity. The results are summarized in Table 6.

Experimental molar enthalpy results are summarized in Table 7. The Table includes molar enthalpies of fusion and results of measurements in single-phase regions, which serve as checks on the integration of the molar heat capacity values. Corrections for premelting 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.

Equilibrium was reached in less than 1 h for all measurements in the liquid phase and for measurements in the solid phase more than 50 K below T_tp. As the triple-point temperature was approached equilibration times increased for both samples. For 8-methylquinoline, equilibration times increased gradually from 1 h near 210 K to 6 h near 240 K, while for 2-methylquinoline, equilibration times increased gradually from 1 h near 220 K to 20 h near 265 K. The greater increase for 2-methylquinoline might be related to processes associated with equilibration involving the indicated solid-soluble impurities.

The experimental molar heat capacities under vapor saturation pressure $C_\mathrm{sat,m}$ determined by adiabatic calorimetry are listed in Table 8 and shown in Figures 1 and 2. Values in Table 8 were corrected for effects of sample vaporization into the gas space of the calorimeter, although the size of the correction is small, as indicated in Table 1. The values listed in Table 8 were not corrected for premelting, but an independent calculation can be made with the temperature increments provided. The temperature increments were small enough to obviate the need for corrections for nonlinear variation of $C_\mathrm{sat,m}$ with temperature. Combined uncertainties (95% level of confidence) for the heat capacity measurements ranged from approximately 3% at 5 K to 0.5% at 10 K and improved gradually to better than 0.1% above 30 K. Extrapolation of the heat capacity results to $T \rightarrow 0$ was made with a plot of $C_\mathrm{sat,m}/T$ against T^2 for temperatures below 10 K.

Table 7. Measurements of Molar Energy Increment $\Delta_\mathrm{tot}U_\mathrm{m}$ ($R = 8.314472\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)

		T_i	T_f	T_trs	$\Delta_\mathrm{tot}U_\mathrm{m}{}^c$	$\Delta_\mathrm{trs}H_\mathrm{m}{}^d$
N^a	h^b	K	K	K	$\mathrm{kJ{\cdot}mol^{-1}}$	$\mathrm{kJ{\cdot}mol^{-1}}$
2-Methylquinoline						
Single-Phase Measurements in the Crystal Phase						
5	1	227.512	263.467		5.423	−0.002
10	1	85.429	187.154		9.482	0.000
10	1	187.167	264.47		10.816	0.015
12	1	168.175	209.079		4.882	−0.002
12	1	209.109	264.035		8.012	0.011
Crystal-to-Liquid Phase Transition						
1	2	267.022	274.237	270.48	13.898	12.520
3	6	265.678	272.483		13.737	12.514[e]
4	2	266.133	273.663		13.921	12.520
12	2	264.027	273.571		14.245	12.519
					average	12.520
Single-Phase Measurements in the Liquid Phase						
15	1	310.026	400.694		22.436	−0.001
15	1	400.706	440.812		11.012	-0.001
8-Methylquinoline						
Single-Phase Measurements in the Crystal Phase						
13	1	61.918	108.746		3.026	0.001
13	1	108.785	186.047		7.543	0.002
13	1	186.059	239.213		7.047	0.000
Crystal-to-Liquid Phase Transition						
10	5	240.423	252.107	246.94	12.760	10.721[e]
13	2	239.174	249.251		12.368	10.732
					selected value	10.732
Single-Phase Measurements in the Liquid Phase						
14	2	189.477	248.47		11.558	0.004
18	1	295.722	378.494		19.806	0.001
18	1	378.513	440.167		16.582	−0.001

[a] Adiabatic series number. [b] Number of heating increments. [c] $\Delta_\mathrm{tot}U_\mathrm{m}$ is the molar energy input from the initial temperature T_i to the final temperature T_f. [d] $\Delta_\mathrm{trs}H_\mathrm{m}$ is the net molar enthalpy of transition at the transition temperature T_trs or the excess enthalpy for single-phase measurements relative to the heat capacity curve described in the text and defined in Table 13. [e] This series included a fractional-melting study, which involved long equilibration times resulting in relatively large uncertainties in heat leaks. Therefore, this value was not included in the average.

Table 9 lists two-phase heat capacities for 2- and 8-methylquinoline measured by DSC for three cell fillings. Slow decomposition of the sample at temperatures above approximately $T = 700$ K precluded reliable heat capacity measurements in this region. However, sample decomposition was sufficiently slow to allow a rapid heating method[33,34] to be used to determine the temperature of conversion from the two-phase (liquid + gas) to the one-phase (fluid) region for a series of filling densities of the hermetically sealed dsc cells. The conversion temperature is indicated by a sudden decrease in heat capacity when the phase boundary is crossed during heating. The heating rate used was 0.33 $\mathrm{K{\cdot}s^{-1}}$. The filling densities and phase boundary temperatures are listed in Table 10 and are shown in Figures 3 and 4. The experimental critical temperature corresponds

Table 8. Molar Heat Capacities $C_{\mathrm{sat,m}}$ at the Vapor-Saturation Pressure Measured with Adiabatic Calorimetry (R = 8.314472 J·K^{-1}·mol^{-1})

	$\langle T\rangle$	$C_{\mathrm{sat,m}}$	ΔT		$\langle T\rangle$	$C_{\mathrm{sat,m}}$	ΔT		$\langle T\rangle$	$C_{\mathrm{sat,m}}$	ΔT		$\langle T\rangle$	$C_{\mathrm{sat,m}}$	ΔT
N^a	K	R^b	K	N^a	K	R^b	K	N^a	K	R^b	K	N^a	K	R^b	K
2-Methylquinoline															
Crystal															
9	5.565	0.075	0.776	9	32.521	3.413	3.392	6	89.020	8.388	7.836	6	199.527	15.043	12.017
9	6.404	0.115	0.949	9	36.118	3.866	3.802	7	92.314	8.597	8.485	11	205.563	15.427	17.924
9	7.354	0.168	0.999	9	39.676	4.287	3.316	6	97.212	8.896	8.534	6	211.512	15.810	11.947
9	8.354	0.236	1.028	9	43.663	4.732	4.658	7	101.283	9.148	9.439	3	222.269	16.476	12.932
9	9.372	0.317	1.020	9	48.556	5.235	5.127	6	106.317	9.452	9.657	6	223.465	16.571	11.954
9	10.395	0.418	1.045	7	52.536	5.622	4.447	7	110.830	9.720	9.646	11	223.489	16.601	17.917
9	11.525	0.530	1.214	8	53.493	5.707	4.766	6	116.092	10.027	9.882	3	235.038	17.354	12.581
9	12.800	0.680	1.340	9	53.982	5.763	5.725	6	125.969	10.602	9.856	6	235.463	17.397	12.043
9	14.207	0.853	1.473	7	57.457	6.081	5.364	6	135.922	11.183	9.894	4	239.039	17.656	12.159
9	15.748	1.056	1.609	8	58.644	6.189	5.506	6	145.887	11.765	9.963	11	241.522	17.837	18.143
9	17.456	1.296	1.803	9	60.029	6.289	6.368	6	155.924	12.362	10.051	3	247.485	18.275	12.241
9	19.364	1.568	2.014	7	63.196	6.551	6.087	6	166.033	12.967	10.123	4	250.701	18.532	11.139
9	21.488	1.872	2.236	8	64.469	6.650	6.119	6	176.218	13.582	10.182	11	257.751	19.137	14.289
9	23.827	2.212	2.444	7	69.557	7.057	6.612	6	187.413	14.277	12.203	3	259.671	19.323	11.891
9	26.425	2.586	2.753	7	76.519	7.555	7.294	11	190.571	14.461	12.051	4	261.219	19.430	9.879
9	29.313	2.985	3.025	7	84.084	8.068	7.820								
Liquid															
13	251.778	24.755	1.525	4	278.519	25.981	9.720	14	310.635	27.524	16.469	14	393.311	31.667	16.599
13	256.023	24.958	6.966	13	285.396	26.306	15.152	14	327.127	28.348	16.487	14	409.824	32.485	16.571
13	263.547	25.304	8.081	3	286.607	26.362	9.639	14	343.642	29.171	16.510	14	426.331	33.299	16.478
13	272.705	25.711	10.236	14	294.192	26.720	16.381	14	360.173	30.004	16.534	14	439.475	33.944	9.871
3	277.131	25.913	9.292	13	300.519	27.028	15.156	14	376.729	30.837	16.566				
8-Methylquinoline															
Crystal															
12	6.105	0.097	0.891	12	25.981	2.564	2.678	11	69.002	6.647	6.677	10	160.436	12.559	13.933
12	7.027	0.152	0.936	12	28.806	2.909	2.974	11	75.986	7.151	7.276	10	174.360	13.450	13.919
12	8.004	0.224	0.976	12	31.942	3.275	3.301	11	83.657	7.685	8.053	9	175.636	13.523	10.141
12	9.004	0.317	1.010	12	35.444	3.661	3.705	10	86.444	7.873	6.779	9	186.907	14.255	12.396
12	10.058	0.431	1.098	12	39.363	4.071	4.134	11	91.886	8.239	8.279	10	188.792	14.379	14.953
12	11.207	0.569	1.201	12	43.726	4.505	4.589	10	94.092	8.380	8.516	9	199.749	15.112	13.293
12	12.474	0.728	1.325	12	48.586	4.956	5.124	11	100.745	8.813	9.267	10	203.201	15.350	13.870
12	13.870	0.921	1.472	11	52.434	5.302	4.281	10	103.064	8.960	9.427	9	212.458	15.991	12.161
12	15.424	1.139	1.636	12	53.968	5.437	5.639	10	112.708	9.570	9.861	10	215.194	16.182	10.084
12	17.144	1.384	1.807	11	57.175	5.709	5.177	10	123.652	10.253	12.026	9	224.456	16.898	11.770
12	19.041	1.649	1.986	12	59.941	5.936	6.302	10	135.628	11.004	11.925	10	225.286	16.955	10.074
12	21.132	1.933	2.192	11	62.717	6.161	5.879	10	147.533	11.744	11.886	10	235.367	18.150	10.105
12	23.437	2.242	2.413												
Liquid															
14	175.791	22.338	5.385	13	253.723	24.874	8.944	16	282.822	26.157	14.145	17	357.579	29.789	16.206
14	181.223	22.437	5.462	15	254.073	24.883	8.351	16	296.934	26.817	14.076	17	373.800	30.595	15.945
14	186.716	22.561	5.508	10	256.362	24.987	8.519	16	310.972	27.489	14.006	17	389.626	31.383	15.700
15	232.541	24.008	5.985	16	257.672	25.036	11.941	17	312.230	27.552	13.982	17	405.689	32.173	16.431
15	238.699	24.260	6.322	10	265.240	25.358	9.244	17	326.773	28.262	15.059	17	422.454	32.993	17.130
15	245.879	24.536	8.034	16	269.688	25.560	12.043	17	341.893	29.006	15.129	17	437.107	33.707	12.207
14	253.584	24.860	10.226												

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

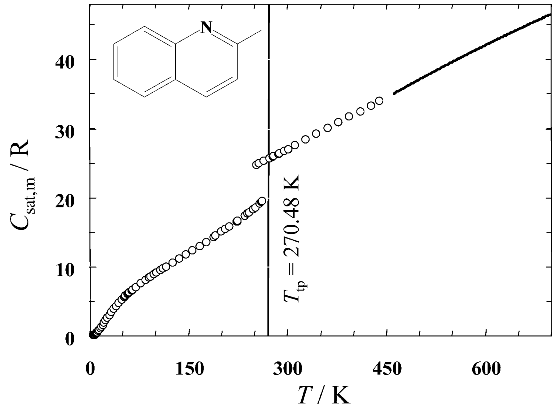


Figure 1. Molar heat capacities at saturation pressure $C_{\mathrm{sat,m}}$ for 2-methylquinoline measured in this research. The vertical line indicates the triple-point temperature.

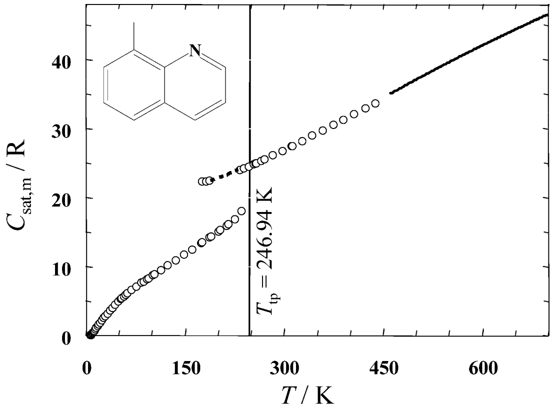


Figure 2. Molar heat capacities at saturation pressure $C_{\mathrm{sat,m}}$ for 8-methylquinoline measured in this research. The vertical line indicates the triple-point temperature.

to the maximum in the curve of temperature against filling density. The experimental critical temperature for 2-methylquinoline is T_c = (778 ± 2) K, and for 8-methylquinoline the value is T_c = (787 ± 2) K.

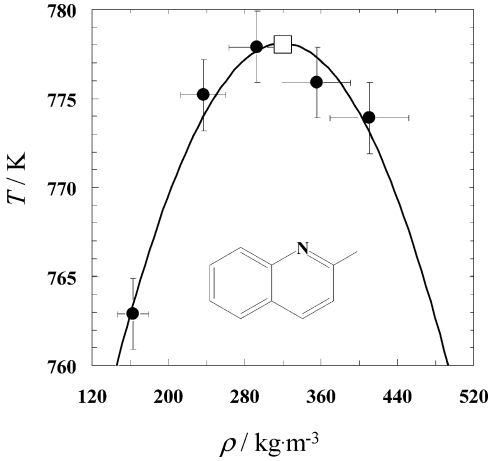


Figure 3. (Vapor + liquid) coexistence region for 2-methylquinoline. ρ denotes density. ●, Experimental values of this research listed in Table 10. □, Experimental critical temperature and estimated critical density determined in this research. The curve represents a fit of a second-order polynomial to the experimental values.

The Wagner equation,[35] as formulated by Ambrose,[36] was used to represent the vapor pressures

$$\ln\left(\frac{p}{p_c}\right) = \left(\frac{1}{T_r}\right)\{A(1 - T_r) + B(1 - T_r)^{1.5} + C(1 - T_r)^{2.5} + D(1 - T_r)^5\} \quad (5)$$

where $T_r = T/T_c$. The fitting procedure has been described.[27] The critical temperatures measured in this research were used in the fits. The critical pressures p_c were selected with Waring's criterion for $T_r = 0.85$.[37] Application of this criterion was discussed previously by Steele.[27] The critical density listed in Table 11 was chosen to optimize agreement between the measured densities listed in Table 2 and values calculated with the extended corresponding states equation of Riedel,[38] as formulated by Hales and Townsend[10]

$$\frac{\rho}{\rho_c} = 1.0 + 0.85(1.0 - T_r) + (1.6916 + 0.9846\omega)(1.0 - T_r)^{1/3} \quad (6)$$

Deviations of the experimental densities from the corresponding states equation are included in Table 2.

Molar enthalpies of vaporization $\Delta_l^g H_m$ were derived from the Wagner-equation fit by means of the Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta_l^g H_m}{T\Delta_l^g V_m} \quad (7)$$

where $\Delta_l^g V_m$ is the increase in molar volume from the liquid to the real vapor. The Wagner-equation fit was employed to derive dp/dT. Estimates of liquid-phase volumes were made with eq 6. 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,[39] and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera.[40] Our research group has successfully applied this formulation for third virial coefficients in analyses of the thermodynamic properties of a range of compounds in recent years. A list of compounds studied successfully was included in a recent publication by the group.[2] In all cases the agreement between the entropies for the ideal gas-state derived using this formulation and those obtained from statistical thermodynamics via accurate spectroscopic measurements was

Table 9. Measured Two-Phase (Liquid + Vapor) Heat Capacities[a]

T/K	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$
	2-Methylquinoline		
V(cell)/cm^3	0.0561	0.0534	0.0561
mass/g	0.01165	0.01629	0.02194
335.0	28.9	28.9	28.9
355.0	30.0	29.9	29.7
375.0	30.7	30.9	30.7
395.0	32.0	32.1	31.9
415.0	33.1	32.8	33.3
435.0	34.2	33.9	34.4
455.0	35.2	34.9	35.4
475.0	36.6	36.2	36.3
495.0	38.1	37.2	37.3
515.0	39.5	38.5	38.6
535.0	41.0	39.5	39.6
555.0	42.4	40.5	40.7
575.0	44.2	41.7	41.7
595.0	45.2	43.1	42.5
615.0	47.2	44.4	43.5
635.0	48.7	45.2	44.6
655.0	50.2	46.5	45.7
675.0	52.1	47.8	46.9
695.0	53.9	49.1	47.9
715.0	55.6	50.2	48.9
735.0	59.1	52.3	51.4
755.0	57.0	55.8	
	8-Methylquinoline		
V(cell)/cm^3	0.0561	0.0534	0.0561
mass/g	0.01079	0.01638	0.02362
315.0		25.8	26.1
335.0	29.9	29.1	27.5
355.0	30.1	30.5	29.5
375.0	29.6	30.8	30.4
395.0	32.0	31.8	31.2
415.0	33.5	33.1	32.4
435.0	34.3	34.2	33.5
455.0	35.3	35.2	34.3
475.0	36.3	36.2	35.5
495.0	37.8	37.5	36.5
515.0	39.4	38.7	37.3
535.0	40.7	39.5	38.5
555.0	41.7	40.9	39.5
575.0	42.8	42.4	40.2
595.0	44.4	43.6	41.2
615.0	45.6	44.7	42.3
635.0	47.1	45.3	42.8
655.0	49.3	46.5	44.4
675.0	50.6	47.8	44.6
695.0	53.0	48.9	45.8
715.0	54.3	50.1	46.9
735.0	56.3	51.9	47.2
755.0	60.0	52.5	49.6

[a] m is the mass of the sample, and V(cell) is the volume of the dsc cell at $T = 298.15$ K after sealing ($R = 8.314472$ J·K^{-1}·mol^{-1})

Table 10. Densities and Temperatures Used to Define the Two-Phase Coexistence Curve near T_c

T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}
	2-Methylquinoline		
773.9	410.8	775.9	355.4
762.9	163.3	775.2	236.6
777.9	292.9		
	8-Methylquinoline		
784.0	244.7	785.1	349.8
769.9	160.5	775.8	444.6
786.0	318.7		

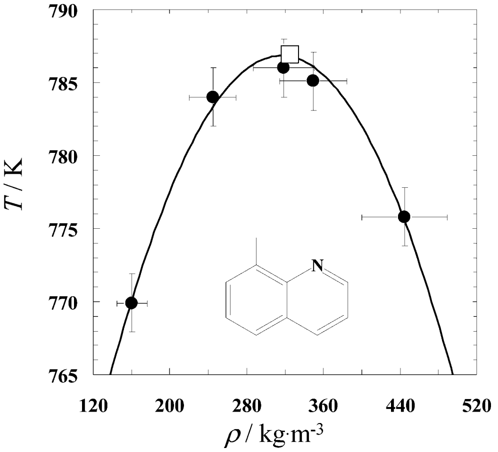


Figure 4. (Vapor + liquid)coexistence region for 8-methylquinoline. ρ denotes density. ●, Experimental values of this research listed in Table 10. □, Experimental critical temperature and estimated critical density determined in this research. The curve represents a fit of a second-order polynomial to the experimental values.

Table 11. Parameters for the Wagner Vapor-Pressure Equation, Selected Critical Constants, and Acentric Factor

	2-methylquinoline	
A	−8.370206	$T_c = 778$ K
B	2.914441	$p_c = 4030$ kPa
C	−3.761685	$\rho_c = 320.5$ kg·m^{-3}
D	−3.195981	$\omega = 0.3807$
	8-methylquinoline	
A	−8.203810	$T_c = 787$ K
B	2.794040	$p_c = 4300$ kPa
C	−3.571108	$\rho_c = 326.1$ kg·m^{-3}
D	−3.142968	$\omega = 0.3561$

Table 12. Enthalpies of Vaporization ΔH_m Obtained from the Wagner and Clapeyron Equations

T / K	$\Delta_l^g H_m$ / kJ·mol^{-1}	T / K	$\Delta_l^g H_m$ / kJ·mol^{-1}	T / K	$\Delta_l^g H_m$ / kJ·mol^{-1}
		2-Methylquinoline			
298.15[a]	62.64 ± 0.13	440.00	53.01 ± 0.09	600.00[a]	41.40 ± 0.49
300.00[a]	62.50 ± 0.13	460.00	51.72 ± 0.10	620.00[a]	39.57 ± 0.59
320.00	61.04 ± 0.12	480.00	50.42 ± 0.12	640.00[a]	37.61 ± 0.70
340.00	59.62 ± 0.12	500.00	49.08 ± 0.16	660.00[a]	35.49 ± 0.81
360.00	58.23 ± 0.11	520.00	47.70 ± 0.20	680.00[a]	33.21 ± 0.95
380.00	56.89 ± 0.10	540.00	46.25 ± 0.26	700.00[a]	30.70 ± 1.09
400.00	55.57 ± 0.09	560.00[a]	44.72 ± 0.32		
420.00	54.29 ± 0.09	580.00[a]	43.11 ± 0.41		
		8-Methylquinoline			
298.15[a]	62.18 ± 0.13	440.00	52.78 ± 0.09	600.00[a]	41.51 ± 0.47
300.00[a]	62.05 ± 0.13	460.00	51.53 ± 0.10	620.00[a]	39.75 ± 0.57
320.00[a]	60.62 ± 0.12	480.00	50.26 ± 0.12	640.00[a]	37.86 ± 0.67
340.00	59.23 ± 0.11	500.00	48.96 ± 0.15	660.00[a]	35.84 ± 0.77
360.00	57.89 ± 0.10	520.00	47.61 ± 0.19	680.00[a]	33.66 ± 0.90
380.00	56.57 ± 0.10	540.00	46.20 ± 0.25	700.00[a]	31.28 ± 1.03
400.00	55.29 ± 0.09	560.00[a]	44.73 ± 0.31		
420.00	54.04 ± 0.09	580.00[a]	43.17 ± 0.38		

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

Table 13. Molar Thermodynamic Functions at Vapor-Saturation Pressure (R = 8.314472 J·K^{-1}·mol^{-1})[a]

T / K	$C_{sat,m}$ / R	$\Delta_0^T S_m$ / R	$\Delta_0^T H_m$ / RT	T / K	$C_{sat,m}$ / R	$\Delta_0^T S_m$ / R	$\Delta_0^T H_m$ / RT
			2-Methylquinoline				
			Crystal				
5.00[b]	0.055	0.018	0.014	100.00	9.071	8.818	4.892
10.00	0.378	0.138	0.102	120.00	10.255	10.578	5.688
20.00	1.659	0.764	0.539	140.00	11.421	12.246	6.424
30.00	3.079	1.708	1.152	160.00	12.605	13.848	7.122
40.00	4.325	2.770	1.794	180.00	13.814	15.402	7.798
50.00	5.379	3.851	2.408	200.00	15.073	16.922	8.463
60.00	6.295	4.915	2.982	220.00	16.345	18.418	9.121
70.00	7.088	5.946	3.513	240.00	17.716	19.898	9.779
80.00	7.794	6.939	4.004	260.00	19.258	21.376	10.448
90.00	8.451	7.896	4.462	270.48[b]	20.140	22.154	10.806
			Liquid				
250.00[b]	24.680	25.742	15.654	460.00[c]	35.019	43.571	22.095
260.00	25.141	26.718	16.010	480.00[c]	36.049	45.083	22.655
270.48	25.614	27.721	16.373	500.00[c]	37.080	46.575	23.212
280.00	26.049	28.615	16.695	520.00[c]	38.111	48.050	23.765
298.15	26.914	30.278	17.290	540.00[c]	39.135	49.507	24.315
300.00	27.003	30.444	17.350	560.00[c]	40.144	50.949	24.863
320.00	27.991	32.218	17.984	580.00[c]	41.130	52.375	25.407
340.00	28.990	33.945	18.602	600.00[c]	42.087	53.786	25.947
360.00	29.996	35.631	19.207	620.00[c]	43.010	55.181	26.482
380.00	31.002	37.280	19.801	640.00[c]	43.900	56.560	27.013
400.00	31.999	38.895	20.386	660.00[c]	44.769	57.925	27.538
420.00	32.987	40.480	20.963	680.00[c]	45.653	59.274	28.058
440.00[c]	33.975	42.038	21.532	700.00[c]	46.635	60.611	28.574
			8-Methylquinoline				
			Crystal				
5.00[b]	0.054	0.018	0.014	100.00	8.764	8.597	4.701
10.00	0.425	0.145	0.108	120.00	10.021	10.307	5.483
20.00	1.780	0.843	0.598	140.00	11.269	11.945	6.221
30.00	3.051	1.812	1.209	160.00	12.522	13.531	6.930
40.00	4.136	2.842	1.809	180.00	13.794	15.080	7.622
50.00	5.085	3.869	2.371	200.00	15.097	16.600	8.304
60.00	5.941	4.874	2.896	220.00	16.432	18.101	8.982
70.00	6.720	5.849	3.388	240.00	17.798	19.589	9.659
80.00	7.434	6.793	3.849	246.94[b]	18.280	20.103	9.894
90.00	8.115	7.709	4.286				
			Liquid				
170.00[b]	22.239	16.678	11.444	420.00	32.874	40.342	20.689
180.00	22.414	17.954	12.048	440.00[c]	33.845	41.894	21.265
200.00	22.910	20.340	13.108	460.00[c]	34.802	43.419	21.833
220.00	23.551	22.553	14.028	480.00[c]	35.763	44.921	22.393
240.00	24.309	24.634	14.852	500.00[c]	36.720	46.400	22.947
246.94	24.581	25.330	15.121	520.00[c]	37.666	47.859	23.495
260.00	25.136	26.611	15.611	540.00[c]	38.598	49.298	24.037
280.00	26.027	28.506	16.322	560.00[c]	39.511	50.718	24.574
298.15	26.875	30.167	16.939	580.00[c]	40.399	52.120	25.104
300.00	26.963	30.334	17.000	600.00[c]	41.256	53.504	25.628
320.00	27.930	32.105	17.653	620.00[c]	42.080	54.871	26.146
340.00	28.913	33.827	18.287	640.00[c]	42.874	56.219	26.656
360.00	29.910	35.508	18.905	660.00[c]	43.646	57.550	27.159
380.00	30.905	37.152	19.510	680.00[c]	44.426	58.865	27.656
400.00	31.894	38.762	20.104	700.00[c]	45.275	60.165	28.147

[a] Values are reported with one digit more than is justified by the experimental uncertainty. This is to avoid round-off errors in calculations based on these results. [b] Values at this temperature were calculated with graphically extrapolated heat capacities. [c] Values at this temperature are based on the fits of the dsc and vapor-pressure measurements described in the text. All other values are based on the adiabatic calorimetric results.

better than 0.1% over a temperature range of greater than 250 K. Third virial coefficients are required for accurate calculation of the volume of gas for pressures greater than 0.1 MPa. Standard uncertainties in the virial coefficients were assumed to be 10% in the calculation results reported here for each methylquinoline. Derived enthalpies of vaporization are reported in Table 12. For $p > 0.1$ MPa, the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived molar enthalpies of vaporization.

Calculation of $C_{sat,m}$ values from the values listed in Table 9 has been described.[26,41] Reliable vapor pressures and densities for the liquid phase are required for the calculation of $C_{sat,m}$ values. The Wagner equation (equation 5) was used with the parameters listed in Table 11 for the

Table 14. Standard Molar Thermodynamic Properties in the Gaseous State at $p = p^\circ = 101.325$ kPa ($R = 8.314472$ $J \cdot K^{-1} \cdot mol^{-1}$)

T	$\Delta_0^T H_m^\circ$	$\Delta_{imp} H_m^\circ$	$\Delta_0^T S_m^\circ$	$\Delta_{imp} S_m^\circ$	$\Delta_f H_m^\circ$	$\Delta_f S_m^\circ$	$\Delta_f G_m^\circ$
K	RT	RT[a]	R	R[b]	RT	R	RT
2-Methylquinoline							
298.15[c]	42.56 ± 0.06	0.00	45.77 ± 0.06	0.00	63.65 ± 0.19	−43.32 ± 0.06	106.98 ± 0.18
300.00[c]	42.41 ± 0.06	0.00	45.88 ± 0.06	0.00	63.20 ± 0.19	−43.38 ± 0.06	106.58 ± 0.18
320.00	40.93 ± 0.05	0.00	47.08 ± 0.06	0.00	58.66 ± 0.18	−43.99 ± 0.06	102.65 ± 0.17
340.00	39.69 ± 0.05	0.00	48.29 ± 0.05	0.00	54.68 ± 0.16	−44.54 ± 0.05	99.22 ± 0.16
360.00	38.66 ± 0.04	0.00	49.50 ± 0.05	0.00	51.16 ± 0.15	−45.03 ± 0.05	96.19 ± 0.15
380.00	37.81 ± 0.04	0.01	50.72 ± 0.05	0.01	48.04 ± 0.15	−45.47 ± 0.05	93.51 ± 0.15
400.00	37.11 ± 0.03	0.01	51.94 ± 0.05	0.01	45.26 ± 0.14	−45.86 ± 0.05	91.12 ± 0.14
420.00	36.53 ± 0.03	0.02	53.15 ± 0.05	0.02	42.76 ± 0.13	−46.21 ± 0.05	88.97 ± 0.14
440.00	36.06 ± 0.03	0.04	54.37 ± 0.05	0.03	40.51 ± 0.13	−46.53 ± 0.05	87.04 ± 0.13
460.00	35.67 ± 0.03	0.05	55.58 ± 0.05	0.04	38.47 ± 0.12	−46.81 ± 0.05	85.28 ± 0.13
480.00	35.37 ± 0.04	0.08	56.79 ± 0.06	0.06	36.62 ± 0.12	−47.06 ± 0.06	83.68 ± 0.12
500.00	35.13 ± 0.05	0.11	57.98 ± 0.06	0.08	34.94 ± 0.12	−47.29 ± 0.06	82.22 ± 0.12
520.00	34.95 ± 0.06	0.15	59.18 ± 0.07	0.11	33.40 ± 0.12	−47.48 ± 0.07	80.88 ± 0.12
540.00	34.81 ± 0.07	0.20	60.36 ± 0.08	0.14	31.98 ± 0.12	−47.66 ± 0.08	79.65 ± 0.12
560.00	34.72 ± 0.09	0.25	61.54 ± 0.10	0.19	30.69 ± 0.13	−47.82 ± 0.10	78.50 ± 0.12
580.00	34.67 ± 0.11	0.32	62.71 ± 0.12	0.24	29.49 ± 0.14	−47.95 ± 0.11	77.44 ± 0.13
600.00	34.65 ± 0.13	0.40	63.87 ± 0.13	0.30	28.39 ± 0.15	−48.07 ± 0.13	76.46 ± 0.14
620.00	34.65 ± 0.15	0.50	65.02 ± 0.16	0.37	27.36 ± 0.17	−48.17 ± 0.16	75.54 ± 0.16
640.00	34.68 ± 0.17	0.60	66.15 ± 0.18	0.44	26.41 ± 0.19	−48.27 ± 0.18	74.67 ± 0.17
660.00	34.72 ± 0.19	0.72	67.28 ± 0.20	0.53	25.52 ± 0.21	−48.35 ± 0.20	73.86 ± 0.19
680.00	34.78 ± 0.22	0.85	68.38 ± 0.23	0.63	24.68 ± 0.23	−48.42 ± 0.22	73.10 ± 0.20
700.00	34.84 ± 0.24	0.99	69.47 ± 0.25	0.74	23.89 ± 0.26	−48.49 ± 0.25	72.38 ± 0.22
8-Methylquinoline							
298.15[c]	42.02 ± 0.06	0.00	45.53 ± 0.06	0.00	66.73 ± 0.32	−43.56 ± 0.06	110.29 ± 0.32
300.00[c]	41.88 ± 0.06	0.00	45.64 ± 0.06	0.00	66.26 ± 0.32	−43.62 ± 0.06	109.88 ± 0.32
320.00[c]	40.44 ± 0.05	0.00	46.86 ± 0.06	0.00	61.54 ± 0.30	−44.22 ± 0.06	105.76 ± 0.30
340.00	39.24 ± 0.04	0.00	48.07 ± 0.05	0.00	57.39 ± 0.28	−44.76 ± 0.05	102.15 ± 0.28
360.00	38.25 ± 0.04	0.00	49.29 ± 0.05	0.00	53.74 ± 0.27	−45.24 ± 0.05	98.98 ± 0.27
380.00	37.42 ± 0.04	0.01	50.51 ± 0.05	0.01	50.48 ± 0.25	−45.68 ± 0.05	96.16 ± 0.25
400.00	36.74 ± 0.03	0.01	51.73 ± 0.05	0.01	47.58 ± 0.24	−46.06 ± 0.05	93.65 ± 0.24
420.00	36.18 ± 0.03	0.02	52.96 ± 0.05	0.02	44.98 ± 0.23	−46.41 ± 0.05	91.39 ± 0.23
440.00	35.73 ± 0.03	0.03	54.17 ± 0.05	0.03	42.63 ± 0.22	−46.72 ± 0.05	89.35 ± 0.22
460.00	35.36 ± 0.03	0.05	55.38 ± 0.05	0.04	40.50 ± 0.21	−47.01 ± 0.05	87.50 ± 0.21
480.00	35.06 ± 0.04	0.07	56.58 ± 0.05	0.05	38.56 ± 0.20	−47.26 ± 0.05	85.82 ± 0.20
500.00	34.83 ± 0.04	0.10	57.78 ± 0.06	0.08	36.79 ± 0.19	−47.49 ± 0.06	84.28 ± 0.20
520.00	34.65 ± 0.05	0.14	58.96 ± 0.07	0.10	35.17 ± 0.19	−47.70 ± 0.07	82.87 ± 0.19
540.00	34.51 ± 0.07	0.19	60.14 ± 0.08	0.14	33.68 ± 0.19	−47.89 ± 0.08	81.57 ± 0.19
560.00	34.42 ± 0.08	0.24	61.30 ± 0.09	0.18	32.31 ± 0.19	−48.06 ± 0.09	80.37 ± 0.19
580.00	34.36 ± 0.10	0.31	62.45 ± 0.11	0.22	31.04 ± 0.19	−48.21 ± 0.11	79.25 ± 0.19
600.00	34.33 ± 0.12	0.38	63.59 ± 0.13	0.28	29.86 ± 0.20	−48.35 ± 0.13	78.21 ± 0.19
620.00	34.33 ± 0.14	0.47	64.71 ± 0.15	0.34	28.77 ± 0.21	−48.48 ± 0.15	77.25 ± 0.20
640.00	34.34 ± 0.16	0.57	65.82 ± 0.17	0.42	27.75 ± 0.22	−48.59 ± 0.17	76.34 ± 0.21
660.00	34.37 ± 0.19	0.67	66.92 ± 0.19	0.50	26.79 ± 0.23	−48.70 ± 0.19	75.49 ± 0.22
680.00	34.41 ± 0.21	0.80	68.00 ± 0.22	0.59	25.89 ± 0.25	−48.80 ± 0.22	74.69 ± 0.23
700.00	34.45 ± 0.23	0.93	69.06 ± 0.24	0.69	25.04 ± 0.27	−48.90 ± 0.24	73.94 ± 0.24

[a] Gas-imperfection correction included in the standard molar enthalpy for the gas. The standard molar enthalpy of the gas is calculated relative to that of the crystals at $T \to 0$. [b] Gas-imperfection correction included in the standard molar entropy of the gas. [c] Values at this temperature were calculated with extrapolated vapor pressures calculated from the fitted parameters of the Wagner equation.

vapor pressures, and densities were calculated with eq 6, also with the parameters in Table 11. A polynomial was fit to the liquid phase heat capacities derived from the DSC results. Values of $C_{sat,m}$ determined with adiabatic calorimetry in this research for the temperature range $300 < (T/K) < 445$ were included and weighted by a factor of 100 greater than the DSC values. These were included to ensure a smooth junction between the values determined with the two methods.

Condensed-phase molar entropies and molar enthalpies relative to those of the crystals at $T \to 0$ for the solid and liquid phases under vapor saturation pressure are listed in Table 13. These were derived by integration of the smoothed molar heat capacities corrected for premelting, together with the molar entropy and molar enthalpy of fusion. The molar 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. Because of limitations in the spline-function procedure, some acceptable values from Table 8 were not included in the fit, while in other regions graphical values were introduced to ensure that the second derivative of the heat capacity with respect to temperature was a smooth function of temperature. Premelting corrections were made using standard methods[31] for solid-insoluble impurities and the mole fraction impurity value shown in Table 1. The presence of solid-soluble impurities in the sample of 2-methylquinoline results in this value ($x_{pre} = 0.00008$) being much smaller than the mole fraction impurity ($x = 0.0004$) listed in Table 6.

Standard molar enthalpies and standard molar entropies for the methylquinolines ($C_{10}H_9N$) at selected temperatures for the ideal gas at $p = 101.325$ kPa were calculated with values in Tables 12 and 13 and are listed in columns 2 and 4 of Table 14. The derived standard molar enthalpies and standard molar entropies for the methylquinolines in the ideal gaseous state were combined with the standard molar

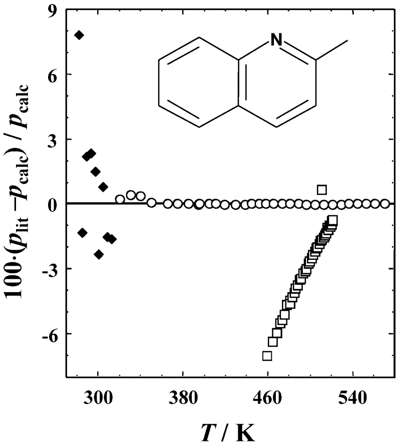


Figure 5. Deviation plot for vapor pressures of 2-methylquinoline reported in the literature from values calculated with the Wagner equation (equation 5) and the parameters listed in Table 11. ○, This research; □, Malanowski;[46] ♦, Van de Rostyne and Prausnitz.[47]

enthalpies of formation for the liquid (Table 4) to calculate the standard molar enthalpies, standard molar entropies, and standard molar Gibbs free energies of formation listed in columns 6, 7, and 8, respectively, of Table 14. Standard molar enthalpies and standard molar entropies for H_2(equilibrium, g), N_2(g), and C(graphite) were calculated with parameters from JANAF tables.[42] All combined uncertainties in Table 14 represent one standard deviation and do not include uncertainties in the properties of the elements.

Discussion

The enthalpies of formation in the liquid phase for 2- and 8-methylquinoline were determined previously by Ribeiro da Silva et al.[43] The values reported there are $\{\Delta_f H^\circ_m = (93.0 \pm 2.5)\ \text{kJ} \cdot \text{mol}^{-1})\}$ for 2-methylquinoline and $\{\Delta_f H^\circ_m = (102.0 \pm 2.4)\ \text{kJ} \cdot \text{mol}^{-1})\}$ for 8-methylquinoline. The values are in good accord with those reported here (Table 4), $\{\Delta_f H^\circ_m = (95.15 \pm 0.90)\ \text{kJ} \cdot \text{mol}^{-1})\}$ for 2-methylquinoline and $\{\Delta_f H^\circ_m = (103.23 \pm 1.58)\ \text{kJ} \cdot \text{mol}^{-1})\}$ for 8-methylquinoline. Samples used by Ribeiro da Silva were purchased commercially and purified by repeated vacuum distillation "until the combustion results were consistent and the carbon-dioxide recovery ratios were satisfactory".[43] This method of analysis does not detect isomeric impurities, which might account partially for the small differences from the present research.

Critical properties for 2- and 8-methylquinoline have not been determined by experiment previously. The group-contribution method of Joback[44,45] provides the estimate $T_c = 776$ K for both compounds, which is in excellent accord with the experimental value for 2-methylquinoline, but differs by 11 K for 8-methylquinoline. The new experimental values provided here can be used to develop improved group parameters.

Deviations of literature vapor pressures from those of this research are shown in Figures 5 and 6. The ebulliometric results reported by Malanowski in 1961[46] show surprisingly large deviations from those of the present research for both compounds. Analogous large deviations were seen previously for quinoline and isoquinoline.[1] The origin of the large differences is unknown, but the consistently large differences suggest the existence of systematic errors in the earlier work.[46] Vapor pressures reported by Van De Rostyne and Prausnitz[47] determined by a gas-saturation method at temperatures below the lowest values of this research show excellent agreement with the extrapolated values of the present research, as shown in Figure 5. The scatter in the literature values is as expected for gas-saturation studies.

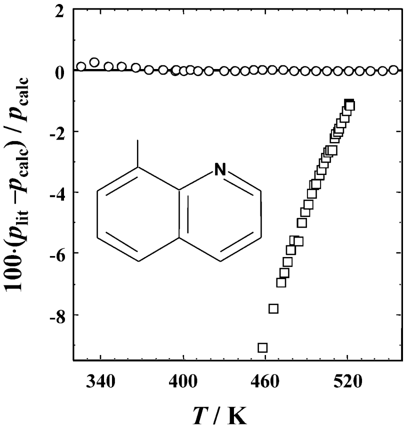


Figure 6. Deviation plot for vapor pressures of 8-methylquinoline reported in the literature from values calculated with the Wagner equation (eq 5) and the parameters listed in Table 11. ○, This research; □ , Malanowski.[46]

Ribeiro da Silva et al.[43] determined the enthalpy of vaporization at the temperature $T = 298.15$ K for 2- and 8-methylquinoline by measuring enthalpy increments between the gas at temperatures near 373 K and the liquid at 298.15 K together with an estimated enthalpy increment for the gas phase between $T = 373$ K and 298.15 K. The reported values for $\Delta_l^g H_m$(298.15 K) are roughly 3.5 $\text{kJ} \cdot \text{mol}^{-1}$ higher than those determined in the present research. Uncertainties claimed by Ribeiro da Silva et al.[43] were 1.9 $\text{kJ} \cdot \text{mol}^{-1}$; however, uncertainties associated with the estimate of the gas-phase enthalpy increment were not considered. Combined uncertainties (95% level of confidence) for $\Delta_l^g H_m$(298.15 K) in the present research are 0.3 $\text{kJ} \cdot \text{mol}^{-1}$. A short extrapolation of the measured vapor pressures was involved in the calculation of $\Delta_l^g H_m$(298.15 K) in the present research; however, any uncertainty associated with this extrapolation is too small to account for the difference in the reported values.

Thermodynamic property measurements similar to those reported here were completed also for 2,6-dimethylquinoline by the Bartlesville Thermodynamics Group. Comparisons with statistical calculations of ideal-gas properties and other generalizations for the family of methylquinolines will be discussed together with publication of the results for 2,6-dimethylquinoline.

Acknowledgment

We acknowledge Professor E. J. "Pete" Eisenbraun and his research group at Oklahoma State University for preparing the methylquinoline samples. We acknowledge the contributions of Stephen E. Knipmeyer to the DSC studies, An (Andy) Nguyen to the vapor-pressure measurements, and Aaron P. Rau to vapor transfer of the samples prior to the property measurements.

Literature Cited

(1) Steele, W. V.; Archer, D. G.; Chirico, R. D.; Collier, W. B.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Gammon, B. E. The Thermodynamic Properties of Quinoline and Isoquinoline. *J. Chem. Thermodyn.* **1988**, *20*, 1233−1264.

(2) Steele, W. V.; Chirico, R. D.; Cowell, A. B.; Nguyen, A.; Knipmeyer, S. E. Possible Precursors and Products of Deep Hydrodesulfurization of Gasoline and Distillate Fuels III. The Thermodynamic

Properties of 1,2,3,4-Tetrahydrodibenzothiophene. *J. Chem. Thermodyn.* **2004**, *36*, 497−509.

(3) Coursey, J. S.; Schwab, D. J.; Dragoset, R. A. *Atomic Weights and Isotopic Compositions*, version 2.4; 2003; Available at http://physics.nist.gov/Comp (September 16, 2004); National Institute of Standards and Technology, Gaithersburg, MD. Originally published as Coplen, T. B. Atomic Weights of the Elements 1999. *Pure Appl. Chem.* **2001**, *73*, 667; Rosman, K. J. R.; Taylor, P. D. P. Isotopic Compositions of the Elements. *J. Phys. Chem. Ref. Data* **1997**, *27*, 1275; and Audi, G.; Wapstra, A. H. The 1995 Update To The Atomic Mass Evaluation. *Nucl. Phys. A* **1995**, *595*, 409.

(4) Mohr, P. J.; Taylor, B. N. CODATA Recommended Values for the Fundamental Constants 1998. *J. Phys. Chem. Ref. Data* **1999**, *28*, 1713−1852.

(5) Metrologia **1969**, *5*, 35−44.

(6) Goldberg, R. N.; Weir, R. D. Conversion of Temperatures and Thermodynamic Properties to the Basis of the International Temperature Scale of 1990. *Pure Appl. Chem.* **1992**, *64*, 1545−1562.

(7) McCrackin, F. L.; Chang, S. S. Simple Calibration Procedures for Platinum Resistance Thermometers from 2.5 to 14 K. *Rev. Sci. Instrum.* **1975**, *46*, 550−553.

(8) Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Smith, N. K.; Steele, W. V. The Thermodynamic Properties of 4,5,9,10-Tetrahydropyrene and 1,2,3,6,7,8-Hexahydropyrene. *J. Chem. Thermodyn.* **1993**, *25*, 729−761.

(9) Chirico, R. D.; Steele, W. V. Reconciliation of Calorimetrically and Spectroscopically Derived Thermodynamic Properties at Pressures Greater Than 0.1 MPa for Benzene and Methylbenzene. The Importance of the Third Virial Coefficient. *Ind. Eng. Chem. Res.* **1994**, *33*, 157−167.

(10) Hales, J. L.; Townsend, R. Liquid Densities from 293 K to 490 K of Nine Aromatic Hydrocarbons. *J. Chem. Thermodyn.* **1972**, *4*, 763−772.

(11) Good, W. D.; Moore, R. T. Enthalpies of Formation of Ethylenediamine, 1,2-Propanediamine, 1,2-Butanediamine, 2-Methyl-1,2-propanediamine and Isobutylamine. *J. Chem. Eng. Data* **1970**, *15*, 150−154.

(12) Good, W. D. Enthalpies of Combustion of Nine Organic Nitrogen Compounds Related to Petroleum. *J. Chem. Eng. Data* **1972**, *17*, 28−31.

(13) Good, W. D.; Scott, D. W.; Waddington, G. Combustion Calorimetry of Organic Fluorine Compounds by a Rotating-Bomb Method. *J. Phys. Chem.* **1956**, *60*, 1080−1089.

(14) Good, W. D.; Douslin, D. R.; Scott, D. W.; George, A.; Lacina, J. L.; Dawson, J. P. Thermochemistry and Vapor Pressures of Aliphatic Fluorocarbons. A Comparison of the C−F and C−H Thermochemical Bond Energies. *J. Phys. Chem.* **1959**, *63*, 1133−1138.

(15) Guthrie, G. B.; Scott, D. W.; Hubbard, W. N.; Katz, C.; McCullough, J. P.; Gross, M. E.; Williamson, K. D.; Waddington, G. Thermodynamic Properties of Furan. *J. Am. Chem. Soc.* **1952**, *74*, 4662−4669.

(16) Smith, N. K.; Stewart, R. C., Jr.; Osborn, A. G.; Scott, D. W. Pyrene: Vapor Pressures, Enthalpy of Combustion, and Chemical Thermodynamic Properties. *J. Chem. Thermodyn.* **1980**, *12*, 919−926.

(17) Chirico, R. D.; Hossenlopp, I. A.; Nguyen, A.; Strube, M. M.; Steele W. V. Thermochemical and Thermophysical Properties of Organic Compounds Derived From Fossil Substances. Thermodynamic Studies Related to the Hydrogenation of Phenanthrene. Department of Energy Report No. NIPER-247, April 1987 (NTIS Report No. DE87001252).

(18) Goldberg, R. N.; Nuttall, R. N.; Prosen, E. J.; Brunetti, A. P. NBS Report 10437, U.S. Department of Commerce, National Bureau of Standards, June 1971.

(19) Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Chapter 5, pp 75−128. For those who cannot obtain a copy of this reference, the following source details the items in question, but in an earlier version in which some of the ancillary data are inaccurate. Hubbard, W. N.; Scott, D. W.; Waddington, W. Reduction to Standard States (at 25 °C) of Bomb Calorimetric Data for Compounds of Carbon, Hydrogen, Oxygen, and Sulfur *J. Phys. Chem.* **1954**, *58*, 152−162.

(20) Good, W. D.; Smith, N. K. Enthalpies of Combustion of Toluene, Benzene, Cyclohexane, Cyclohexene, Methylcyclopentane, 1-Methylcyclopentene, and *n*-Hexane. *J. Chem. Eng. Data* **1969**, *14*, 101−106.

(21) Swietoslawski, W. *Ebulliometric Measurements*; Reinhold: New York, 1945.

(22) Osborn A. G.; Douslin, D. R. Vapor Pressure Relations for 36 Sulfur Compounds Present in Petroleum. *J. Chem. Eng. Data* **1966**, *11*, 502−509.

(23) Wagner, W.; Pruss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387−535.

(24) Douslin, D. R.; McCullough, J. P. Report of Investigation 6149. U.S. Bureau of Mines, 1963; p 11.

(25) Douslin, D. R.; Osborn A. G. Pressure Measurements in the 0.01−0.30 mm Range with an Inclined-Piston Gauge. *J. Sci. Instrum.* **1965**, *42*, 369−373.

(26) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Smith, N. K. High-Temperature Heat-Capacity Measurements and Critical Property Determinations Using a Differential Scanning Calorimeter. (Development of Methodology and Application to Pure Organic Compounds) NIPER-360, December 1988. Published by DOE Fossil Energy, Bartlesville Project Office. Available from NTIS Order No. DE89000709.

(27) Steele, W. V. Fifty Years of Thermodynamics Research at Bartlesville. The Hugh M. Huffman Legacy. *J. Chem. Thermodyn.* **1995**, *27*, 135−162.

(28) Rossini, F. D. Assignment of Uncertainities to Thermochemical Data. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Chapter 14, pp 297−320.

(29) *CODATA Key Values for Thermodynamics*; Cox, J. D., Wagman, D. D., Medvedev, V. A., Eds.; Hemisphere: New York, 1989.

(30) McCullough, J. P.; Waddington, G. Melting-Point Purity Determinations: Limitations Evidenced by Calorimetric Studies in the Melting Region. *Anal. Chim. Acta* **1957**, *17*, 80−96.

(31) Westrum, E. F., Jr.; Furukawa, G. T.; McCullough, J. P. In *Experimental Thermodynamics*; McCullough, J. P., Scott, D. W., Eds.; Butterworths: London, 1968; Vol. 1, Chapter 5.

(32) Mastrangelo, S. V. R.; Dornte, R. W. Solid Solutions Treatment of Calorimetric Purity Data. *J. Am. Chem. Soc.* **1955**, *77*, 6200−6201.

(33) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. The Thermodynamic Properties of 2-Aminobiphenyl. *J. Chem. Thermodyn.* **1991**, *23*, 957−977.

(34) Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Steele, W. V. The Thermodynamic Properties of Dibenzothiophene. *J. Chem. Thermodyn.* **1991**, *23*, 431−450.

(35) Wagner, W. New Vapor Pressure Measurements for Argon and Nitrogen and a New Method of Establishing Rational Vapor Pressure Equations. *Cryogenics* **1973**, *13*, 470−482.

(36) Ambrose, D.; Walton, J. Vapor Pressures up to Their Critical Temperatures of Normal Alkanes and 1-Alkanols. *Pure Appl. Chem.* **1989**, *61*, 1395−1403.

(37) Waring, W. Form of a Wide-Range Vapor Pressure Equation. *Ind. Eng. Chem.* **1954**, *46*, 762−763.

(38) Riedel, L. Liquid Density in the Saturated State. Extension of the Theorem of Corresponding States II. *Chem.-Ing.-Tech.* **1954**, *26*, 259−264.

(39) Pitzer, K. S.; Curl, R. F., Jr. The Volumetric and Thermodynamic Properties of Fluids. III. Empirical Equation for the Second Virial Coefficent. *J. Am. Chem. Soc.* **1957**, *79*, 2369−2370.

(40) Orbey, H.; Vera, J. H. Correlation for the Third Virial Coefficient Using T_c, p_c, and ω as Parameters. *AIChE J.* **1983**, *29*, 107−113.

(41) Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Steele, W. V. Thermodynamic Properties of the Methylpyridines. Part 2: Vapor Pressures, Heat Capacities, Critical Properties, Derived Thermodynamic Functions between the Temperatures T = 250 K and T = 560 K, and Equilibrium Isomer Distributions for all Temperatures T = 250 K. *J. Chem. Thermodyn.* **1999**, *31*, 339−378.

(42) Chase, M. W., Jr. *NIST-JANAF Thermochemical Tables*, 4th ed.; Springer-Verlag: New York. 1998; Part I. Al−Co and Part II. Cr−Zr.

(43) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Amaral, L. M. P. F. Thermochemical Study of 2-, 4-, 6-, and 8-Methylquinoline. *J. Chem. Thermodyn.* **1995**, *27*, 565−574.

(44) Joback, K. G. S. M. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1984. The equations and parameters are listed in ref 45.

(45) Poling, B. E.; O'Connell, J.; Prausnitz, J. M. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2000.

(46) Malanowski, S. Vapor Pressures and Boiling Temperatures for Some Quinoline Bases. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1961**, *9*, 71−76.

(47) Van De Rostyne, C.; Prausnitz, J. M. Vapor Pressures of some Nitrogen-Containing, Coal-Derived Liquids. *J. Chem. Eng. Data* **1980**, *25*, 1−3.

Received for review November 16, 2004. Accepted December 29, 2004. We gratefully acknowledge the financial support of the Office of Fossil Energy of the U.S. Department of Energy (DOE). This research was funded within the Processing and Downstream Operations section of the Advanced Oil Recovery (AOR) program. The Bartlesville portion of the experiments was completed through BDM-Oklahoma under its contract with DOE for Management and Operations of the National Oil and Related Programs (NORP), Contract Number DE-AC22-94C91008. Manuscript preparation at Oak Ridge National Laboratory was completed under DOE Contract Number DE-AC05-00OR22725 with ORNL, which is managed and operated by UT-Battelle, LLC. Preparation of the manuscript at the National Institute of Standards and Technology (U.S. Department of Commerce in Boulder, Colorado) was supported by the National Petroleum Technology Office of DOE, Interagency Agreement number DE-AI26-02NT15338.

JE049595U