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**THE THERMODYNAMIC PROPERTIES OF 2-METHYLANILINE AND
TRANS-(R,S)-DECAHYDROQUINOLINE**

Topical Report

**By
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February 1990

Performed Under Cooperative Agreement No. FC22-83FE60149

**IIT Research Institute
National Institute for Petroleum and Energy Research
Bartlesville, Oklahoma**

**Bartlesville Project Office
U. S. DEPARTMENT OF ENERGY
Bartlesville, Oklahoma**

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EXECUTIVE SUMMARY

Catalytic hydrodenitrogenation (HDN) is a key step in upgrading processes for conversion of heavy petroleum, shale oil, tar sands, and the products of the liquefaction of coal to economically viable products. Organic nitrogen and sulfur are commonly removed via reaction at 300 to 400° C and 50 to 150 atm. of hydrogen. Under these severe conditions, hydrogen is consumed not only in breaking carbon-nitrogen and carbon-sulfur bonds but also in saturating aromatic components in the feed. Hydrogen consumption in excess of 1500 scf/bbl (standard cubic feet per barrel) is common in hydrotreating shale oil, while the amount theoretically required for selective heteroatom removal is only about 600 scf/bbl. Hence, the saving in expensive hydrogen could be enormous, if a process for denitrogenation without saturation of the aromatic rings in the feedstock could be developed.

This research program, funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Extraction and Process Technology (AEPT), provides accurate experimental thermochemical and thermophysical properties for "key" organic nitrogen-containing compounds present in the range of alternative feedstocks, and applies the experimental information to thermodynamic analyses of key HDN reaction networks (e.g., quinoline/hydrogen, indole/hydrogen, acridine/hydrogen, etc.) Thermodynamic analyses, based on accurate information, provide insights for the design of cost-effective methods of nitrogen removal.

This topical report details the thermodynamic properties of 2-methylaniline and trans-(R,S)-decahydroquinoline. The thermodynamic properties were measured using adiabatic heat-capacity calorimetry, differential-scanning calorimetry (d.s.c.), comparative ebulliometry, inclined-piston gauge manometry, and combustion calorimetry. Critical properties were determined for 2-methylaniline using the d.s.c. All measured properties were compared with literature values, and Gibbs energies of formation were derived. With these Gibbs energies, sufficient information is now available for a comprehensive thermodynamic analysis of the quinoline/hydrogen reaction network. This analysis will be published as the next topical report within this research program.

The results of the property measurements reported here indicate; 1) a recent API monograph on the mono-methylanilines needs major revision, 2) corresponding-states correlations provide a reliable means of calculation of thermophysical properties *provided* accurate critical constants such as those determined here for 2-methylaniline are available, and 3) group-additivity methods can be developed to predict accurately Gibbs energies for polycyclic nitrogen-containing compounds *provided* experimentally-determined properties for key compounds, such as those reported here for trans-(R,S)-decahydroquinoline, continue to become available to allow extension of the empirical correlations.

ABSTRACT

Measurements leading to the calculation of the ideal-gas thermodynamic properties for 2-methylaniline and trans-(R,S)-decahydroquinoline are reported. Experimental methods included combustion calorimetry, adiabatic heat-capacity calorimetry, comparative ebulliometry, inclined-piston gauge manometry, and differential-scanning calorimetry (d.s.c.). Entropies, enthalpies, and Gibbs energies of formation were derived for the ideal gas at selected temperatures for both compounds. Critical properties were determined for 2-methylaniline with the d.s.c. Measured combustion enthalpies, vapor pressures, critical properties, and ideal-gas entropies were compared with estimated and experimental literature values.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the Office of Fossil Energy of the U.S. Department of Energy. This research was funded within the Advanced Extraction and Process Technology (AEPT) program as part of the Cooperative Agreement DE-FC22-83FE60149. The authors gratefully acknowledge Professor E. J. "Pete" Eisenbraun and his research group at Oklahoma State University for purification of the calorimetric samples, and I. Alex Hossenlopp for vapor-transfer of the samples to the measuring apparatus.

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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 issue of the Journal of Chemical Thermodynamics. This glossary attempts to summarize the main points, especially 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 $\rho/(\text{kg}\cdot\text{m}^{-3})$ rather than " ρ (kg/m^3)" or " ρ kg/m^3 ". Molar values, i.e., intensive functions, are denoted by the subscript m e.g., $C_{\text{sat},m}$ 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 (the standard atmosphere in the days before SI units).

M = molar mass in $\text{g}\cdot\text{mol}^{-1}$

T = temperature in Kelvin

p = pressure in Pascals (Pa)

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

$\Delta_c U_m^\circ$ = molar energy of combustion and $\Delta_c U_m^\circ/M$ = energy of combustion per gram

$\Delta_c H_m^\circ$ = molar enthalpy of combustion

$\Delta_f H_m^\circ$ = molar enthalpy of formation

$\Delta_l^g H_m$ = molar enthalpy of vaporization, hence the subscript l (for liquid) and superscript g (for gas)

$\Delta_l^g V_m$ = the change in molar volume going 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

$C_{\text{sat},m}$ = molar heat capacity at saturated pressure

μ = chemical potential

n = number of moles of substance

S_m = molar entropy (see below since measured relative to some standard state)

V_x = volume of DSC 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

$C_V^{\text{II}}(p = p_{\text{sat}})$ = 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 = $[-\lg (P_X/P_c) - 1.000]$ where P_X is the vapor pressure

at $T_r = 0.700$

$\Delta_0^T S_m^o$ = molar entropy at temperature T/K (relative to entropy at T=0 K)

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

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

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

$T \rightarrow 0$ = 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) or h (hours).

1. INTRODUCTION

This laboratory has a research program, funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Extraction and Process Technology (AEPT), in which thermochemical and thermophysical properties are determined for "key" organic nitrogen-containing compounds present in heavy petroleum, shale oil, tar sands, and the products of the liquefaction of coal. Catalytic hydrodenitrogenation (HDN) is a key step in the upgrading of these fuel sources.⁽¹⁻⁴⁾§ They are typically rich in nitrogen, and their conversion produces distillates that are also rich in nitrogen, making them poor distillate fuels without severe denitrogenation pre-treatment.

Hydrodenitrogenation (HDN) reaction mechanisms for aromatic systems contain steps where the aromatic ring structures are hydrogenated. These reaction steps are all reversible within the temperature and pressure ranges of hydrogenation reactors used commercially. Therefore, a knowledge of the thermodynamic equilibria among the species is necessary for the proper interpretation of reaction data, for comparing different catalysts, and for accurate modelling of the overall reaction.

The HDN of quinoline has been used as a model system in kinetics, catalysis, and equilibria studies designed to provide insights into the fundamental processes involved. Figure 1 shows part of the most recently proposed reaction scheme for the HDN of quinoline.⁽⁵⁾ The thermodynamic properties of quinoline and isoquinoline were reported in an earlier topical report⁽⁶⁾ and journal publication⁽⁷⁾ from this group. A recent topical report⁽⁸⁾ and journal publication⁽⁹⁾ detail the thermodynamic properties of 1,2,3,4- and 5,6,7,8-tetrahydroquinoline. The present report covers the experimental measurements made to determine the thermodynamic properties of 2-methylaniline and trans-(R,S)-decahydroquinoline. The research included adiabatic heat-capacity calorimetry, differential-scanning calorimetry (d.s.c.) to determine high-temperature heat capacities and critical properties, comparative ebulliometry, inclined-piston gauge manometry, and combustion calorimetry.

With the thermochemical and thermophysical properties of 2-methylaniline and trans-(R,S)-decahydroquinoline provided in this report, sufficient data are now available to undertake an accurate and detailed equilibrium thermodynamic analysis of the HDN of quinoline. The next topical report (due February 1990) will cover that topic.

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§ References are listed in numerical order at the end of this Report.

Figure 1. Partial reaction network for the hydrodenitrogenation (HDN) of quinoline over Ni-W Y-type zeolite catalyst.⁽⁵⁾

2. EXPERIMENTAL

MATERIALS

A commercial sample of 2-methylaniline was purified in the following manner. The impure samples were treated with oxalic acid dihydrate in hot propan-2-ol (molecular proportions 1.4 to 1 to 50 for 2-methylaniline, oxalic acid dihydrate, and propan-2-ol, respectively). The resulting oxalate was recrystallized from propan-2-ol/water (molar ratio 4:1), and cleaved using $2 \text{ mol} \cdot \text{dm}^{-3}$ KOH(aq). The liberated 2-methyl-aniline was extracted with ether, dried (Na_2CO_3), filtered, and concentrated. Final purification was achieved by double distillation at 337 K and 270 Pa.

Commercial trans-(R,S)-decahydroquinoline was eluted through alumina in a Soxhlet apparatus, under an argon atmosphere, using hexane. The eluate was refrigerated, and the resulting crystals were filtered and pumped at 323 K to remove traces of solvent.

The mole-fraction impurities were estimated to be 0.001 for 2-methylaniline and < 0.001 for trans-(R,S)-decahydroquinoline, using g.l.c. and d.s.c. purity analyses, respectively. The high purities of both samples were confirmed in fractional-melting studies completed as part of the adiabatic heat-capacity studies.

The water used as a reference material in the ebulliometric vapor-pressure 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 $M = 107.1554 \text{ g} \cdot \text{mol}^{-1}$ for 2-methylaniline and $M = 139.2412 \text{ g} \cdot \text{mol}^{-1}$ for trans-(R,S)-decahydroquinoline and are based on the relative atomic masses of 1981^{(10)†} and the gas constant, $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, adopted by CODATA.⁽¹¹⁾ 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.⁽¹²⁾ The platinum resistance thermometers used in the adiabatic heat-capacity studies were calibrated below 13.81 K using the method of McCrackin and

---

† The 1981 relative atomic masses were used because the CODATA Recommended Key Values for Thermodynamics (reference 34) are based on them.

Chang.⁽¹³⁾ Measurements of mass, time, electrical resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

APPARATUS AND PROCEDURES

Combustion Calorimetry. The experimental procedures used in the combustion calorimetry of organic nitrogen compounds at the National Institute for Petroleum and Energy Research have been described.⁽¹⁴⁻¹⁶⁾ A rotating-bomb calorimeter (laboratory designation BMR II)⁽¹⁷⁾ and platinum-lined bombs (laboratory designations Pt-3b and B57-I)⁽¹⁸⁾ with internal volumes of 0.3934 dm³ and 0.3930 dm³, respectively, were used without rotation. Pt-3b was used for the trans-(R,S)-decahydroquinoline combustion measurements, and B57-I was used for the 2-methylaniline combustions. The calorimetric samples of 2-methylaniline were confined in borosilicate glass ampoules.^(14,19) Bags of polyester film⁽²⁰⁾ were used to confine the crystalline samples of trans-(R,S)-decahydroquinoline before combustion. For each experiment 1.0x10⁻³ dm³ of water was added to the bomb, and the bomb was flushed and charged to 3.04 MPa with pure oxygen. Judicious choice of sample and auxiliary masses allowed the temperature rise in each 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.^(21,22) 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.⁽²³⁾

NBS benzoic acid (sample 39i) was used for calibration of the calorimeter; its specific energy of combustion is $-(26434.0 \pm 3.0)$ J·g⁻¹ under certificate conditions. Conversion to standard states⁽²⁴⁾ gives $-(26413.7 \pm 3.0)$ J·g⁻¹ for $\Delta_c U_m^0/M$, the specific energy of the idealized combustion reaction. Calibration experiments were interspersed with each series of 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 each calibration series, $\epsilon(\text{calor})$, was (16641.6 ± 0.7) J·K⁻¹ (mean and standard deviation of the mean) for the 2-methylaniline and (16770.6 ± 0.9) J·K⁻¹ for the trans-(R,S)-decahydroquinoline measurements.

The auxiliary oil (laboratory designation TKL66) had the empirical formula $\text{CH}_{1.913}$. For this material $\Delta_c U_m^0/M$ was $-(46042.5 \pm 1.8) \text{ J} \cdot \text{g}^{-1}$. For the cotton fuse, empirical formula $\text{CH}_{1.774}\text{O}_{0.887}$, $\Delta_c U_m^0/M$ was $-16945 \text{ J} \cdot \text{g}^{-1}$. The value for $\Delta_c U_m^0/M$ obtained for the polyester film, empirical formula $\text{C}_{10}\text{H}_8\text{O}_4$, was a function of the relative humidity (RH) in the laboratory during weighings:⁽²⁰⁾

$$\{(\Delta_c U_m^0/M)/(\text{J} \cdot \text{g}^{-1})\} = -22912.0 - 1.0560(\text{RH}) . \quad (1)$$

Auxiliary information, necessary for reducing weights measured in air to masses, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states,⁽²⁴⁾ included densities of $985 \text{ kg} \cdot \text{m}^{-3}$ and $960 \text{ kg} \cdot \text{m}^{-3}$, and estimated values of $1.7 \text{ m}^3 \cdot \text{K}^{-1}$ and $1.6 \text{ m}^3 \cdot \text{K}^{-1}$ for $(\delta V_m/\delta T)_p$ for 2-methylaniline and trans-(R,S)-decahydroquinoline, respectively. The densities at 298.15 K were obtained by weighing an ampoule of known volume (2-methylaniline) or a pellet (trans-(R,S)-decahydroquinoline). Values of the molar heat capacities at 298.15 K for both compounds used in the corrections to standard states are given as part of the heat-capacity study results later in this report.

Nitric acid formed during the nitrogen-containing compound combustions was determined by titration with standard sodium hydroxide.⁽²⁵⁾ Carbon dioxide was also recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as absorbent.⁽¹⁵⁾ The combustion products were checked for unburned carbon and other products of incomplete combustion, but none were detected. Carbon dioxide percentage recoveries for the calibrations and main combustions were 100.001 ± 0.005 (mean and standard deviation of the mean) for calibrations, 100.000 ± 0.002 for the corresponding 2-methylaniline combustions, 99.996 ± 0.006 for calibrations, and 99.998 ± 0.003 for the corresponding trans-(R,S)-decahydroquinoline combustions.

Ebulliometric Vapor-Pressure Measurements. The essential features of the ebulliometric equipment and procedures are described in the literature.^(26,27) 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 using the condensation temperature of the standard.⁽²⁸⁾

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

$$\sigma(p) = (0.001 \text{ K}) \{ (dp_{\text{ref}}/dT)^2 + (dp_{\Xi}/dT)^2 \}^{1/2}, \quad (2)$$

where p_{ref} is the vapor pressure of the reference substance and p_{Ξ} 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⁽²⁹⁾ to vapor pressures of the reference materials (decane and water) reported in reference 28.

Inclined-Piston Vapor-Pressure Measurements. The equipment for these measurements has been described by Douslin and McCullough,⁽³⁰⁾ and Douslin and Osborn.⁽³¹⁾ Recent revisions to the equipment and procedures are given in references 6 and 7. The low pressure range of the inclined-piston measurements, 10 to 3500 Pa, necessitated diligent outgassing of the sample prior to introduction into the apparatus. Also prior to the sample introduction, all parts of the cell in contact with the sample were baked at 623 K under high vacuum ($< 10^{-4}$ Pa). The thoroughly outgassed samples were placed in the apparatus, and additional outgassing was performed prior to commencing measurements. Finally, prior to each measurement, a small amount of sample was pumped off. Measurements were made as a function of time to extrapolate the pressure to the time when the pumping valve was closed; i.e., to the time when insignificant amounts of light gas had leaked into the system or diffused out of the sample.

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 the expression:

$$\sigma(p) = 1.5 \times 10^{-4} p + 0.2 \text{ Pa}. \quad (3)$$

The uncertainties in the temperatures are 0.001 K.

Adiabatic Heat-Capacity Calorimetry. Adiabatic heat-capacity and enthalpy measurements were made with a calorimetric system that has been described previously.^(6,7) The calorimeter characteristics and sealing conditions are given in

table 1.[†] Energy measurement procedures were the same as those described[†] for studies on quinoline.^(6,7) 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 calorimeters were corrected for enthalpy changes in the empty calorimeter, for the helium exchange gas, and for vaporization of the samples. The maximum correction to the measured energy for the helium exchange gas was less than 0.4 per cent near 5 K for both compounds. The sizes of the other two corrections are indicated in table 1.

Differential-Scanning Calorimetry. Differential-scanning calorimetric measurements were made with a Perkin-Elmer DSC-2. Experimental methods were described previously.⁽³²⁾

3. RESULTS

COMBUSTION CALORIMETRY

A typical combustion experiment for each compound is summarized in table 2. It is impractical to list summaries for each combustion, but values of $\Delta_c U_m^0/M$ for all the experiments are reported in table 3. All values of $\Delta_c U_m^0/M$ in table 3 refer to the reaction:

Table 3 also gives derived values of the standard molar energy of combustion $\Delta_c U_m^0$, the standard molar enthalpy of combustion $\Delta_c H_m^0$, and the standard molar enthalpy of formation $\Delta_f H_m^0$, for 2-methylaniline and trans-(R,S)-decahydroquinoline. Values of $\Delta_c U_m^0$ and $\Delta_c H_m^0$ refer to reaction 4. The values of $\Delta_f H_m^0$ refer to reaction 5:

Uncertainties given in table 3 are the "uncertainty interval" defined in reference 33. The enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ were taken to be $-(393.51 \pm 0.13)$ and $-(285.830 \pm 0.042) \text{ kJ} \cdot \text{mol}^{-1}$, respectively, as assigned by CODATA.⁽³⁴⁾

[†] All tables are given at the end of this Report.

VAPOR-PRESSURE MEASUREMENTS

Vapor pressures for 2-methylaniline and trans-(R,S)-decahydroquinoline are reported in table 4. Following previous practice,⁽²⁷⁾ 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 for the samples are reported. The small differences between the boiling and condensation temperatures for 2-methylaniline indicated correct operation of the equipment and the high purity of the samples. The larger differences for trans-(R,S)-decahydroquinoline are due to the sample being an R,S pair. Above 520 K for trans-(R,S)-decahydroquinoline, the difference between the boiling and condensation temperatures increased rapidly with time indicative of sample decomposition. Sample decomposition was also seen when d.s.c. heat capacity measurements were attempted above 520 K.

Cox Equation Fits to Vapor Pressures. Previous studies by Scott and Osborn⁽³⁵⁾ showed that the Cox equation⁽³⁶⁾ can represent measured vapor pressures adequately from the triple-point pressure to 0.3 MPa. Scott and Osborn also showed that the Antoine equation, the most commonly used to represent vapor pressures, does not extrapolate well outside the experimental range. In contrast, the Cox equation extrapolates with reasonable precision over a 50 K range.⁽³⁵⁾

The Cox equation in the form:

$$\ln(p/p_{\text{ref}}) = \{1 - (T_{\text{ref}}/T)\} \exp\{A + B(T/K) + C(T/K)^2\}, \quad (6)$$

was fitted to the experimental vapor pressures with p_{ref} chosen to be 101.325 kPa so that T_{ref} was the normal-boiling temperature. In those fits, the sums of the weighted squares in the function:

$$\Delta = \ln\{\ln(p/p_{\text{ref}})/(1 - T_{\text{ref}}/T)\} - A - B(T/K) - C(T/K)^2. \quad (7)$$

were minimized. The weighting factors W , the reciprocals of the variance in Δ derived from the propagation of errors in the temperature and pressure determinations, are defined by:

$$1/W = (\delta\Delta/\delta T)_p^2 \sigma(T)^2 + (\delta\Delta/\delta p)_T^2 \sigma(p)^2. \quad (8)$$

Parameters derived from the fits are given in table 5. Details of the Cox equation fits are given in table 4.

Derived Enthalpies of Vaporization. Enthalpies of vaporization $\Delta_1^g H_m$ were derived from the Cox equation fits using the Clapeyron equation:

$$dp/dT = \Delta_1^g H_m / (T \Delta_1^g V_m) , \quad (9)$$

where $\Delta_1^g V_m$ is the increase in molar volume from the liquid to the real vapor. For trans-(R,S)-decahydroquinoline $\Delta_1^g V_m$ was calculated using estimates of the second virial coefficients (the correlation of Scott et al.,⁽³⁷⁾) a liquid-phase density of 894 kg·m⁻³ at 338 K, and an estimated coefficient of expansion of 0.0009 in the temperature range 290 to 600 K. The liquid-phase density for trans-(R,S)-decahydroquinoline was measured during loading of the heat-capacity calorimeter. Generally, we have found such density measurements to be within 3 per cent of precisely determined values. For 2-methylaniline, $\Delta_1^g V_m$ was calculated using estimates of the second virial coefficients derived from the extended corresponding-states equation of Pitzer and Curl.⁽³⁸⁾ Liquid-phase densities for 2-methylaniline were obtained from extended corresponding-states estimates and measured critical parameters (see below). For trans-(R,S)-decahydroquinoline, uncertainties in the second virial coefficients and liquid-phase densities were estimated to be 20 and 5 per cent of the calculated values, respectively. For 2-methylaniline, the corresponding uncertainties were estimated to be 10 and 3 per cent, respectively. Derived enthalpies of vaporization and the corresponding entropies of compression are reported in table 6.

ADIABATIC HEAT-CAPACITY CALORIMETRY

Crystallization and Melting Studies. Crystallization of trans-(R,S)-decahydroquinoline was initiated by slowly cooling (approximately 6 K·h⁻¹) the liquid sample 10 to 12 K below the triple-point temperature. The crystals were annealed by maintaining the sample under adiabatic conditions in the partially melted state (15 to 25 per cent liquid) for approximately 20 h. No spontaneous warming was observed. The sample was cooled at an effective rate of 1 K·h⁻¹ to crystallize the remaining liquid. As a final step, the sample was thermally cycled between <100 K and within 2 K of the triple-point temperature, where it was held for a minimum of 24 h to provide further tempering. All of the solid-phase measurements were performed upon crystals pre-treated in this manner.

Crystallization of 2-methylaniline was initiated by slowly cooling (approximately $4\text{ K}\cdot\text{h}^{-1}$) the liquid sample 35 to 40 K below the triple-point temperature. The sample crystallized initially into a metastable form with a triple-point temperature near 251.1 K. When partially remelted, the sample transformed to the stable form over approximately a two-day period. On one occasion the sample did not transform to the stable form when partially remelted, and the approximate triple-point temperature was obtained. After transformation to the stable form, the crystals were annealed as described above for the trans-(R,S)-decahydroquinoline sample.

The triple-point temperatures T_{tp} and sample purities were determined from the measurement of the equilibrium melting temperatures $T(F)$ as a function of fraction F of the samples in the liquid state.⁽³⁹⁾ Equilibrium melting temperatures were determined by measuring temperatures at approximately 300-s intervals for 0.75 to 1 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 7.

The results for trans-(R,S)-decahydroquinoline indicated the presence of a solid-soluble impurity, and published procedures⁽⁴⁰⁾ were used to derive the mole fraction of impurity, triple-point temperature, and effective distribution coefficient for the impurity between the two phases. The results are summarized in table 7.

Phase Transformations and Enthalpy Measurements. Experimental molar enthalpy results are summarized in table 8. The table includes both phase-transition enthalpies 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 8 and 9 were taken without interruption of adiabatic conditions.

Heat Capacities Measurements. The experimental molar heat capacities under vapor saturation pressure $C_{\text{sat},m}$ determined by adiabatic calorimetry are listed in table 9. Values in table 9 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 $C_{\text{sat},m}$ with temperature. The precision of the heat-capacity measurements ranged from approximately 5 per cent at 5 K, to 2 per cent at 11 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 phase near the triple-point temperatures where

equilibration times were long. The heat capacities in table 9 have not been corrected for pre-melting, but from the temperature increments provided an independent calculation can be made.

For heat-capacity measurements in the liquid phase, equilibrium was reached in less than 1 h. Equilibration times for the crystal phase of trans-(R,S)-decahydroquinoline were all less than 1 h for temperatures below 270 K, and increased smoothly to 16 h near 320 K. For 2-methylaniline, equilibration times for the crystal phase were less than 1 h for temperatures below 220 K, and increased smoothly to 40 h near 250 K.

Extrapolation of the heat-capacity results to $T \rightarrow 0$ for 2-methylaniline was made using a least-squares fit of the Debye heat-capacity equation to results below 12 K. The derived Debye characteristic temperature was $\Theta = 82.2$ K with 2.31 degrees of freedom. For trans-(R,S)-decahydroquinoline linear extrapolation of a plot of $C_{\text{sat,m}}/T$ against temperature squared for results below 8 K was used to estimate heat capacities below the measured range.

DIFFERENTIAL SCANNING CALORIMETRY

Theoretical Background. The theoretical background for the determination of heat capacities at vapor-saturation pressure, $C_{\text{sat,m}}$, with results obtained with a d.s.c. has been described.⁽³²⁾ If two phases are present and the liquid is a pure substance, then the vapor pressure p and the chemical potential μ are independent of the amount of substance n and the cell volume V_x , and are equal to p_{sat} and μ_{sat} . The two-phase heat capacities at cell volume V_x , $C_{x,m}^{\text{II}}$, can be expressed in terms of the temperature derivatives of these quantities:

$$n C_{x,m}^{\text{II}} / T = -n(\delta^2 \mu / \delta T^2)_{\text{sat}} + V_x (\delta^2 p / \delta T^2)_{\text{sat}} + \{(\delta V_x / \delta T)_x (\delta p / \delta T)_{\text{sat}}\}. \quad (10)$$

The third term on the right-hand side of equation (10) includes the thermal expansion of the cell. In this research the thermal expansion of the cells was expressed as:

$$V_x(T) / V_x(298.15 \text{ K}) = 1 + ay + by^2, \quad (11)$$

where, $y = (T - 298.15) \text{ K}$, $a = 3.216 \times 10^{-5} \text{ K}^{-1}$, and $b = 5.4 \times 10^{-8} \text{ K}^{-2}$.

$(dp/dT)_{\text{sat}}$ can be calculated based on the vapor pressures measured in this research. Therefore, with a minimum of two different filling levels of the cell $(\delta^2 p / \delta T^2)_{\text{sat}}$ and $(\delta^2 \mu / \delta T^2)_{\text{sat}}$ can be determined. In this research 5 (five) fillings were used. To obtain the saturation heat capacity $C_{\text{sat,m}}$ at vapor pressures greater than

0.1 MPa, the limit where the cell is full of liquid is required, i.e., $(n/V_x) = \{1/V_m(l)\}$ where $V_m(l)$ is the molar volume of the liquid:

$$\lim_{(n/V_x) \rightarrow \{1/V_m(l)\}} (n C_{V,m}^{II}/T) = V_m(l)(\delta^2 p/\delta T^2)_{\text{sat}} - n(\delta^2 \mu/\delta T^2)_{\text{sat}}. \quad (12)$$

$C_{\text{sat},m}$ is obtained using the expression:

$$\lim_{(n/V_x) \rightarrow \{1/V_m(l)\}} (n C_{V,m}^{II}) = n[C_{\text{sat},m} - \{T(\delta p/\delta T)_{\text{sat}} (dV_m(l)/dT)\}]. \quad (13)$$

Thus, reliable liquid density values are also required to determine $C_{\text{sat},m}$.

DSC Measurement Results. Table 10 lists the experimental two-phase heat capacities $C_{x,m}^{II}$ for 2-methylaniline obtained for 5 cell fillings. The temperature at which conversion to a single phase occurred for 2-methylaniline was measured for 5 additional cell fillings. Table 11 reports the filling density, obtained from the mass of sample and the cell volume calculated using equation (11), and the measured temperatures at which conversion to a single phase was observed for all 10 fillings. A critical temperature of (716.5 ± 1) K and critical density of (305 ± 3) kg·m⁻³ were derived graphically for 2-methylaniline using these results, as seen in figure 2. Critical-property determinations for trans-(R,S)-decahydroquinoline were precluded by rapid sample decomposition near 520 K.

Simultaneous Fit of Vapor-pressure and Two-phase Heat-capacity Results. The critical pressure for 2-methylaniline was not measured directly, but was estimated by means of simultaneous non-linear least-squares fits using the vapor pressures listed in table 4 and the $C_{x,m}^{II}$ values given in table 10. $C_{\text{sat},m}$ values were derived using results of the fit and equation (13). Experimental $C_{x,m}^{II}$ were converted to $C_{V,m}^{II}$ values by means of equation (11) for the cell expansion and the vapor-pressure fit described below for $(dp/dT)_{\text{sat}}$. The values of $C_{V,m}^{II}$ were used to derive functions for $(\delta^2 p/\delta T^2)_{\text{sat}}$ and $(\delta^2 \mu/\delta T^2)_{\text{sat}}$. The Cox equation⁽³⁶⁾ was used to represent the vapor pressures in the form:

$$\ln(p/p_c) = (1 - 1/T_r) \exp(A + BT_r + CT_r^2), \quad (14)$$

with $T_r = T/T_c$, where T_c and p_c are the critical temperature and critical pressure. The critical pressure was included as a variable in the non-linear least-squares analysis.

Figure 2. Vapor-liquid coexistence region for 2-methylaniline. The crosses span the range of uncertainty.

The functional form chosen for variation of the second derivative of the chemical potential with temperature was:

$$(\delta^2\mu/\delta T^2)_{\text{sat}} = \sum_{i=0}^n b_i(1 - T/T_C)^i. \quad (15)$$

[For compounds where sufficient information was available to evaluate reliably $(d^2\mu/dT^2)_{\text{sat}}$ (e.g., benzene⁽⁴¹⁾), four terms (i.e., expansion to $n=3$) were required to represent the function. Thus, four terms were used in this research.] In these fits the sum of the weighted squares in the following function was minimized:

$$\Delta = C_{V,m}^{\text{II}}/R - \{V_m(l)T/nR\}(\delta^2p/\delta T^2)_{\text{sat}} + (T/R)(\delta^2\mu/\delta T^2)_{\text{sat}}. \quad (16)$$

For the vapor-pressure fits, the functional forms of the weighting factors used have been reported.^(6,7) Within the heat-capacity results the weighting factors were proportional to the square of the mass of sample used in the measurements.

Table 12 lists the coefficients determined in the non-linear least-squares fit. A weighting factor of 20 was used to increase the relative weights of the vapor-pressure measurements in the fit. The weighting factor reflects the higher precision of the vapor-pressure values relative to the experimental heat capacities.

Values of $C_{\text{sat},m}$ for 2-methylaniline were derived from $C_{V,m}^{\text{II}}(p=p_{\text{sat}})$ with the densities obtained from the corresponding-states equation in the form:⁽⁴²⁾

$$(p/p_C) = 1.0 + 0.85\{1.0 - (T/T_C)\} + (1.692 + 0.986\omega)\{1.0 - (T/T_C)\}^{1/3}, \quad (17)$$

with $p_C = 305 \text{ kg}\cdot\text{m}^{-3}$, $T_C = 716.5 \text{ K}$, and the acentric factor $\omega = 0.386$. The acentric factor is defined as $\{-\lg(p/p_C) - 1.0\}$, where p is the vapor pressure at $T_r = 0.7$ and p_C is the critical pressure. The Cox equation coefficients given in table 12 were used to calculate p . The results for $C_{V,m}^{\text{II}}(p = p_{\text{sat}})/R$ and $C_{\text{sat},m}/R$ are reported in table 13. The estimated uncertainty in these values is 1 per cent.

THERMODYNAMIC PROPERTIES IN THE CONDENSED STATE

Condensed-phase entropies and enthalpies relative to that of the crystals at $T \rightarrow 0$ for the solid and liquid phases under vapor saturation pressure are listed in table 14. These were derived by integration of the smoothed heat capacities corrected for pre-melting, together with the entropies and enthalpies of transition and 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 9 and 13 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 using standard methods for solid-insoluble impurities and the mole-fraction impurity 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 6 and 14 and are listed in columns 2 and 4 of table 15. Values above 600 K are not reported for 2-methylaniline because gas-imperfection corrections are large and cannot be determined with sufficient accuracy. The derived ideal-gas enthalpies and entropies were combined with the condensed-phase enthalpies of formation given in table 3 to calculate the enthalpies, entropies, and Gibbs energies of formation listed in columns 6, 7, and 8, respectively, of table 15. Enthalpies and entropies for nitrogen, equilibrium hydrogen, and graphite were determined from JANAF tables.⁽⁴³⁾ All uncertainties in table 15 represent one standard deviation, and include uncertainties in the properties of the elements as assessed in the JANAF tables.

4. DISCUSSION

2-METHYLANILINE

The physical and thermodynamic properties of the methyl substituted anilines were the subject of a recent report in the API Monograph Series.⁽⁴⁴⁾ In several areas the results reported here are in serious disagreement with the assessed values in the API Report. These differences are detailed in the following comparisons with available literature values.

ENERGY OF COMBUSTION

The energy of combustion of 2-methylaniline was measured by Petit⁽⁴⁵⁾ in 1889. The value obtained, $\Delta_c U_m^0 / M = -37661 \text{ J} \cdot \text{g}^{-1}$, (corrected to modern units) is in remarkable agreement with that obtained in this research, $\Delta_c U_m^0 / M = -(37625.2 \pm 3.2) \text{ J} \cdot \text{g}^{-1}$. However, Petit's result translates to a standard enthalpy of formation of $-0.9 \text{ kJ} \cdot \text{mol}^{-1}$ for 2-methylaniline in the liquid phase compared to a value of $-(4.72 \pm 0.96) \text{ kJ} \cdot \text{mol}^{-1}$ obtained in this research. This illustrates the need for accurate and precise energy of combustion measurements. In this case a percentage

difference of 0.1 in the energy of combustion translates into a greater than five hundred percent difference in the standard enthalpy of formation. The API Monograph⁽⁴⁴⁾ lists a value of $-5.4 \text{ kJ}\cdot\text{mol}^{-1}$ for the standard enthalpy of formation of 2-methylaniline in the liquid phase with no details on the source of the value.

CRITICAL PROPERTIES

Glaser and Ruland⁽⁴⁶⁾ reported a critical temperature of 694 K with a corresponding critical pressure of 3750 kPa for 2-methylaniline. In this research the experimental value obtained for the critical temperature is $(716.5 \pm 1.0) \text{ K}$ with a corresponding critical pressure of $(4476 \pm 45) \text{ kPa}$ derived in the fitting procedure. The vapor-pressure measurements reported by Glaser and Ruland in their "critical region" (near 690 K) agree with those estimated in this research (see below in VAPOR PRESSURE section) and extrapolate to the critical pressure obtained here at 716.5 K. Hence, Glaser and Ruland appear not to have reached the true critical temperature in their measurements. Indirect collaboration of this conclusion is supplied by the critical property estimation schemes of Ambrose⁽⁴⁷⁾ and Somayajulu.⁽⁴⁸⁾ Critical temperatures of 706.1 and 707.7 K, respectively, are obtained using the estimation methods with a correspondingly higher critical pressure in the range of 4600 kPa. The API Monograph⁽⁴⁴⁾ reports the critical property values of Glaser and Ruland.

DENSITY

Although no experimental measurements of the density of 2-methylaniline were made in this research, it is of interest to compare the available measurements reported in the literature⁽⁴⁹⁻⁵²⁾ with values derived using extended corresponding-states, p_{corr} , using the critical properties obtained here. Comparisons of this type are rarely reported in the literature although extended corresponding-states is a major tool used in process design. Figure 3 is a difference plot between densities reported in the literature ρ_{lit} for 2-methylaniline and those calculated ρ_{corr} using the equation:

$$(\rho_{\text{corr}}/\rho_{\text{C}}) = 1.0 + 0.85\{1.0 - (T/T_{\text{C}})\} + (1.692 + 0.986\omega)\{1.0 - (T/T_{\text{C}})\}^{1/3}, \quad (18)$$

with $\rho_{\text{C}} = 305 \text{ kg}\cdot\text{m}^{-3}$, $T_{\text{C}} = 716.5 \text{ K}$, and $\omega = 0.386$. The percentage difference $100\{\rho_{\text{lit}} - \rho_{\text{corr}}\}/\rho_{\text{corr}}$ ranges from 0.75 to 1.1 per cent with the majority of the values congregated in the region 0.9 to 1.0 per cent. An adjustment of the critical density by 1 per cent would bring the experimental and estimated values into near

Figure 3. Percentage deviation plot for 2-methylaniline densities. ρ_{corr} was calculated using equation 18 and the constants reported in the text. $\circ$, Bingham et al.;⁽⁴⁹⁾ $\bullet$, Kremann et al.;⁽⁵⁰⁾ $\square$, Dreisbach and Martin;⁽⁵¹⁾ and $\blacksquare$, Buehler et al.⁽⁵²⁾

Figure 4. Percentage deviation plot for 2-methylaniline vapor pressures below 473 K. p_{corr} is the vapor pressure calculated using equation 14 and the constants reported in table 12. ○, Berliner and May;⁽⁵⁴⁾ ●, Dreisbach and Shrader;⁽⁵⁵⁾ and +, Kahlbaum⁽⁵³⁾

Figure 5. Percentage deviation plot for 2-methylaniline vapor pressures above 473 K. p_{corr} is the vapor pressure calculated using equation 14 and the constants reported in table 12. $\circ$, Glaser and Ruland⁽⁴⁶⁾

perfect agreement. Such a difference is within the assigned uncertainty on the experimentally determined critical density $\rho_c = (305 \pm 3) \text{ kg} \cdot \text{m}^{-3}$.

VAPOR PRESSURE

Liquid phase vapor-pressure measurements on 2-methylaniline have been reported by several groups.⁽⁵³⁻⁵⁵⁾ Figures 4 and 5 show the vapor pressures reported in the literature. In the figures the experimental vapor pressures are compared with values calculated using equation 14 with the constants reported in table 12. At temperatures below 400 K the measurements of Kahlbaum⁽⁵³⁾ and Berliner and May⁽⁵⁴⁾ are in serious disagreement with each other and with those obtained in this research. Above 400 K the results of Kahlbaum,⁽⁵³⁾ Berliner and May,⁽⁵⁴⁾ Dreisbach and Shrader,⁽⁵⁵⁾ and this research are all in reasonable agreement (see figure 4).

The measurements of Glaser and Ruland⁽⁴⁶⁾ extend from the normal-boiling temperature (473 K) to 690 K. From 473 to 630 K their measured pressures are 4 per cent lower than those of this research. Within the upper 60 K of the experimental range the agreement improves to almost coincidence at 690 K. The API Monograph⁽⁴⁴⁾ listed vapor pressures for 2-methylaniline which appear to be a weighted mean of those of Kahlbaum,⁽⁵³⁾ Berliner and May,⁽⁵⁴⁾ and Dreisbach and Shrader⁽⁵⁵⁾ below 473 K and the values of Glaser and Ruland⁽⁴⁶⁾ above that temperature.

HEAT CAPACITY

In figure 6 the liquid-phase heat capacities for 2-methylaniline reported in the API Monograph⁽⁴⁴⁾ are compared with those obtained in this research. The API values are, "Based on combination of experimental heat capacity and correlation of difference between heat capacity of liquid and of ideal gas." As the figure shows, the percentage difference between the heat capacities reported here and the API values ranges from 5.5 per cent at 270 K to -1.1 per cent at 500 K. The experimental heat capacity used by API in their correlation was the *single* value of de Kolossowsky and Udowensko⁽⁵⁶⁾ ($C_{\text{sat},m} / R = 25.21$ at 302.9 K) which is 4.5 per cent lower than the value interpolated from the results reported here.

IDEAL GAS THERMODYNAMIC FUNCTIONS

Statistical thermodynamic ideal-gas properties for 2-methylaniline have been reported by Draeger⁽⁵⁷⁾ and Kudchadker and Wilhoit⁽⁴⁴⁾ (the API Monograph). The values for the standard entropy reported in the API Monograph are

Figure 6. Deviation plot for 2-methylaniline liquid-phase heat capacities. API is reference 44.

Figure 7. Comparison of experimental calorimetric and spectroscopic ideal-gas entropies for 2-methylaniline. The solid lines represent the error limits (one standard deviation) assigned to the calorimetric entropies. The open circles are values of $\{\Delta_0^T S_m^o(\text{reference 57}) - \Delta_0^T S_m^o(\text{calorimetric})\}/R$.

lower than those calculated by Draeger by a constant $R \cdot \ln 2$ term. It would appear that the authors of the API report miscalculated the overall symmetry number for 2-methylaniline by using a value of 3 and not the correct value of 6 (3 for the methyl group and 2 for the NH_2 inversion). Figure 7 compares the results reported by Draeger with those obtained in this research. The differences all lie within two standard deviations of the uncertainty in the calorimetric values. Some portion of the differences may be due to uncertainty in the barrier for hindered internal rotation. Draeger used as an approximation the barrier for adjacent methyl groups in substituted benzenes.⁽⁵⁸⁾

TRANS-(R,S)-DECAHYDROQUINOLINE

No thermochemical or thermophysical measurements were found in the literature for trans-(R,S)-decahydroquinoline. The properties listed in this report refer to the racemic mixture of R and S trans-decahydroquinoline. For compounds with optical isomers, there is a residual entropy at 0 K of $R \cdot \ln 2$ for each (R,S) center in the molecule. Therefore, the thermodynamic properties both in the condensed and ideal-gas states reported here for trans-(R,S)-decahydroquinoline include the residual entropy. To obtain the thermodynamic properties of either the pure (R)- or (S) enantiomers, $\ln 2 = 0.693$ should be subtracted from both the entropy and free energy columns of tables 14 and 15. Since there is no enthalpy of mixing of enantiomers, the enthalpy of formation (column 6 of table 15) remains the same as that given for the (R,S) mixture for both the (R) and (S) forms of trans-decahydroquinoline.

One of the goals of this research program is to obtain thermodynamic property values for "key" compound types such that a minimum of measurements will enable the estimation of the whole range of nitrogen-containing compounds present in heavy petroleum, shale oil, tar sands, and the products of the liquefaction of coal. To that end the second-order group-contribution methodology for the calculation of thermodynamic properties has been outlined in detail by Benson.⁽⁵⁹⁾ However, that text lacks parameters for a number of important groups and correction terms for several important ring structures. Also parameters for some structural groups were derived from data which have since been shown to be incorrect. In the absence of new data, application of the methodology for the estimation of thermochemical properties for some important organic compound types is impossible.

Analysis of compounds into group types and the derivation of temperature-dependent group parameters is beyond the scope of this project, and is being studied at NIPER as part of a project for the Division of Department of Energy/Office of Energy Research (OER)/Basic Energy Sciences entitled, "Thermodynamic Properties by Non-

Calorimetric Methods." However, sufficient group values are available in reference 59 to permit the estimation of the ideal-gas enthalpy of formation of trans-decahydroquinoline at 298.15 K. Using the available group terms the estimated value is $\Delta_f H_m^0 (\text{C}_9\text{H}_{17}\text{N}, \text{g}) = -112.5 \text{ kJ}\cdot\text{mol}^{-1}$ in excellent agreement with the value obtained in this research $\Delta_f H_m^0 (\text{C}_9\text{H}_{17}\text{N}, \text{g}) = -(113.09 \pm 1.34) \text{ kJ}\cdot\text{mol}^{-1}$ (see column 6 of table 15). Estimation of other properties such as standard entropies and even the enthalpy of formation at temperatures other than 298.15 K is not possible at present due to the absence of essential group-additivity terms. Evaluation of the needed parameters using the results of this research is in progress within the OER research program. The excellent agreement seen for the ideal gas enthalpy of formation at 298.15 K augurs well for the development of a full set of group-additivity terms.

5. CONCLUSIONS

The results given in this report highlight several points. They are:

- The API monograph on the mono-methylanilines needs major revision.
- With the accurate knowledge of critical constants (T_c , p_c , and ρ_c) the variation with temperature of other thermophysical properties can be estimated with a high degree of accuracy.
- Initial results augur well for the development of group-additivity terms to estimate both thermochemical and thermophysical properties for the range of organic nitrogen-containing compounds present in heavy petroleum, shale oil, tar sands, and the products of the liquefaction of coal.
- Sufficient data are now available to undertake a comprehensive thermodynamic analysis of the HDN of quinoline. (This analysis will be published in a separate topical report in the first quarter of 1990.)

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TABLE 1. Calorimeter and sample characteristics; 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, $\delta C/C$ is the vaporization correction, and x_{pre} is the mole-fraction impurity used for pre-melting corrections

	2-Methylaniline	trans-(R,S)-Decahydroquinoline
m/g	47.466	44.686
$V_i(298.15\text{ K})/\text{cm}^3$	62.47	59.06
T_{cal}/K	297.2	297.0
p_{cal}/kPa	4.20	5.32
$r(T_{max})$	3.8	3.4
r_{min}	2.0	1.8
$10^2(\delta C/C)_{max}$	0.054	0.022
x_{pre}	0.00075	0.0

TABLE 2. Typical combustion experiments at 298.15 K ($p^\circ = 101.325 \text{ kPa}$) ^a

	2-Methylaniline	trans-(R,S)-Decahydro-quinoline
$m(\text{compound})/\text{g}$	0.878512	0.998716
$m''(\text{oil})/\text{g}$	0.073619	0.0
$m'''(\text{film})/\text{g}$	0.0	0.054888
$m''''(\text{fuse})/\text{g}$	0.001439	0.001923
$n_i(\text{H}_2\text{O})/\text{mol}$	0.05535	0.05535
$m(\text{Pt})/\text{g}$	32.716	20.804
$m(\text{glass})/\text{g}$	0.034265	0.0
$\Delta T = (t_i - t_f + \Delta t_{\text{corr}})/\text{K}$	2.19073	2.54685
$\epsilon(\text{calor})(\Delta T)/\text{J}$	-36457.3	-42712.1
$\epsilon(\text{cont})(\Delta T)/\text{J}$ ^b	-45.9	-47.4
$\Delta U_{\text{ign}}/\text{J}$	0.8	0.8
$\Delta U_{\text{dec}}(\text{HNO}_3)/\text{J}$	29.6	66.0
$\Delta U(\text{corr. to std. states})/\text{J}$ ^c	17.9	16.4
$-m''(\Delta_c U_m^\circ/M)(\text{oil})/\text{J}$	3389.6	0.0
$-m'''(\Delta_c U_m^\circ/M)(\text{film})/\text{J}$	0.0	1254.2
$-m''''(\Delta_c U_m^\circ/M)(\text{fuse})/\text{J}$	24.4	32.6
$m'(\Delta_c U_m^\circ/M)(\text{compound})/\text{J}$	-33041.0	-41389.5
$(\Delta_c U_m^\circ/M)(\text{compound})/\text{J}\cdot\text{g}^{-1}$	-37610.1	-41442.6

^a The symbols and abbreviations of this table are those of reference 24 except as noted.

^b $\epsilon_i(\text{cont})(t_i - 298.15 \text{ K}) + \epsilon_f(\text{cont})(298.15 \text{ K} - t_f + \Delta t_{\text{corr}})$

^c Items 81 to 85, 87 to 90, 93, and 94 of the computational form of reference 24.

TABLE 4. Summary of 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 calculated value of pressure from the observed value of pressure; σ_i is the propagated error calculated from equations (2) and (3); ΔT is the difference between the boiling and condensation temperatures ($T_{\text{boil}} - T_{\text{cond}}$) for the sample in the ebulliometer

Method	T K	p kPa	Δp kPa	σ_i kPa	ΔT K
2-Methylaniline					
IP	290.002	0.0210	0.0002	0.0002	
IP	300.001	0.0464	0.0001	0.0002	
IP	309.923	0.0964	-0.0001	0.0002	
IP	319.997	0.1922	0.0001	0.0002	
IP	329.999	0.3620	0.0000	0.0003	
IP	340.000	0.6519	0.0001	0.0003	
IP	350.000	1.1263	-0.0001	0.0004	
IP	360.000	1.8759	0.0002	0.0005	
decane	361.313	2.0000	-0.0004	0.0001	0.057
IP	365.000	2.3896	0.0003	0.0006	
decane	367.321	2.6660	0.0000	0.0002	0.032
IP	370.004	3.0202	0.0002	0.0007	
decane	382.895	5.3330	0.0006	0.0003	0.015
decane	392.794	7.9989	0.0007	0.0005	0.008
decane	400.216	10.6661	0.0013	0.0006	0.007
decane	406.220	13.332	0.001	0.001	0.006
decane	412.453	16.665	0.000	0.001	0.004
decane	417.628	19.933	0.000	0.001	0.003
decane	424.439	25.023	0.000	0.001	0.002
water	424.440 ^a	25.023	-0.001	0.002	0.000
water	431.296	31.177	-0.002	0.002	0.000

TABLE 4. Continued

Method	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma_i}{kPa}$	$\frac{\Delta T}{K}$
2-Methylaniline (cont.)					
water	438.194	38.565	-0.004	0.002	-0.002
water	445.132	47.375	-0.005	0.002	-0.003
water	452.113	57.817	-0.004	0.003	-0.003
water	459.137	70.120	-0.004	0.003	-0.003
water	466.204	84.533	-0.002	0.004	-0.003
water	473.313 ^a	101.325	0.002	0.004	-0.004
water	480.464	120.79	0.01	0.01	-0.002
water	487.663	143.25	0.01	0.01	-0.003
water	494.899	169.02	0.01	0.01	-0.003
water	502.182	198.49	0.01	0.01	-0.003
water	509.505	232.02	0.00	0.01	-0.004
water	516.870	270.02	-0.03	0.01	-0.004
trans-(R,S)-Decahydroquinoline					
IP	325.001	0.3748	-0.0005	0.0003	
IP	335.002	0.6595	-0.0005	0.0003	
IP	345.003	1.1149	-0.0005	0.0004	
IP	349.999	1.4295	-0.0006	0.0004	
IP	355.001	1.8189	0.0005	0.0005	
IP	360.000	2.2934	0.0004	0.0006	
IP	364.997	2.8691	0.0002	0.0006	
decane	357.031	2.0000	0.0000	0.0001	0.030
decane	363.344	2.6660	-0.0001	0.0002	0.034
decane	372.731	3.9999	0.0002	0.0002	0.031
decane	379.781	5.3330	0.0002	0.0003	0.029
decane	390.243	7.9989	0.0005	0.0004	0.024
decane	398.130	10.6661	0.0005	0.0007	0.023
decane	404.521	13.332	0.000	0.001	0.023
decane	411.173	16.665	0.000	0.001	0.023
decane	416.709	19.933	-0.001	0.001	0.023

TABLE 4. Continued

Method	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma_i}{kPa}$	$\frac{\Delta T}{K}$
trans-(R,S)-Decahydroquinoline (cont.)					
decane	424.010	25.023	-0.002	0.001	0.023
water	424.007 ^a	25.023	0.000	0.002	0.024
water	431.371	31.177	-0.000	0.002	0.024
water	438.799	38.565	-0.002	0.002	0.023
water	446.288	47.375	-0.003	0.002	0.022
water	453.838	57.817	-0.001	0.003	0.023
water	461.453	70.120	0.001	0.003	0.023
water	469.130	84.533	0.004	0.004	0.024
water	476.871 ^a	101.325	0.008	0.004	0.023
water	484.674	120.79	0.01	0.01	0.021
water	492.542	143.25	0.01	0.01	0.021
water	500.467	169.02	0.00	0.01	0.020
water	508.459	198.49	-0.02	0.01	0.020
water	516.508 ^a	232.02	-0.06	0.01	0.021
water	524.617 ^a	270.02	-0.14	0.01	0.023

^a The value at this temperature was given zero weight in the Cox equation fit.

TABLE 5. Cox equation coefficients

	2-Methylaniline	trans-(R,S)-Decahydro-quinoline
T_{ref}/K	473.314	476.874
$P_{\text{ref}}/\text{kPa}$	101.325	101.325
A	2.96783	2.88316
10^3B	-1.63732	-1.66425
10^6C	1.24373	1.33444
T/K^{a}	290 to 517	325 to 508

^a Temperature range of the vapor pressures used in the fit.

TABLE 6. Enthalpies of vaporization and entropies of compression obtained from the Cox and Clapeyron equations ^a
($R=8.31451 \text{ J}\cdot\text{K}^{-1}\text{mol}^{-1}$ and $p^\circ=101.325 \text{ kPa}$)

T/K	$\Delta_l^g H_m/RK$	$\Delta S_{\text{comp},m}/R$	T/K	$\Delta_l^g H_m/RK$	$\Delta S_{\text{comp},m}/R$
2-Methylaniline					
240.00 ^b	7494±17	-13.705±0.002	420.00	5853±7	-1.546±0.000
260.00 ^b	7296±12	-11.334±0.001	440.00	5682±11	-0.912±0.000
280.00 ^b	7101±7	-9.356±0.001	460.00	5509±15	-0.345±0.000
298.15	6928±5	-7.830±0.001	480.00	5334±21	0.165±0.000
300.00	6910±5	-7.687±0.001	500.00	5156±29	0.625±0.000
320.00	6724±3	-6.266±0.000	520.00 ^b	4975±37	1.043±0.000
340.00	6543±2	-5.046±0.000	540.00 ^b	4790±47	1.425±0.000
360.00	6367±2	-3.989±0.000	560.00 ^b	4601±59	1.776±0.000
380.00	6194±2	-3.068±0.000	580.00 ^b	4408±71	2.100±0.000
400.00	6023±4	-2.260±0.000	600.00 ^b	4209±85	2.402±0.000
trans-(R,S)-Decahydroquinoline					
298.15 ^b	6408±4	-7.344±0.001	460.00	5106±34	-0.404±0.000
300.00 ^b	6392±4	-7.211±0.001	480.00	4945±47	0.071±0.000
320.00 ^b	6221±2	-5.897±0.000	500.00	4779±64	0.502±0.000
340.00	6055±2	-4.767±0.000	520.00 ^b	4607±83	0.895±0.000
360.00	5892±3	-3.788±0.000	540.00 ^b	4425±107	1.255±0.000
380.00	5733±6	-2.935±0.000	560.00 ^b	4231±135	1.587±0.000
400.00	5576±10	-2.185±0.000	580.00 ^b	4021±169	1.896±0.000
420.00	5420±16	-1.522±0.000	600.00 ^b	3788±210	2.184±0.000
440.00	5264±24	-0.932±0.000			

^a $\Delta S_{\text{comp}}/R = \ln(p/p^\circ)$

^b Values at this temperature were calculated with extrapolated vapor pressures derived from the fitted Cox coefficients.

TABLE 7. 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; K_d is the distribution coefficient for the impurity as defined in reference 40.

2-Methylaniline		trans-(R,S)-Decahydroquinoline	
F	T(F)/K	F	T(F)/K
0.238	258.584	0.162	321.2990
0.337	258.629	0.312	321.3044
0.485	258.660	0.513	321.3072
0.634	258.677	0.664	321.3085
0.783	258.687		
T_{tp}/K	258.73		321.314
K_d	0.0		0.10
x	0.00075		0.00016

TABLE 8. Experimental enthalpy measurements ($R=8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

N^a	h^b	$\frac{T_i}{\text{K}}$	$\frac{T_f}{\text{K}}$	$\frac{T_{\text{trs}}}{\text{K}}$	$\frac{\Delta_{\text{tot}}H_m^c}{\text{R}\cdot\text{K}}$	$\frac{\Delta_{\text{trs}}H_m^d}{\text{R}\cdot\text{K}}$
2-Methylaniline						
Single-phase measurements in cr						
16	1	98.373	150.793		469.87	0.03
16	1	150.843	201.603		618.56	0.36
19	1	55.709	118.425		915.83	0.20
cr(l) to liquid						
4	2	253.259	262.060	258.73	1591.89	1403.37
20	6	248.635	261.562		1661.38	1401.80
					Average:	1402.59
Single-phase measurements in liquid						
22	1	267.950	307.637		1034.37	0.11
24	1	307.778	385.898		2152.33	-0.28
24	1	385.874	419.335		979.18	-0.17
trans-(R,S)-Decahydroquinoline						
Single-phase measurements in cr						
2	1	230.845	315.852		1799.32	0.14
5	1	62.915	159.207		887.84	0.34
5	1	159.234	261.248		1645.87	0.40
5	1	261.321	315.167		1209.12	1.14
cr to liquid						
1	6	317.101	326.713	321.314	3370.78	3093.06
2	2	315.864	324.743		3338.80	3092.75
5	2	315.213	324.155		3336.78	3093.11
					Average:	3092.98
Single-phase measurements in liquid						
7	1	329.145	420.293		3143.34	-0.40
7	1	420.285	444.219		913.88	-0.08

TABLE 8. Continued

- a Adiabatic series number
- b Number of heating increments
- c $\Delta_{\text{tot}}H_m$ is the molar energy input from the initial temperature T_i to the final temperature T_f .
- d $\Delta_{\text{trs}}H_m$ is the net molar enthalpy of transition at the transition temperature T_{trs} .

TABLE 9. Experimental molar heat capacities at vapor-saturation pressure
($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

N^a	$\frac{\langle T \rangle}{\text{K}}$	$\frac{\Delta T}{\text{K}}$	$\frac{C_{\text{sat},m}^b}{R}$	N^a	$\frac{\langle T \rangle}{\text{K}}$	$\frac{\Delta T}{\text{K}}$	$\frac{C_{\text{sat},m}^b}{R}$
2-Methylaniline							
cr							
18	5.088	0.9833	0.039	17	86.585	8.2565	6.651
18	6.010	0.8254	0.071	17	95.224	8.7908	7.176
18	6.909	0.9730	0.107	14	99.191	9.9564	7.418
18	7.901	1.0289	0.159	17	104.493	9.3321	7.738
18	8.981	1.0875	0.225	15	105.605	8.9897	7.805
18	10.036	1.1060	0.298	14	109.147	9.8972	8.020
18	11.165	1.2530	0.393	17	113.849	9.3591	8.305
18	12.429	1.3223	0.516	15	115.200	10.1136	8.387
18	13.807	1.3694	0.658	14	119.350	9.8896	8.637
18	15.270	1.5326	0.810	15	126.344	12.1021	9.065
18	16.874	1.6743	0.987	14	129.296	9.9405	9.249
18	18.626	1.7986	1.184	15	139.150	13.0386	9.854
18	20.516	1.9848	1.395	14	139.308	10.0216	9.864
18	22.619	2.2017	1.639	14	149.396	10.1237	10.490
18	24.973	2.4917	1.907	15	152.359	13.3452	10.672
18	27.630	2.8067	2.199	15	166.223	14.3472	11.544
18	30.568	3.0568	2.505	15	180.416	14.0040	12.442
18	33.883	3.5757	2.844	20	181.572	26.3227	12.514
18	37.644	3.9425	3.201	15	194.455	14.0530	13.350
18	41.785	4.3186	3.570	20	202.658	15.7583	13.877
18	46.330	4.7514	3.947	15	208.239	13.4910	14.223
18	51.379	5.3429	4.342	19	210.730	20.0487	14.405
17	54.614	4.6230	4.579	20	218.425	15.4046	14.899
18	56.985	5.8686	4.749	15	221.842	13.5982	15.122
17	59.582	5.2194	4.932	20	232.203	11.7907	15.968
17	65.258	6.0608	5.311	15	233.756	10.1663	16.245
17	71.622	6.6197	5.723	20	243.410	10.1777	17.378
17	78.672	7.4430	6.165	15	243.854	10.1466	17.461

TABLE 9. Continued

N^a	$\frac{\langle T \rangle}{K}$	$\frac{\Delta T}{K}$	$\frac{C_{sat,m}^b}{R}$	N^a	$\frac{\langle T \rangle}{K}$	$\frac{\Delta T}{K}$	$\frac{C_{sat,m}^b}{R}$
liquid							
21	235.216	4.0422	25.289	24	302.403	10.6992	26.360
21	241.020	7.5416	25.355	23	313.416	8.8614	26.625
21	248.907	8.2106	25.443	23	324.909	14.0844	26.921
21	257.204	8.3642	25.550	23	339.380	14.8315	27.318
21	265.741	8.6974	25.665	23	354.150	14.6914	27.746
11	269.871	7.4758	25.721	23	369.198	15.4021	28.200
21	273.631	7.0844	25.780	23	385.297	16.9315	28.699
11	277.758	8.3051	25.856	23	400.879	14.2356	29.212
12	277.795	8.6596	25.855	23	415.038	14.0966	29.681
11	286.099	8.4505	26.013	24	423.846	9.0688	29.963
12	286.523	8.8055	26.021	24	432.847	9.0113	30.272
11	294.700	8.7700	26.193	23	440.323	9.4054	30.534
12	295.300	8.7691	26.198	24	441.163	7.7005	30.557
trans-(R,S)-Decahydroquinoline							
cr							
4	5.019	1.4773	0.023	3	86.752	7.1635	7.566
4	6.131	0.8653	0.042	3	94.940	9.1971	8.137
4	7.083	1.1227	0.066	1	96.368	8.8457	8.233
4	8.170	1.0862	0.106	3	104.501	9.6833	8.790
4	9.242	1.0936	0.158	1	105.577	9.5633	8.869
4	10.362	1.1590	0.229	1	115.229	9.7329	9.526
4	11.539	1.2050	0.315	1	125.067	9.9382	10.190
4	12.820	1.3601	0.429	1	135.045	10.0086	10.859
4	14.250	1.4931	0.576	1	145.499	10.1436	11.561
4	15.820	1.6565	0.750	1	155.602	10.0521	12.231
4	17.576	1.8505	0.974	1	165.636	10.0095	12.908
4	19.529	2.0610	1.227	1	175.636	9.9840	13.589
4	21.696	2.2719	1.525	1	185.627	9.9939	14.282

TABLE 9. Continued

N^a	$\frac{\langle T \rangle}{K}$	$\frac{\Delta T}{K}$	$\frac{C_{sat,m}^b}{R}$	N^a	$\frac{\langle T \rangle}{K}$	$\frac{\Delta T}{K}$	$\frac{C_{sat,m}^b}{R}$
4	24.090	2.5160	1.855	1	195.632	10.0109	14.991
4	26.744	2.7948	2.215	1	205.656	10.0322	15.715
4	29.693	3.1043	2.601	1	215.721	10.0562	16.460
4	32.956	3.4228	3.010	1	225.742	9.9842	17.225
4	36.550	3.7635	3.434	1	235.742	10.0124	18.003
4	40.562	4.2605	3.862	1	245.779	10.0623	18.807
4	45.031	4.6774	4.311	1	255.819	10.0213	19.629
4	49.999	5.2564	4.783	1	265.865	10.0751	20.464
3	54.180	5.1332	5.144	1	275.918	10.0392	21.316
4	55.525	5.7938	5.244	1	285.934	10.0988	22.161
3	59.581	5.6026	5.579	1	295.854	10.1694	23.064
3	65.488	6.1818	6.040	1	306.032	10.1039	24.091
3	72.039	6.8956	6.511	1	314.101	5.9541	24.826
3	79.331	7.6614	7.049				
liquid							
5	328.934	9.5542	31.940	6	374.068	14.6122	34.368
2	329.422	9.3582	31.960	6	389.006	15.2667	35.302
1	330.318	7.1789	31.997	6	404.522	15.8826	36.305
6	334.656	15.2089	32.213	6	418.086	11.2927	37.215
1	338.361	8.9074	32.384	6	429.703	12.0007	38.009
6	347.207	9.3931	32.839	6	440.336	9.3148	38.749
6	359.336	14.8452	33.505				

a Adiabatic series number.

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

TABLE 10. Experimental $C_{x\ m}^{\parallel}/R$ values for 2-methylaniline
($R = 8.31451\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

mass / g	0.008152	0.014253	0.024464	0.015667	0.024042
Vol. cell / cm ³ ^a	0.05374	0.05409	0.05576	0.05576	0.05374
T/K	$C_{x\ m}^{\parallel}/R$	$C_{x\ m}^{\parallel}/R$	$C_{x\ m}^{\parallel}/R$	$C_{x\ m}^{\parallel}/R$	$C_{x\ m}^{\parallel}/R$
315.00	26.94			26.70	26.44
335.00	27.11			27.09	27.07
355.00	27.72			27.69	27.65
375.00	28.37			28.26	28.23
395.00	29.23			29.06	28.97
415.00	30.12	29.85	29.70	29.76	29.68
435.00	31.09	30.68	30.38	30.61	30.42
455.00	32.16	31.54	31.09	31.50	31.16
475.00	33.35	32.47	31.97	32.41	31.96
495.00	34.57	33.40	32.62	33.28	32.69
515.00	35.90	34.37	33.57	34.16	33.48
535.00	37.21	35.12	34.05	34.95	34.06
555.00	38.57	35.96	34.66	35.84	34.63
575.00	40.53	37.36	35.79	37.15	35.65
595.00	42.31	38.45	36.44	38.23	36.35
615.00	44.43	39.70	37.19	39.35	37.18
635.00	47.05	41.43	38.37	40.92	38.22
655.00	50.00	43.06	39.33	42.52	39.26
675.00		45.16	40.57	44.49	40.42
695.00		47.75	42.10	46.88	42.18

^a Volume measured at 298.15 K

TABLE 11. Densities and temperatures for the conversion from two phases to a single phase for 2-methylaniline

$\rho/(\text{kg}\cdot\text{m}^{-3})$	T/K
165.8	708.6
188.8	712.8
214.5	713.6
257.6	715.9
274.7	716.2
280.6	716.2
354.8	714.8
370.1	713.2
429.2	707.8
437.6	708.8

TABLE 12. Parameters for equations (14) and (15) and critical constants for 2-methylaniline

A	2.55910	b_0	-0.37322
B	-1.45473	b_1	-0.76654
C	0.95355	b_2	1.36936
		b_3	-1.86367
T_c	716.5 K	p_c	4476 kPa
		ρ_c	305 kg·m ⁻³

TABLE 13. Values of $C_{V,m}^{\text{II}}(\rho = \rho_{\text{sat}})/R$ and $C_{\text{sat},m}/R$ ($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

T/K	$C_{V,m}^{\text{II}}(\rho = \rho_{\text{sat}})/R$	$C_{\text{sat},m}/R$	T/K	$C_{V,m}^{\text{II}}(\rho = \rho_{\text{sat}})/R$	$C_{\text{sat},m}/R$
2-Methylaniline					
340.0	27.34	27.34	540.0	33.93	34.03
360.0	27.95	27.96	560.0	34.62	34.78
380.0	28.57	28.57	580.0	35.30	35.54
400.0	29.19	29.20	600.0	35.98	36.34
420.0	29.83	29.83	620.0	36.66	37.22
440.0	30.48	30.49	640.0	37.37	38.25
460.0	31.15	31.16	660.0	38.16	39.62
480.0	31.83	31.86	680.0	39.17	41.88
500.0	32.53	32.57	700.0	40.76	47.59
520.0	33.23	33.29			

TABLE 14. Molar thermodynamic functions at vapor-saturation pressure

(R = 8.31451 J·K⁻¹·mol⁻¹)

$\frac{T}{K}$	$\frac{C_{\text{sat,m}}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{RT}$	$\frac{T}{K}$	$\frac{C_{\text{sat,m}}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{RT}$
2-Methylaniline							
cr							
5.000	0.041	0.014	0.010	80.000	6.247	5.506	3.173
6.000	0.070	0.023	0.017	90.000	6.859	6.277	3.549
7.000	0.111	0.037	0.028	100.000	7.465	7.031	3.910
8.000	0.164	0.055	0.041	110.000	8.072	7.771	4.261
9.000	0.226	0.078	0.058	120.000	8.677	8.500	4.604
10.000	0.296	0.105	0.079	130.000	9.292	9.218	4.941
12.000	0.473	0.174	0.129	140.000	9.906	9.929	5.273
14.000	0.678	0.262	0.193	150.000	10.525	10.634	5.603
16.000	0.890	0.367	0.266	160.000	11.151	11.333	5.930
18.000	1.114	0.484	0.348	170.000	11.782	12.028	6.256
20.000	1.338	0.613	0.436	180.000	12.416	12.720	6.580
25.000	1.910	0.973	0.673	190.000	13.053	13.408	6.904
30.000	2.447	1.370	0.925	200.000	13.683	14.094	7.228
35.000	2.952	1.785	1.179	210.000	14.311	14.776	7.550
40.000	3.414	2.210	1.430	220.000	14.979	15.457	7.872
45.000	3.839	2.637	1.674	230.000	15.768	16.140	8.198
50.000	4.236	3.062	1.911	240.000	16.749	16.831	8.533
60.000	4.960	3.900	2.360	250.000 ^a	17.988	17.539	8.885
70.000	5.619	4.715	2.779	258.730 ^a	19.332	18.178	9.214
liquid							
240.000	25.343	21.687	13.791	380.000	28.533	33.889	18.539
250.000	25.456	22.724	14.256	400.000	29.182	35.369	19.054
258.730	25.568	23.599	14.635	420.000	29.844	36.809	19.552
260.000	25.584	23.725	14.689	440.000	30.516	38.213	20.035
270.000	25.724	24.693	15.095	460.000	31.166	39.584	20.505
280.000	25.897	25.631	15.477	480.000	31.859	40.925	20.964

TABLE 14. Continued

$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m^o}{R}$	$\frac{\Delta_0^T H_m^o}{RT}$	$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m^o}{R}$	$\frac{\Delta_0^T H_m^o}{RT}$
290.000	26.093	26.543	15.840	500.000	32.570	42.240	21.414
298.150	26.266	27.269	16.123	520.000	33.291	43.531	21.857
300.000	26.307	27.432	16.185	540.000	34.030	44.801	22.294
320.000	26.793	29.144	16.833	560.000	34.780	46.052	22.726
340.000	27.335	30.785	17.434	580.000	35.540	47.286	23.155
360.000	27.921	32.364	18.000	600.000	36.340	48.504	23.581

trans-(R,S)-Decahydroquinoline

cr

5.000	0.023	0.701	0.006	120.000	9.849	10.022	5.176
6.000	0.039	0.706	0.010	130.000	10.521	10.836	5.561
7.000	0.064	0.714	0.016	140.000	11.192	11.641	5.939
8.000	0.099	0.724	0.024	150.000	11.859	12.436	6.312
9.000	0.145	0.739	0.035	160.000	12.527	13.222	6.679
10.000	0.204	0.757	0.049	170.000	13.204	14.002	7.043
12.000	0.354	0.807	0.086	180.000	13.890	14.776	7.405
14.000	0.549	0.876	0.138	190.000	14.590	15.546	7.764
16.000	0.773	0.963	0.203	200.000	15.304	16.312	8.123
18.000	1.028	1.069	0.280	210.000	16.034	17.077	8.483
20.000	1.291	1.190	0.368	220.000	16.784	17.840	8.843
25.000	1.980	1.553	0.622	230.000	17.554	18.603	9.205
30.000	2.640	1.973	0.904	240.000	18.342	19.366	9.569
35.000	3.255	2.426	1.196	250.000	19.151	20.131	9.936
40.000	3.805	2.898	1.489	260.000	19.975	20.899	10.306
45.000	4.309	3.375	1.774	270.000	20.814	21.668	10.680
50.000	4.781	3.854	2.052	280.000	21.656	22.440	11.057
60.000	5.612	4.800	2.577	290.000	22.522	23.215	11.437
70.000	6.367	5.723	3.065	298.150	23.298	23.850	11.750
80.000	7.095	6.621	3.524	300.000	23.484	23.995	11.822
90.000	7.792	7.497	3.959	310.000	24.457	24.781	12.214

TABLE 14. Continued

$\frac{T}{K}$	$\frac{C_{\text{sat},m}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{RT}$	$\frac{T}{K}$	$\frac{C_{\text{sat},m}}{R}$	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_0^T H_m^\circ}{RT}$
100.000	8.485	8.354	4.377	320.000 ^a	25.353	25.571	12.611
110.000	9.171	9.195	4.782	321.314 ^a	25.471	25.676	12.663
liquid							
298.150 ^a	30.638	32.975	21.605	380.000	34.733	40.842	23.954
300.000 ^a	30.708	33.165	21.661	400.000	36.009	42.656	24.525
310.000 ^a	31.104	34.178	21.959	420.000	37.345	44.445	25.103
320.000 ^a	31.530	35.172	22.251	440.000	38.725	46.214	25.691
321.314 ^a	31.588	35.302	22.289	460.000 ^a	40.142	47.966	26.288
330.000	31.982	36.149	22.539	480.000 ^a	41.602	49.705	26.896
340.000	32.467	37.111	22.824	500.000 ^a	43.102	51.434	27.514
360.000	33.543	38.997	23.389				

^a Values at this temperature were calculated with graphically extrapolated heat capacities.

TABLE 15. Thermodynamic properties in the ideal-gas state
($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $p^\circ = 101.325 \text{ kPa}$)

$\frac{T}{\text{K}}$	$\frac{\Delta_0 H_m^\circ}{R T}$	$\frac{\Delta_{\text{imp}} H_m^\circ}{R T}^a$	$\frac{\Delta_0 S_m^\circ}{R}$	$\frac{\Delta_{\text{imp}} S_m^\circ}{R}^b$	$\frac{\Delta_f H_m^\circ}{R T}$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_f G_m^\circ}{R T}$
2-Methylaniline							
240.00 °	45.016±0.072	0.000	39.902±0.076	0.000	28.32±0.26	-42.02±0.15	70.34±0.28
260.00 °	42.750±0.048	0.000	41.145±0.051	0.000	25.58±0.23	-43.61±0.15	69.19±0.27
280.00 °	40.838±0.029	0.000	42.328±0.037	0.000	23.21±0.21	-43.19±0.16	66.40±0.26
298.15	39.360±0.023	0.001	43.368±0.032	0.001	21.33±0.19	-43.65±0.18	64.98±0.26
300.00	39.219±0.023	0.001	43.473±0.032	0.001	21.15±0.19	-43.69±0.18	64.84±0.26
320.00	37.847±0.019	0.002	44.586±0.031	0.002	19.35±0.18	-44.19±0.20	63.54±0.27
340.00	36.683±0.018	0.005	45.681±0.031	0.004	17.78±0.17	-44.65±0.21	62.43±0.28
360.00	35.696±0.019	0.010	46.761±0.033	0.008	16.39±0.17	-45.06±0.23	61.45±0.29
380.00	34.856±0.019	0.018	47.827±0.035	0.014	15.16±0.17	-45.43±0.25	60.59±0.30
400.00	34.142±0.022	0.030	48.882±0.037	0.023	14.07±0.16	-45.78±0.27	59.85±0.31
420.00	33.535±0.026	0.047	49.927±0.040	0.036	13.10±0.17	-46.09±0.29	59.19±0.33
440.00	33.020±0.032	0.071	50.960±0.045	0.053	12.22±0.17	-46.37±0.30	58.59±0.35
460.00	32.583±0.040	0.102	51.984±0.052	0.075	11.44±0.18	-46.61±0.32	58.05±0.37
480.00	32.216±0.054	0.140	52.998±0.065	0.102	10.74±0.19	-46.85±0.34	57.59±0.39
500.00	31.912±0.071	0.187	54.004±0.080	0.134	10.10±0.20	-47.06±0.36	57.16±0.41
520.00 °	31.667±0.088	0.243	55.006±0.097	0.173	9.54±0.21	-47.24±0.39	56.78±0.43
540.00 °	31.473±0.107	0.309	56.009±0.116	0.220	9.03±0.22	-47.39±0.41	56.42±0.45
560.00 °	31.331±0.127	0.388	57.015±0.136	0.277	8.58±0.24	-47.51±0.43	56.09±0.47
580.00 °	31.238±0.147	0.483	58.027±0.158	0.347	8.20±0.28	-47.60±0.45	55.80±0.49
600.00 °	31.193±0.168	0.597	59.048±0.179	0.434	7.86±0.28	-47.65±0.48	55.51±0.51

TABLE 15. Continued

$\frac{T}{K}$	$\frac{\Delta_f H_m^\circ}{R T}$	$\frac{\Delta_{imp} H_m^\circ}{R T}$ ^a	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_{imp} S_m^\circ}{R}$ ^b	$\frac{\Delta_f H_m^\circ}{R T}$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_f G_m^\circ}{R T}$
trans-(R,S)-Decahydroquinoline							
298.15 ^{c,d}	43.099±0.025	0.001	46.430±0.035	0.001	-45.62±0.27	-104.78±0.23	59.16±0.36
300.00 ^{c,d}	42.969±0.025	0.001	46.567±0.035	0.001	-45.46±0.27	-104.90±0.23	59.44±0.36
320.00 ^{c,d}	41.695±0.023	0.003	48.026±0.035	0.003	-43.76±0.26	-106.08±0.25	62.32±0.36
340.00	40.640±0.024	0.007	49.465±0.037	0.006	-42.25±0.24	-107.18±0.28	64.93±0.37
360.00	39.769±0.025	0.013	50.895±0.040	0.011	-40.88±0.24	-108.18±0.30	67.30±0.38
380.00	39.064±0.029	0.023	52.319±0.043	0.018	-39.62±0.23	-109.10±0.32	69.48±0.40
400.00	38.502±0.035	0.037	53.746±0.049	0.028	-38.45±0.23	-109.93±0.35	71.48±0.41
420.00	38.063±0.046	0.055	55.175±0.058	0.040	-37.35±0.23	-110.68±0.37	73.33±0.43
440.00	37.733±0.060	0.078	56.608±0.071	0.056	-36.32±0.24	-111.36±0.39	75.04±0.45
460.00 ^d	37.495±0.078	0.107	58.043±0.089	0.074	-35.34±0.25	-111.97±0.42	76.63±0.48
480.00 ^d	37.339±0.102	0.141	59.480±0.110	0.095	-34.40±0.26	-112.52±0.45	78.11±0.50
500.00 ^d	37.253±0.131	0.181	60.920±0.137	0.119	-33.51±0.28	-113.01±0.48	79.50±0.52

^a Gas-imperfection correction to the ideal-gas enthalpy.

^b Gas-imperfection correction to the ideal-gas entropy.

^c Values at this temperature were calculated with extrapolated vapor pressures calculated from the fitted Cox coefficients.

^d Values at this temperature were calculated with graphically extrapolated values of the liquid-phase heat capacities.