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CRITICAL PROPERTY AND HIGH-TEMPERATURE HEAT-CAPACITY MEASUREMENTS ON QUINOLINE AND 5,6,7,8-TETRAHYDROQUINOLINE

Topical Report

By
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June 1990

Performed Under Cooperative Agreement No. FC22-83FE60149

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

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U. S. DEPARTMENT OF ENERGY
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Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy

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EXECUTIVE SUMMARY

In petroleum refining process streams contain materials ranging from hydrogen to some that decompose well before reaching their normal boiling point which is extrapolated to be in excess of 1000°F. To characterize such streams process engineers use "defined compounds" and "fractions." "Defined compounds" are identifiable chemical substances: hydrogen, methane, phenol, quinoline, etc. A "fraction" is a narrow boiling-range cut or "petroleum fraction" which can be treated as a single pseudo-component with a boiling point equal to the average boiling point of the fraction. This method of characterization is very successful for paraffinic crude oils.

Arabian light crude contains approximately 80 wt % saturates and 20 wt % aromatics with approximately 1.8 wt % sulfur and little or no nitrogen or oxygen. As the spectrum of fossil energy materials shifts from Arabian light through heavy petroleum, shale oil, tar sands, and the products of the liquefaction of coal, the compound type distribution changes. At the end of the spectrum, liquids derived from the liquefaction of coal contain only 35 wt % saturates and 60 wt % aromatics. In addition, while the sulfur content has decreased to approximately 0.2 wt %, other heteroatoms have been introduced in large quantities. On the average, coal liquids contain 0.3 wt % nitrogen and 2.0 wt % oxygen. This means that the wt % of compounds containing heteroatoms has shifted from 10 wt % in Arabian light crude to greater than 25 wt % in liquids derived from the liquefaction of coal. The shift is gradual across the whole spectrum of fossil materials.

Because of these changes in composition, process design correlations derived for Arabian light crude will need, at best, modification to make them applicable to the changing fossil materials. It may be the case that new correlations will be needed to adequately represent the process streams. Model or "key" compounds are especially important in testing existing correlations and developing new ones for characterization and property prediction for the different fossil sources. Accurate and precise thermophysical property values for "key" compound types are essential in the testing and development of the process design equations. However, the literature on thermochemical and thermophysical property values for "key" nitrogen-containing heterocyclic aromatic compounds is sparse. Greater than 90 per cent of the available measurements are those obtained in this research project funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Extraction and Process Technology (AEPT).

This report details results of thermophysical property measurements (high-temperature heat capacities, and critical properties) made on quinoline and 5,6,7,8-

tetrahydroquinoline. Both are "key" compounds in process design engineering for hydrodenitrogenation of fossil materials. These results, in conjunction with values for other major nitrogen-containing compound types under study in this project, provide a sound basis for the analysis and development of correlations. Such correlations are necessary for the cost-effective, energy-efficient design of process equipment such as distillation towers, heat-exchangers, and gas-liquid reactors.

ABSTRACT

Critical property and high-temperature heat capacity measurements on quinoline and 5,6,7,8-tetrahydroquinoline are reported. From the measurements, critical temperatures of (787±2) K and (746±2) K, and critical densities of (336±3) $kg \cdot mol^{-1}$ and (304±3) $kg \cdot mol^{-1}$ were obtained for quinoline and 5,6,7,8-tetrahydroquinoline, respectively. Critical pressures of (4820±50) kPa and (3975±40) kPa, respectively, were derived from the fitting procedures used. The results from the high-temperature heat capacity measurements were combined with earlier reported measurements at lower temperatures to obtain ideal-gas thermodynamic functions for both quinoline and 5,6,7,8-tetrahydroquinoline in the temperature range 298.15 K to 700 K. The derived values are compared with literature values. Densities for quinoline, estimated using the experimental critical properties determined in this research and extended corresponding states, are compared with literature measurements. Agreement is excellent with a maximum difference of 0.14 per cent at 298 K. Using critical properties estimated via group-contribution methods the agreement is not so good. The difference between experimental and calculated values averages 4.5 per cent .

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 acknowledge Professor E. J. "Pete" Eisenbraun and his research team at Oklahoma State University for preparation of the samples, and the assistance of I. A. Hossenlopp in vapor-transfer of the materials prior to the calorimetric measurements.

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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 any 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 $\rho/(kg \cdot m^{-3})$ 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., $C_{sat,m}$, 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 $g \cdot mol^{-1}$

T = temperature in Kelvin

p = pressure in Pascals (Pa)

ρ = density in $kg \cdot m^{-3}$

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

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

$\Delta_f H^\circ_m$ = molar enthalpy of formation

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

$\Delta^g_l V_m$ = 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

$C_{sat,m}$ = 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^{II}_x = two-phase heat capacity at cell volume V_x

C^{II}_v = two-phase heat capacity at constant volume

C^{II}_V $(\rho = \rho_{sat})$ = 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

ρ_{cs} = density calculated using extended corresponding states

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)

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

$\Delta_{imp}S_m$ = 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

In this research program, funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Extraction and Process Technology (AEPT), 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 feedstocks.[1-4]§ They are typically rich in nitrogen, and their fractionation produces distillates that are also rich in nitrogen, giving poor quality distillate fuels without denitrogenation.

Hydrodenitrogenation (HDN) reactions of 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. In addition a knowledge of thermophysical properties, particularly the critical temperature, critical volume, and critical pressure is necessary for process-design estimations.

This report is a companion to Topical Report NIPER-468, "Thermodynamics of the Hydrodenitrogenation of Quinoline." The present report provides key experimental information necessary for the thermodynamic analysis presented in NIPER-468. In earlier reports and journal articles the thermodynamic properties of quinoline and isoquinoline,[5,6] 1,2,3,4- and 5,6,7,8-tetrahydroquinoline,[7,8] and 2-methyl-aniline and trans-(R,S)-decahydroquinoline[9] were reported. The present report extends the results for quinoline and 5,6,7,8-tetrahydroquinoline to include the measurement of high-temperature heat capacities and critical properties. These results allow the thermodynamic equilibria calculations in Topical Report NIPER-468 (which are essential to understanding the HDN process) to be based on *experimental* thermodynamic properties in the temperature range of commercial HDN (325 to 425°C). In conjunction with values of the same thermodynamic properties for other "key" organo-nitrogen compound types, a basis for the derivation of new correlations applicable to the streams obtained in the processing of heavy petroleum, oil shale and the products of the liquefaction of coal is provided. Such correlations are necessary for the cost-effective energy-efficient design of process equipment such as distillation towers, heat-exchangers, and gas-liquid reactors.

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

2. EXPERIMENTAL

MATERIALS

Details of the preparation, purification, and purity of the samples of quinoline and 5,6,7,8-tetrahydroquinoline were given in references 5, 6, 7, and 8.

PHYSICAL CONSTANTS AND STANDARDS

Molar values are reported in terms of $M = 129.1613\ g \cdot mol^{-1}$ for quinoline and $M = 133.1931\ g \cdot mol^{-1}$ for 5,6,7,8-tetrahydroquinoline and are based on the relative atomic masses of 1981[10] and the gas constant, $R = 8.31451\ J \cdot K^{-1} \cdot mol^{-1}$, adopted by CODATA.[11] All temperatures reported are in terms of the IPTS-68.[12] Measurements of mass, time, electrical resistance, and potential difference were made in terms of standards traceable to calibrations at the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS).

Differential-Scanning Calorimetry. Differential-scanning calorimetric measurements were made with a Perkin-Elmer DSC II. Experimental methods were described previously.[13]

3. RESULTS

DIFFERENTIAL SCANNING CALORIMETRY

Theoretical Background. The theoretical background for the determination of heat capacities at vapor-saturation pressure, $C_{sat,m}$, with a d.s.c. has been described.[13] 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, $C^{II}_{x,m}$, can be expressed in terms of the temperature derivatives of these quantities:

$$n\,C^{II}_{x,m}/T = -n(\delta^2\mu/\delta T^2)_{sat} + V_x\,(\delta^2 p/\delta T^2)_{sat} + \{(\delta V_x/\delta T)_x\,(\delta p/\delta T)_{sat}\}. \quad (1)$$

The third term on the right-hand side of equation (**1**) includes the thermal expansion of the cell. In this research the thermal expansion of the cells was expressed as:

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

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

$(\delta p/\delta T)_{sat}$ can be calculated based on measured vapor pressures. Therefore, with a minimum of two different filling levels of the cell $(\delta^2 p/\delta T^2)_{sat}$ and $(\delta^2 \mu/\delta T^2)_{sat}$ can be determined. To obtain the saturation heat capacity $C_{sat,m}$ 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:

$$\lim_{(n/V_x) \to \{1/V_m(l)\}} (n\, C^{II}_{v,m}/T) = V_m(l)(\delta^2 p/\delta T^2)_{sat} - n(\delta^2 \mu/\delta T^2)_{sat}. \qquad (3)$$

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

$$\lim_{(n/V_x) \to \{1/V_m(l)\}} (n\, C^{II}_{v,m}) = n[C_{sat,m} - \{T(\delta p/\delta T)_{sat}\, (\delta V_m(l)/\delta T)\}]. \qquad (4)$$

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

DSC Measurement Results. Table 1¶ lists the experimental two-phase heat capacities $C^{II}_{x,m}$ for both quinoline and 5,6,7,8-tetrahydroquinoline obtained using three cell fillings each. Quinoline decomposes in the region of its critical temperature.[14] Preliminary studies showed that the temperature at which conversion from two phases to a single phase occurred was a function of the heating rate below 0.17 $K \cdot s^{-1}$. No such dependence was shown for values obtained at a heating rate of 0.17 $K \cdot s^{-1}$ and greater. Table 2 reports the filling density, obtained from the mass of sample and the cell volume calculated using equation (2), and the measured temperatures at which conversion to a single phase was observed for measurements on quinoline. Figure 1 illustrates the dependence of conversion temperature on the heating rate. Using the values obtained for heating rates of 0.17 $K \cdot s^{-1}$ and greater, a critical temperature of (787±2) K and a corresponding critical density of (336±3) $kg \cdot m^{-3}$, were derived graphically for quinoline, as seen in figure 1.

¶ All tables are listed at the end of this Report.

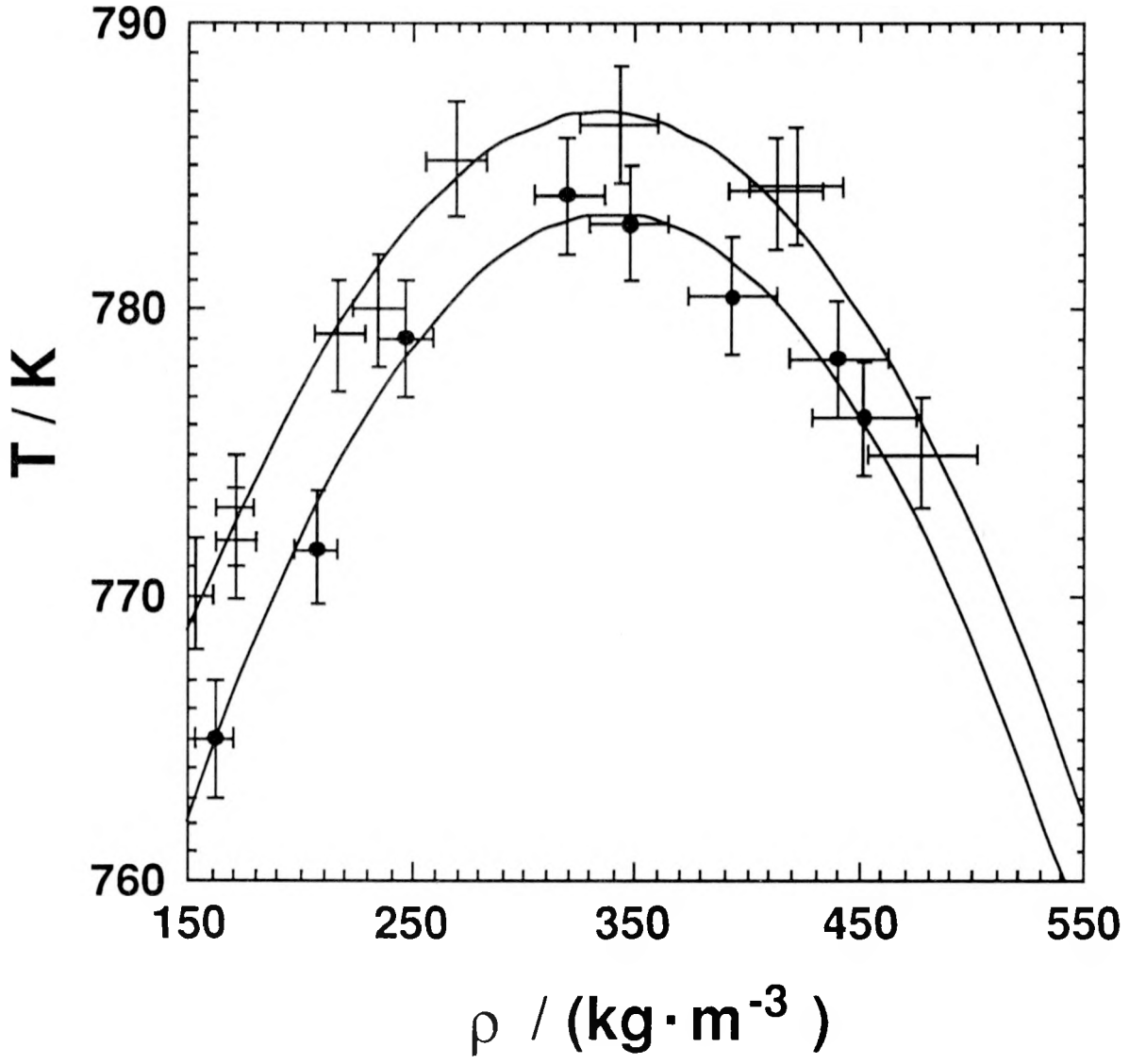

Figure 1. Vapor-liquid coexistence region for quinoline. The crosses span the range of uncertainty; ⊢⊣, represents values obtained at heating rates of 0.17 $K \cdot s^{-1}$, 0.34 $K \cdot s^{-1}$ or 0.68 $K \cdot s^{-1}$; ⊢●⊣,represents values obtained at a heating rate of 0.08 $K \cdot s^{-1}$.

The temperature at which conversion to a single phase occurred for 5,6,7,8-tetrahydroquinoline was measured for seven cell fillings. Table 2 reports the filling density, obtained from the mass of sample and the cell volume calculated using equation (**2**), and the measured temperature at which conversion to a single phase was observed. A critical temperature of (746±2) K and a critical density of (304±3) $kg \cdot m^{-3}$ were derived graphically for 5,6,7,8-tetrahydroquinoline using these results, as seen in figure 2.

High-temperature heat capacity (> 450 K) and critical-property determinations were also attempted for 1,2,3,4-tetrahydroquinoline. However, measurements were precluded by rapid sample decomposition near 550 K.

Simultaneous Fit of Vapor-pressure and Two-phase Heat-capacity Results. The critical pressures for quinoline and 5,6,7,8-tetrahydroquinoline were not measured directly, but were estimated by means of simultaneous non-linear least-squares fits using the vapor pressures listed in references 5, 6 and 7, 8 and the $C^{II}_{x,m}$ values given in table 1. $C_{sat,m}$ values were derived using results of the fit and equation (**4**). Experimental $C^{II}_{x,m}$ were converted to $C^{II}_{v,m}$ values by means of equation (**2**) for the cell expansion and the vapor pressure fit described below for $(\delta p/\delta T)_{sat}$. The values of $C^{II}_{v,m}$ were used to derive functions for $(\delta^2 p/\delta T^2)_{sat}$ and $(\delta^2 \mu/\delta T^2)_{sat}$. The Cox equation[15] was used to represent the vapor pressures in the form:

$$\ln(p/p_c) = (1 - 1/T_r) \exp (A + BT_r + CT_r^2) , \qquad (5)$$

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 least-squares analysis. The functional form chosen for variation of the second derivative of the chemical potential with temperature was:

$$(\delta^2 \mu/\delta T^2)_{sat} = \sum_{i=0}^{n} b_i (1 - T/T_c)^i . \qquad (6)$$

[For compounds where sufficient information was available to evaluate reliably $(\delta^2 \mu/\delta T^2)_{sat}$ (e.g., benzene[16] and toluene[17]), 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:

$$\Delta = C^{II}_{v,m}/R - \{V_m(l)T/nR\}(\delta^2 p/\delta T^2)_{sat} + (T/R)(\delta^2 \mu/\delta T^2)_{sat} . \qquad (7)$$

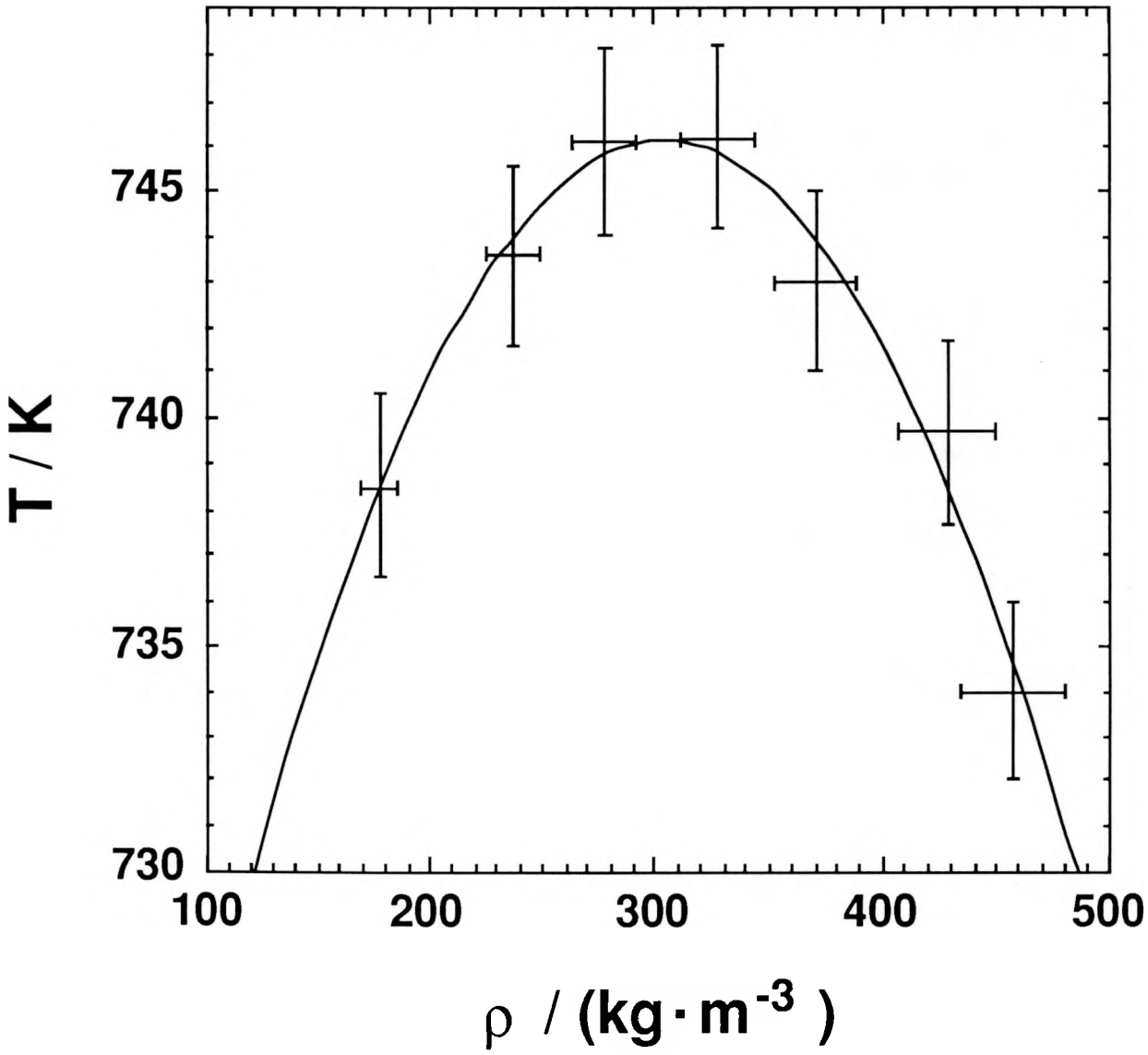

Figure 2. Vapor-liquid coexistence region for 5,6,7,8-tetrahydroquinoline. The crosses span the range of uncertainty.

For the vapor-pressure fits, the functional forms of the weighting factors used have been reported.[5,6] For the heat-capacity results the weighting factors were proportional to the square of the mass of sample used in the measurements.

Table 3 lists the coefficients determined in the least-squares fits. A weighting factor of 20 was used to increase the relative weights of the vapor-pressure measurements. The weighting factor reflects the higher precision of the vapor-pressure values relative to the experimental heat capacities.

Values of $C_{sat,m}$ for quinoline and 5,6,7,8-tetrahydroquinoline were derived from $C^{II}_{v,m}(\rho=\rho_{sat})$ with the densities obtained from the corresponding-states equation in the form:[18]

$$(\rho/\rho_c) = 1.0 + 0.85\{1.0 - (T_r)\} + (1.692 + 0.986\omega)\{1.0 - (T_r)\}^{1/3}, \qquad (8)$$

with $\rho_c = 336\ kg{\cdot}m^{-3}$, $T_c = 787$ K, and acentric factor $\omega = 0.317$ for quinoline and $\rho_c = 304\ kg{\cdot}m^{-3}$, $T_c = 746$ K, and acentric factor $\omega = 0.355$ for 5,6,7,8-tetrahydroquinoline. 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 3 were used to calculate p. The results for $C^{II}_{v,m}(\rho = \rho_{sat})/R$ and $C_{sat,m}/R$ are reported in table 4. The estimated uncertainty in these values is 1 per cent.

ENTHALPIES OF VAPORIZATION

Details of Cox equation fits of the vapor pressures and derived parameters for quinoline and 5,6,7,8-tetrahydroquinoline were reported previously.[5-8] Enthalpies of vaporization $\Delta^g_l H_m$ were derived from the Cox equation fits with the Clapeyron equation:

$$dp/dT = \Delta^g_l H_m / (T \Delta^g_l V_m) , \qquad (9)$$

where $\Delta^g_l V_m$ is the increase in molar volume from the liquid to the real vapor. $\Delta^g_l V_m$ was calculated using estimates of the second virial coefficients derived from the extended corresponding-states equation of Pitzer and Curl.[19] Liquid-phase densities were obtained from extended corresponding-states estimates and measured critical parameters. For both quinoline and 5,6,7,8-tetrahydroquinoline, uncertainties in the second virial coefficients and liquid-phase densities were estimated to be 10 and 3 per cent of the calculated values, respectively. Derived enthalpies of vaporization and the corresponding entropies of compression are reported in table 5.

THERMODYNAMIC PROPERTIES IN THE CONDENSED STATE

Condensed-phase entropies and enthalpies relative to those of the crystals at $T \rightarrow 0$ for the solid and liquid phases under vapor saturation pressure are listed in table 6. These were derived by integration of the smoothed heat capacities reported previously[5-8] corrected for pre-melting, together with the entropies and enthalpies of transition and fusion and the heat capacity values listed in table 4. 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.

THERMODYNAMIC PROPERTIES IN THE IDEAL-GAS STATE

Enthalpies and entropies at selected temperatures for the ideal gas were calculated using values in tables 5 and 6 and are listed in columns 2 and 4 of table 7. Values above 700 K are not reported 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[5-8] to calculate the enthalpies, entropies, and Gibbs energies of formation listed in columns 6, 7, and 8, respectively, of table 7. Enthalpies and entropies for nitrogen and equilibrium hydrogen were determined from JANAF tables.[20] Enthalpies and entropies for graphite were calculated using the polynomial reported in reference 21. All uncertainties in table 7 represent one standard deviation. Uncertainties in the properties of the elements as assessed in the JANAF tables are not included since they cancel in thermodynamic equilibria calculations.

4. DISCUSSION

CRITICAL PROPERTIES

In 1963 Ambrose[14] reported measurements of the critical temperatures of 23 compounds, including quinoline, all of which were unstable in the region of the critical point. Measurements were made using a "rapid heater" method developed at the National Physical Laboratory at Teddington in England. Ambrose made his measurements on a relatively impure sample of quinoline (99.69 mole per cent pure) and reported a critical temperature of (782±2)K. The reported value is close to that obtained in this research (787±2)K. The difference is probably due to the differing purities of the samples studied and the measurement methodology. Recall that at "low" heating rates (see figure 1) the apparent critical temperature was several Kelvin below the value accepted in this report.

In the absence of measured values for the critical density and critical pressure of quinoline values estimated using correlation schemes[22-25] prevail in the literature. Ambrose[14] reported an estimated critical temperature of 771 K obtained using the Lydersen correlation method.[24] A monograph in the API series[26] reported estimated values of 4660 kPa, and 321 $kg \cdot mol^{-1}$ for the critical pressure and critical density, respectively. Those values can be compared with values of (4820±50) kPa, and (336±3) $kg \cdot mol^{-1}$, respectively obtained in this research.

No experimentally measured values for the critical constants for 5,6,7,8-tetrahydroquinoline were found in a search of the literature. Estimated values obtained using the group-additivity type correlation method outlined by Somayajulu[23] are T_c = 750 K, p_c = 4056 kPa, and ρ_c = 308 $kg \cdot mol^{-1}$, which are in excellent agreement with the values measured here, namely, T_c = (746±2) K, p_c = (3975±40) kPa, and ρ_c = (304±3) $kg \cdot mol^{-1}$. This illustrates that group-additivity type correlation schemes are excellent prediction methods provided that the database from which they are derived contains molecules of structure similar to that of the molecules whose properties are being estimated.

DENSITY

Measured values of the density of quinoline in the temperature range 298 to 424 K were made earlier in this research program.[5,6] It is of interest to compare those measurements with densities derived using extended corresponding-states, ρ_{cs}, 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 quinoline and calculated ρ_{cs} using the equation:

$$(\rho_{cs}/\rho_c) = 1.0 + 0.85\{1.0 - (T/T_c)\} + (1.692 + 0.986\omega)\{1.0 - (T/T_c)\}^{1/3}, \quad (10)$$

with ρ_c = 336 $kg \cdot m^{-3}$, T_c = 787 K, and ω = 0.317. The agreement is excellent with the maximum percentage difference, $100\{\rho_{lit} - \rho_{cs}\}/\rho_{lit}$, 0.14 per cent occurring at 298 K. [A similar comparison for 2-methylaniline densities was reported in reference 9 where the average difference was less than 1 per cent.] Such a difference is within the assigned uncertainty in the experimentally determined critical density for 2-methylaniline.[9] If the critical properties reported in the API Monograph on quinoline[26] are used to derive the ρ_{cs} values, the average percentage difference, $100\{\rho_{lit} - \rho_{cs}\}/\rho_{lit}$, is 4.5 per cent. This shows the power of extended corresponding

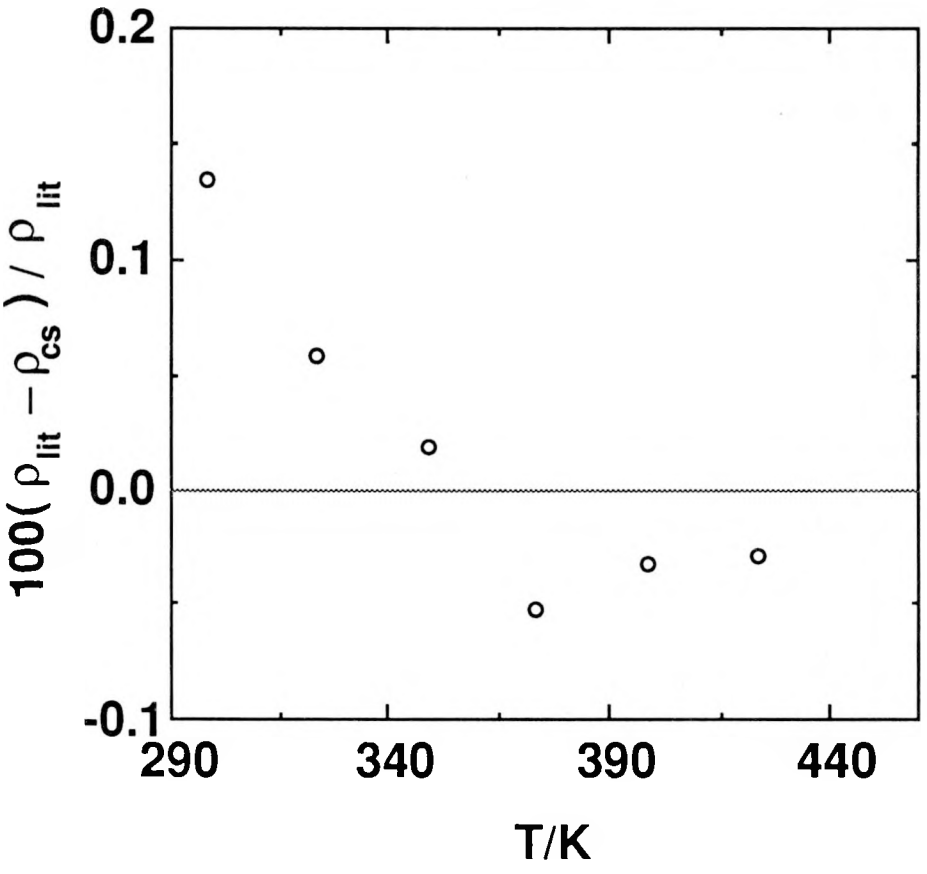

Figure 3. Percentage deviation plot for quinoline densities. ρ_{cs} was calculated using equation **10** and the constants reported in the text. o , Steele et al.;[5,6]

states calculations to estimate values for the thermophysical properties of organic compounds **provided** the critical constants are accurately known.

IDEAL GAS THERMODYNAMIC FUNCTIONS

Ideal-gas properties for quinoline based on molecular spectroscopy and statistical thermodynamics were reported by this research group in references 5 and 6. In the earlier work the statistical thermodynamic values for the ideal gas entropy were compared with values derived using the available heat-capacity and vapor-pressure results. Then, the upper limit for the comparison was 500 K. Figure 4 shows the comparison with the results extended to 700 K. Also included in the figure is a comparison of the Gibbs energies of formation for quinoline derived from the statistical calculations and from the "conventional" calorimetric measurements. The agreement is excellent between the Gibbs energies of formation obtained using both methods. The difference between the derived entropies is larger than that for the Gibbs energies. This is probably due to the use of the virial equation of state truncated at the second virial term to derive the enthalpies of vaporization. At high pressures (above 600 K in this case) introduction of a third virial term would be required to accurately represent the vaporization behavior. However, not enough experimental information is available to derive the third virial coefficient. The excellent agreement between the Gibbs energies of formation for the ideal-gas phase derived by both methods supports the accuracy of the vibrational assignment given in references 5 and 6 and the high temperature heat capacities reported in this research.

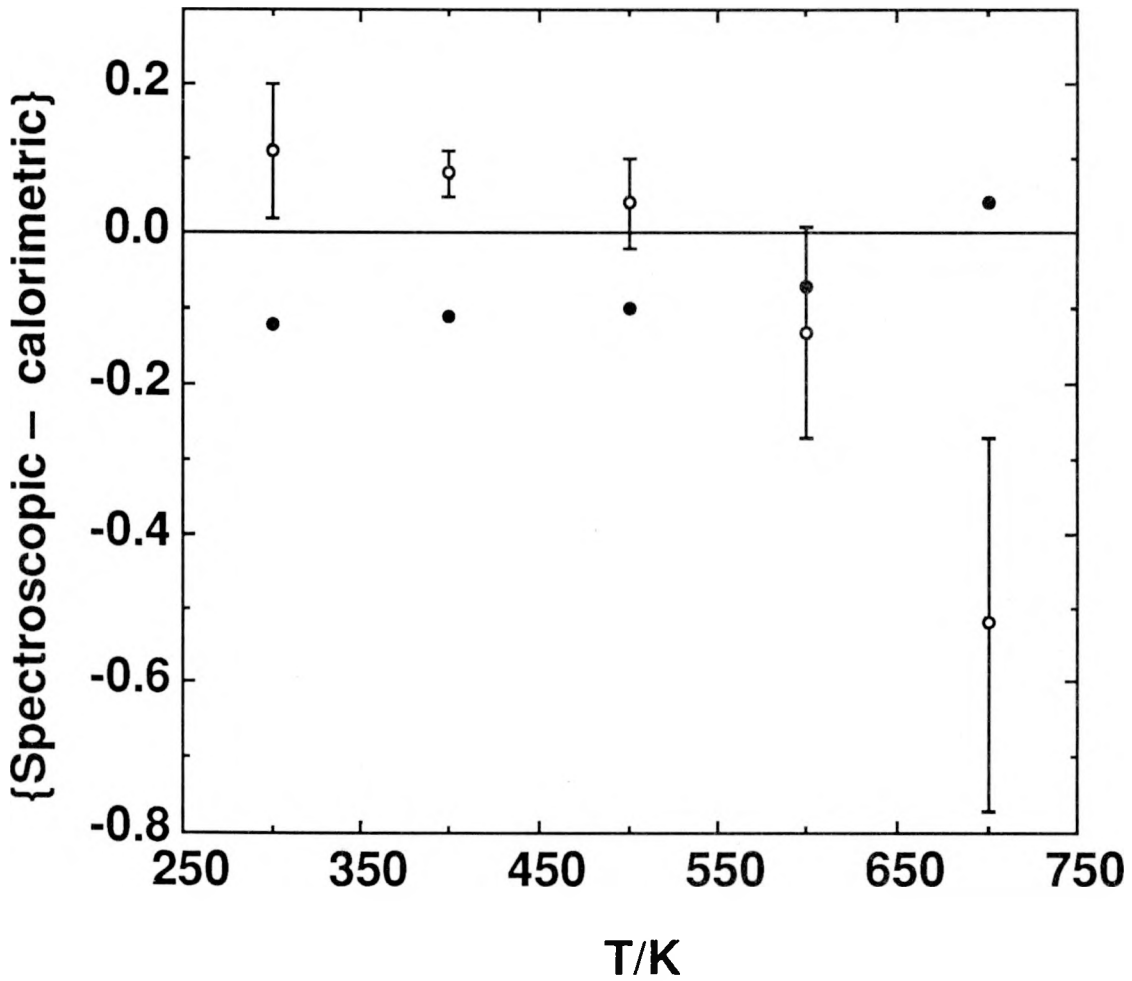

Figure 4. Comparison of experimental calorimetric and spectroscopic[5,6] ideal-gas Gibbs energies of formation and entropies for quinoline. The bars span the range of uncertainty in the calorimetric measurements; o, represents values of $\{\Delta_0^T S_m^\circ(\text{spectroscopic}) - \Delta_0^T S_m^\circ(\text{calorimetric})\}/R$.; ●, represents values of $\{\Delta_0^T G_m^\circ(\text{spectroscopic}) - \Delta_0^T G_m^\circ(\text{calorimetric})\}/RT$.

5. CONCLUSIONS

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

- The API monograph on quinoline[26] needs major revision.
- With an accurate knowledge of critical constants (T_c, p_c, and ρ_c), the variation of other thermophysical properties with temperature can be estimated with a high degree of accuracy.
- For quinoline, the vibrational assignment reported earlier in this research program is accurate. Ideal-gas thermodynamic functions for quinoline derived from calorimetric methods and statistical thermodynamic methods agree within their uncertainty intervals.
- Thermochemical and thermophysical properties for 5,6,7,8-tetrahydroquinoline listed are the first for a partially hydrogenated polycyclic aromatic nitrogen-containing compound with values available to the critical point.

6. REFERENCES

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

mass / g	0.008583	0.015542		0.023745
Vol. cell / cm^3 [a]	0.0547	0.0547		0.0547
T/K	$C^{II}_{x,m}/R$	$C^{II}_{x,m}/R$	T/K	$C^{II}_{x,m}/R$
		Quinoline		
310.0	23.92	23.84	320.0	24.20
330.0	24.79	24.78	340.0	25.22
350.0	25.71	25.49	360.0	25.97
370.0	26.89	26.39	380.0	26.89
390.0	27.53	27.45	400.0	27.82
410.0		28.59	420.0	28.67
430.0	29.43	29.33	440.0	29.55
450.0	30.93	30.56	460.0	30.51
470.0	31.73	31.15		
490.0	33.05	32.41	500.0	32.43
510.0	34.22	33.41	520.0	32.97
530.0	35.30	34.41	540.0	34.01
550.0	36.86	35.40	560.0	34.95
570.0	38.17	36.39	580.0	36.11
590.0	39.61	37.39	600.0	36.86
610.0	41.21	38.50	620.0	37.62
630.0	42.97	39.68	640.0	38.39
650.0	44.74	40.57	660.0	39.21
670.0	46.11		680.0	39.11
690.0	48.07	43.25	700.0	41.41
730.0		45.88	720.0	42.85
770.0		51.74	740.0	43.88
			760.0	46.20

TABLE 1. Continued

mass / g	0.014253	0.015667	0.024042
Vol. cell / cm^3 [a]	0.05409	0.05576	0.05374
T/K	$C^{II}_{x,m}/R$	$C^{II}_{x,m}/R$	$C^{II}_{x,m}/R$
5,6,7,8-Tetrahydroquinoline			
315.0	27.95	27.25	26.67
335.0	29.16	28.38	27.81
355.0	30.38	29.57	28.91
375.0	31.75	30.82	29.99
395.0	32.83	31.90	31.26
415.0	33.81	33.25	32.47
435.0	35.04	34.27	33.53
455.0	36.40	35.36	34.50
475.0	38.14	36.69	35.51
495.0	39.30	37.77	36.56
515.0	40.88	39.00	37.78
535.0	42.61	40.48	38.75
555.0	42.32	41.61	40.09
575.0	44.49	42.55	40.99
595.0	46.64	44.12	42.15
615.0	48.65	45.55	43.42
635.0	50.05	46.64	44.14
655.0	51.53	47.96	45.24
675.0	53.62	48.90	46.60
695.0	55.60	50.66	47.91
715.0	59.30	53.13	49.16
735.0	56.77	58.96	54.89

[a] Volume measured at 298.15 K

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

$\rho/(kg \cdot m^{-3})$	T/K	$\rho/(kg \cdot m^{-3})$	T/K
Quinoline		**5,6,7,8-Tetrahydroquinoline**	
152.8[a]	770.0	177.5	738.5
170.8[a]	773.0	236.7	743.6
171.2[c]	771.8	277.1	746.1
217.0[b]	779.1	327.4	746.2
234.5[a]	780.0	370.7	743.0
269.1[b]	785.2	428.7	739.7
342.7[a]	786.5	457.6	734.0
412.5[c]	784.1		
422.0[b]	784.3		
477.8[b]	775.0		
161.8[d]	765.0		
206.8[d]	771.6		
246.9[d]	779.0		
319.3[d]	784.0		
347.4[d]	783.0		
393.3[d]	780.5		
440.0[d]	778.3		
452.2[d]	776.2		

[a] Sample heating rate 0.17 $K \cdot s^{-1}$: see text.
[b] Sample heating rate 0.34 $K \cdot s^{-1}$: see text.
[c] Sample heating rate 0.68 $K \cdot s^{-1}$: see text.
[d] Sample heating rate 0.08 $K \cdot s^{-1}$: sample decomposition suspected see text.

TABLE 3. Parameters for equations (**5**) and (**6**) and critical constants

Quinoline			
A	2.40764	b_0	−0.37527
B	−1.20874	b_1	−0.66012
C	0.80720	b_2	1.03532
		b_3	−1.11052

T_c (787±2) K p_c (4820±50) kPa ρ_c (336±3) kg·m^{-3}

5,6,7,8-Tetrahydroquinoline			
A	2.47051	b_0	−0.46296
B	−1.28356	b_1	−0.67814
C	0.84302	b_2	1.08516
		b_3	−1.14765

T_c (746±2) K p_c (3975±40) kPa ρ_c (304±3) kg·m^{-3}

TABLE 4. Values of $C^{II}_{V,m}(\rho = \rho_{sat})/R$ and $C_{sat,m}/R$ ($R = 8.31451\ J \cdot K^{-1} \cdot mol^{-1}$)

T/K	$C^{II}_{V,m}(\rho = \rho_{sat})/R$	$C_{sat,m}/R$	T/K	$C^{II}_{V,m}(\rho = \rho_{sat})/R$	$C_{sat,m}/R$
		Quinoline			
300.0	23.47	23.47	560.0	34.78	34.84
320.0	24.42	24.42	580.0	35.58	35.66
340.0	25.34	25.34	600.0	36.35	36.47
360.0	26.25	26.25	620.0	37.09	37.27
380.0	27.13	27.13	640.0	37.81	38.07
400.0	28.01	28.01	660.0	38.50	38.88
420.0	28.88	28.88	680.0	39.18	39.73
440.0	29.74	29.74	700.0	39.86	40.67
460.0	30.60	30.60	720.0	40.57	41.83
480.0	31.45	31.46	740.0	41.37	43.48
500.0	32.30	32.31	760.0	42.44	46.61
520.0	33.14	33.16	780.0	44.43	60.43
540.0	33.97	34.01			
		5,6,7,8-Tetrahydroquinoline			
300.0	26.19	26.19	540.0	39.18	39.25
320.0	27.33	27.33	560.0	40.20	40.30
340.0	28.45	28.45	580.0	41.18	41.33
360.0	29.56	29.56	600.0	42.15	42.37
380.0	30.65	30.65	620.0	43.09	43.42
400.0	31.73	31.73	640.0	44.01	44.50
420.0	32.81	32.82	660.0	44.94	45.68
440.0	33.89	33.90	680.0	45.90	47.08
460.0	34.96	34.97	700.0	46.98	49.00
480.0	36.03	36.05	720.0	48.35	52.49
500.0	37.10	37.12	740.0	50.83	68.71
520.0	38.15	38.19			

TABLE 5. Liquid-phase molar thermodynamic functions at vapor-saturation pressure ($R = 8.31451\ J \cdot K^{-1} \cdot mol^{-1}$)

$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m^o}{R}$	$\frac{\Delta_0^T H_m^o}{RT}$	$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m^o}{R}$	$\frac{\Delta_0^T H_m^o}{RT}$
Quinoline							
298.15	23.44	26.43	15.04	550.0	34.42	43.86	21.44
300.0	23.52	26.57	15.09	600.0	36.47	46.94	22.61
350.0	25.78	30.36	16.46	650.0	38.47	49.94	23.75
400.0	28.03	33.96	17.76	700.0	40.67	52.87	24.88
450.0	30.19	37.39	19.02	720.0	41.83	54.03	25.33
500.0	32.31	40.68	20.25				
5,6,7,8-Tetrahydroquinoline							
298.15	26.15	29.92	16.40	500.0	37.12	46.04	22.56
300.0	26.25	30.08	16.46	550.0	39.77	49.70	24.00
350.0	28.98	34.33	18.05	600.0	42.37	53.28	25.43
400.0	31.75	38.38	19.59	650.0	45.07	56.77	26.83
450.0	34.43	42.27	21.09	700.0	49.00	60.24	28.26

TABLE 6. Enthalpies of vaporization $\Delta_l^g H_m$ and entropies of compression $\Delta S_{comp,m}$ obtained from the Cox and Clapeyron equations (R = 8.31451 $J \cdot K^{-1} \cdot mol^{-1}$) [a]

T/K	$\Delta_l^g H_m/(R \cdot K)$	$\Delta S_{comp,m}/R$	T/K	$\Delta_l^g H_m/(R \cdot K)$	$\Delta S_{comp,m}/R$
		Quinoline			
298.15	7133±26	−9.104±0.003	550.00	5294±33	0.812±0.000
300.00	7119±25	−8.957±0.003	600.00 [b]	4901±57	1.662±0.000
350.00	6743±6	−5.652±0.001	650.00 [b]	4478±89	2.373±0.001
400.00	6382±3	−3.301±0.000	700.00 [b]	3993±129	2.985±0.002
450.00	6028±7	−1.564±0.000	720.00 [b]	3764±149	3.209±0.003
500.00	5668±17	−0.235±0.000			
		5,6,7,8-Tetrahydroquinoline			
298.15 [b]	6924±3	−8.500±0.000	500.00	5381±23	0.074±0.000
300.00 [b]	6909±3	−8.357±0.000	550.00 [b]	4962±44	1.082±0.000
350.00	6524±1	−5.153±0.000	600.00 [b]	4512±72	1.901±0.000
400.00	6150±3	−2.882±0.000	650.00 [b]	4013±108	2.588±0.000
450.00	5775±10	−1.205±0.000	700.00 [b]	3400±154	3.182±0.000

[a] $\Delta S_{comp}/R = \ln(p/p^\circ)$ where p° = 101.325 kPa.

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

TABLE 7. Thermodynamic properties in the ideal-gas state
($R = 8.31451\ J \cdot K^{-1} \cdot mol^{-1}$ and $p^\circ = 101.325\ kPa$)

$\frac{T}{K}$	$\frac{\Delta_0^T H_m^\circ}{R\,T}$	$\frac{\Delta_{imp} H_m^\circ}{R\,T}$ [a]	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_{imp} S_m^\circ}{R}$ [b]	$\frac{\Delta_f H_m^\circ}{R\,T}$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_f G_m^\circ}{R\,T}$
			Quinoline				
298.15	38.96±0.09	0.00	41.25±0.09	0.00	80.89±0.21	−31.44±0.09	112.33±0.19
300.00	38.82±0.08	0.00	41.35±0.09	0.00	80.35±0.20	−31.49±0.09	111.84±0.19
350.00	35.73±0.02	0.00	43.99±0.04	0.00	67.87±0.16	−32.57±0.04	100.44±0.16
400.00	33.73±0.02	0.02	46.63±0.03	0.01	58.61±0.14	−33.39±0.03	92.01±0.14
450.00	32.47±0.02	0.05	49.26±0.04	0.03	51.51±0.12	−34.02±0.04	85.53±0.13
500.00	31.69±0.05	0.11	51.86±0.06	0.08	45.91±0.12	−34.49±0.06	80.40±0.13
550.00	31.27±0.09	0.21	54.45±0.10	0.15	41.42±0.13	−34.82±0.10	76.24±0.14
600.00 [d]	31.13±0.13	0.35	57.02±0.14	0.25	37.77±0.16	−35.01±0.14	72.79±0.16
650.00 [d]	31.18±0.18	0.54	59.59±0.19	0.38	34.79±0.20	−35.08±0.19	69.87±0.19
700.00 [d]	31.37±0.24	0.79	62.12±0.25	0.56	32.30±0.25	−35.05±0.25	67.35±0.23
720.00 [d]	31.47±0.26	0.91	63.12±0.28	0.66	31.42±0.27	−35.03±0.28	66.44±0.24
			5,6,7,8-Tetrahydroquinoline				
298.15 [d]	39.62±0.02	0.00	44.64±0.03	0.00	28.63±0.25	−59.46±0.03	88.09±0.25
300.00 [d]	39.49±0.02	0.00	44.75±0.03	0.00	28.37±0.25	−59.54±0.03	87.91±0.25
350.00	36.69±0.02	0.01	47.82±0.03	0.00	22.72±0.21	−61.26±0.03	83.99±0.22
400.00	34.99±0.02	0.02	50.89±0.04	0.02	18.64±0.19	−62.59±0.04	81.23±0.19
450.00	33.99±0.03	0.07	53.95±0.05	0.05	15.60±0.17	−63.62±0.05	79.22±0.17
500.00	33.47±0.06	0.15	56.99±0.07	0.11	13.30±0.16	−64.40±0.07	77.70±0.16
550.00 [d]	33.31±0.11	0.28	60.01±0.12	0.20	11.55±0.17	−64.96±0.12	76.51±0.18
600.00 [d]	33.41±0.16	0.47	63.03±0.17	0.33	10.23±0.20	−65.32±0.17	75.55±0.20
650.00 [d]	33.71±0.22	0.70	66.04±0.23	0.50	9.24±0.25	−65.51±0.23	74.75±0.23
700.00 [d]	34.13±0.28	1.01	69.01±0.30	0.73	8.48±0.30	−65.57±0.30	74.05±0.27

[a] Formation properties were calculated with values for reference state graphite given in reference 21.

[b] Gas-imperfection correction to the ideal-gas enthalpy.

[c] Gas-imperfection correction to the ideal-gas entropy.

[d] Values at this temperature were calculated with extrapolated vapor pressures calculated from the fitted Cox coefficients.

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