NIPER-399
Distribution Category UC-125

THE THERMODYNAMIC PROPERTIES OF 1,2,3,4-5,6,7,8- TETRAHYDROQUINOLINES

Topical Report

NIPER--399

DE89 000729

By
W. V. Steele
R. D. Chirico
I. A. Hossenlopp
N. K. Smith

April 1989

Work Performed Under Cooperative Agreement No. FC22-83FE60149

Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy

W. D. Peters, Project Manager
Bartlesville Project Office
P.O. Box 1398
Bartlesville, OK 74005

Prepared by
IIT Research Institute
National Institute for Petroleum and Energy Research
P.O. Box 2128
Bartlesville, OK 74005

EXECUTIVE SUMMARY

This is a report of continuing research in a program funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Process Technology (APT), 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. Heteroatom removal is an important processing step in upgrading hydrocarbon feedstocks to commercially useful products. Organic nitrogen and sulfur are commonly removed via reaction at 300-400° C and 50-150 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 used in processing could be enormous if a process for denitrogenation without saturation of the aromatic rings in the feedstock could be developed.

A thermodynamic analysis, based on accurate information, provides insights for the design of cost-effective methods of nitrogen removal. The thermodynamic properties of quinoline, isoquinoline, and the five benzoquinolines were reported in earlier topical reports and journal publications from this group. This topical report details the thermodynamic properties of 1,2,3,4- and 5,6,7,8-tetrahydroquinoline. The thermodynamic properties have been measured in this laboratory using conventional calorimetry. The experimental portion of this research included adiabatic heat-capacity calorimetry, comparative ebulliometry, inclined-piston gauge manometry, and combustion calorimetry.

The results of the thermodynamic property measurements reported in this Topical Report have been used to determine equilibrium constants, and hence equilibrium concentrations, for the quinoline/hydrogen/tetrahydroquinoline system at temperatures of interest in the processing of fuels from crudes with a high nitrogen content. The results prove that under typical processing conditions (see above) there is thermodynamic equilibrium between quinoline and 1,2,3,4-tetrahydroquinoline. The proof that equilibrium conditions exist between quinoline and 5,6,7,8-tetrahydroquinoline in processing is not as unequivocal as in the former case, but there is strong evidence of such an equilibrium. Kinetic modelling of the HDN reaction for quinoline

should be repeated using the results from the thermodynamic studies reported here. Using the results from this report to define the ratios of the rate constants for the equilbria, the remaining rate constants could be determined with greater precision and further insights gained into their relative importance. This in turn could lead to the development of a nitrogen-specific catalyst.

ABSTRACT

Measurements leading to the calculation of the ideal-gas thermodynamic properties for 1,2,3,4- and 5,6,7,8-tetrahydroquinoline are reported. Thermochemical and thermophysical properties were determined by adiabatic heat-capacity calorimetry, comparative ebulliometry, inclined-piston gauge manometry, and combustion calorimetry. Results were used to calculate entropies, enthalpies, and Gibbs energies of formation for the ideal-gas state at selected temperatures to 500 K. The results of the thermodynamic property measurements reported in this Topical Report have been used to determine equilibrium constants, and hence equilibrium concentrations, for the quinoline/hydrogen/tetrahydroquinoline system at temperatures of interest in the processing of fuels from crudes with a high nitrogen content. The results prove that under typical processing conditions (650 K and 7.0 MPa hydrogen pressure) there is thermodynamic equilibrium between quinoline and 1,2,3,4-tetrahydroquinoline. The proof that equilibrium conditions exist between quinoline and 5,6,7,8-tetrahydroquinoline in processing is not as unequivocal as in the former case, but there is strong evidence of such an equilibrium.

ACKNOWLEDGEMENTS

The authors acknowledge the contributions of Bruce E. Gammon, who was group leader until January 1986. Under his direction, much of the early experimental work on 5,6,7,8-tetrahydroquinoline was accomplished. The authors acknowledge the assistance of Robert D. Remke (Associated Western Universities Summer Research Student) in the adiabatic heat-capacity studies, and Stephen E. Knipmeyer for keeping all experimental apparatus in proper functioning order.

TABLE OF CONTENTS

Page

Executive Summary i

Abstract iii

Acknowledgements iv

1. Introduction 1

2. Experimental 3

    Materials 3

    Physical Constants and Standards 3

    Apparatus and Procedures 4

        Combustion Calorimetry 4

        Adiabatic Heat-Capacity Calorimetry 5

        Ebulliometric Vapor Pressure Measurements 6

        Inclined-Piston Vapor Pressure Measurements 6

3. Results 7

    Combustion Calorimetry 7

    Adiabatic Heat-Capacity Calorimetry 7

        Crystallization and Melting Studies 7

        Phase Transformations and Enthalpy Measurements 9

        Heat-Capacity Measurements 14

    Thermodynamic Properties in the Condensed State 18

    Vapor Pressure Measurements 18

        Cox Equation Fits to Vapor Pressures 19

        Derived Enthalpies of Vaporization 19

    Thermodynamic Properties in the Ideal-Gas State 20

4. Discussion 20

5. Conclusions 27

6. References 28

LIST OF TABLES

Page

Table 1. Calorimeter and sample characteristics. 31

Table 2. Typical combustion experiment for the tetrahydroquinolines at 298.15 K. 32

Table 3. Summary of experimental energies of combustion and molar thermochemical functions for the tetrahydroquinolines. 33

Table 4. Melting study summary. 34

Table 5. Experimental enthalpy measurements. 35

Table 6. Experimental molar heat capacities at vapor saturation. 38

Table 7. Molar thermodynamic functions at vapor saturation. 42

Table 8. Summary of vapor pressure results. 46

Table 9. Cox equation coefficients. 49

Table 10. Derived enthalpies of vaporization and entropies of compression obtained from the Cox and Clapeyron equations. 50

Table 11. Thermodynamic properties in the ideal-gas state. 51

Table 12. Comparison of equilibrium constants for the quinoline/tetrahydroquinoline systems. 53

LIST OF FIGURES

Page

Figure 1. Initial steps in the reaction scheme for the HDN of quinoline. 2

Figure 2. Heat capacity against temperature for 1,2,3,4-tetrahydroquinoline. 10

Figure 3. Heat capacity against temperature near the triple point for 5,6,7,8-tetrahydroquinoline. 12

Figure 4. Heat capacity against temperature for 5,6,7,8-tetrahydroquinoline. 13

Figure 5. Experimental average heat capacities in the cr(IV)-to-cr(III) transition region for 1,2,3,4-tetrahydroquinoline. 15

Figure 6. Experimental average heat capacities in the cr(II)-to-cr(I) transition region for 1,2,3,4-tetrahydroquinoline. 16

Figure 7. Experimental average heat capacities in the cr(III)-to-cr(II) transition region for 1,2,3,4-tetrahydroquinoline. 17

Figure 8. Ln K' as a function of inverse temperature for the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline. 21

Figure 9. Ln K' as a function of inverse temperature for the hydrogenation of quinoline to 5,6,7,8-tetrahydroquinoline. 23

Figure 10. Relative percentages of quinoline and its tetrahydro-isomers at thermodynamic equilibrium in the gas phase at different temperatures. 25

Figure 11. Relative percentages of quinoline and 1,2,3,4-tetrahydroquinoline at thermodynamic equilibrium in the gas phase at different temperatures. 26

1. INTRODUCTION

This laboratory has a research program, funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Process Technology (APT), 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. A thermodynamic analysis, based on accurate information, provides insights for the design of cost-effective methods of nitrogen removal.(2) The thermodynamic properties of quinoline and isoquinoline were reported in an earlier topical report(5) and a journal publication(6) from this group. The thermodynamic properties of the five benzoquinolines have been the subject of a recent topical report(7) and journal article.(8) This topical report details the thermodynamic properties of 1,2,3,4- and 5,6,7,8-tetrahydroquinoline. The experimental portion of the research included adiabatic heat-capacity calorimetry, comparative ebulliometry, inclined-piston gauge manometry, and combustion calorimetry.

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 hydrodenitrogenation of quinoline.(9) Cocchetto and Satterfield(10) estimated the equilibrium constants for the hydrogenation reactions of quinoline using the group-additivity schemes of Benson(11) and van Krevelen and Chermin.(12) In a subsequent paper, Cocchetto and Satterfield(13) compared experimental equilibria results with those estimates and showed that the estimates were crude and were probably in error by at least two orders of magnitude for the quinoline/1,2,3,4-tetrahydroquinoline equilibrium.

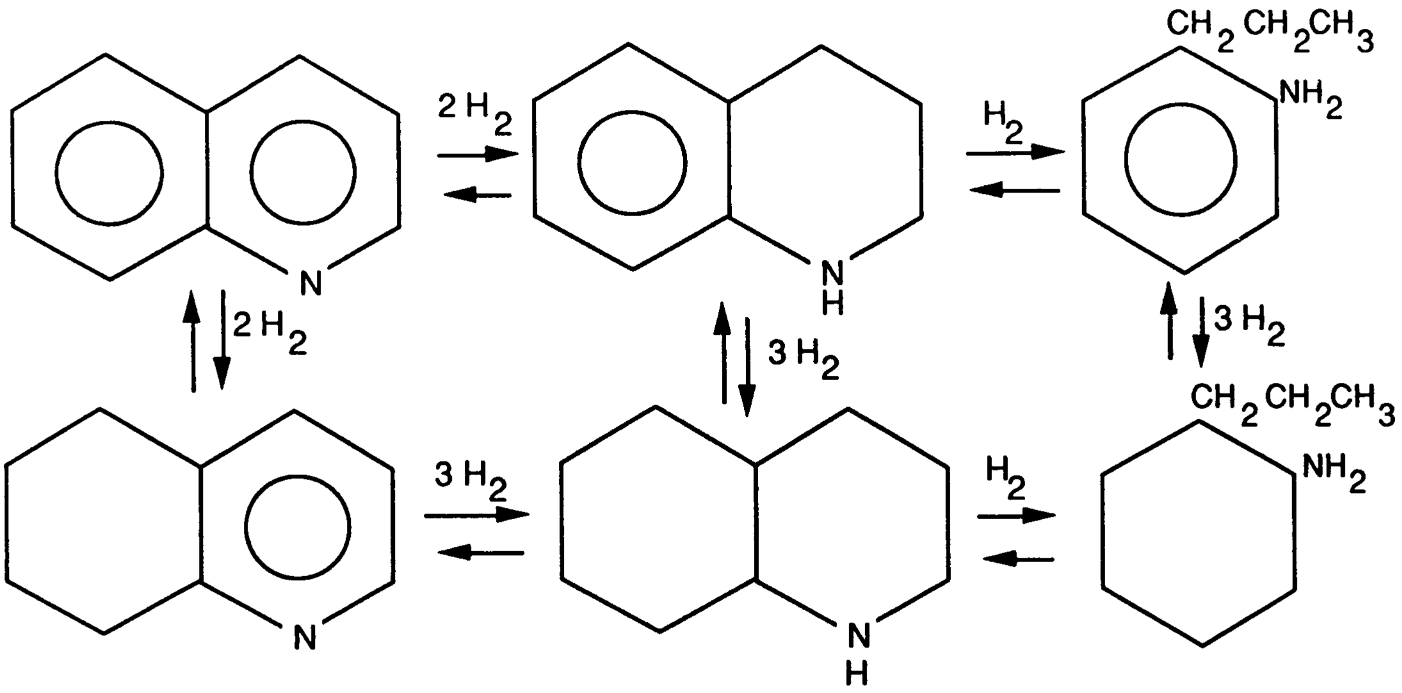


Figure 1. Initial steps in the reaction scheme for the HDN of quinoline

In this report equilibrium constants applicable under the conditions applied by Satterfield's group are derived and compared with the experimentally determined values. In a later paper, Satterfield and Yang(14) developed a kinetic model for the HDN of quinoline using a modular approach. In this report, the ratios of their rate constants for the forward and reverse reactions in the quinoline/tetrahydroquinoline equilibria are discussed and compared with equilibrium constants determined from this research.

2. EXPERIMENTAL

MATERIALS

Commercial samples of both tetrahydroquinolines were 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 tetrahydroquinoline, oxalic acid dihydrate, and propan-2-ol, respectively). The resulting oxalate was recrystallized from propan-2-ol, and cleaved using 2 mol·dm^{-3} KOH(aq). The liberated tetrahydroquinoline was extracted with ether, dried (Na_2CO_3), filtered, and concentrated. For the 1,2,3,4-isomer, final purification was achieved by double distillation at 328 K and 13 Pa. The corresponding conditions used in the double distillation of the 5,6,7,8- isomer were 313 K and 13 Pa. The mole fraction impurities were estimated to be 0.0006 and 0.0001, respectively, using g.l.c. The high purities 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. The benzene used as a reference material for the ebulliometric measurements was obtained from API as Standard Reference Material No. 210X–5s. Prior to its use, it was dried by vacuum transfer through Linde 3A molecular sieves.

PHYSICAL CONSTANTS AND STANDARDS

Molar values are reported in terms of $M = 133.1937$ g·mol^{-1} based on the relative atomic masses of 1969(15)† and the gas constant, $R = 8.31441$ J·K^{-1}·mol^{-1}, adopted by

---

† The 1969 relative atomic masses were used because the CODATA Recommended Key Values for Thermodynamics (reference 38) are based on them.

CODATA.(16) The platinum resistance thermometers used in these measurements were calibrated by comparison with a standard thermometer whose constants were determined at the National Bureau of Standards (NBS). All temperatures are reported in terms of the IPTS-68.(17) Measurements of mass, time, electrical resistance, and potential difference were made in terms of standards traceable to calibrations at NBS.

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.(18-20) A rotating-bomb calorimeter (laboratory designation BMR II)(21) and platinum-lined bombs (laboratory designations Pt-3b and Pt-5)(22) with internal volumes of 0.393_4 dm^3 and 0.393_0 dm^3, respectively, were used without rotation. Pt-3b was used in the 1,2,3,4-tetrahydroquinoline combustion measurements, and Pt-5 was used for the 5,6,7,8-tetrahydroquinoline combustions. For each experiment 1.0×10^{-3} dm^3 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 tetrahydroquinoline combustion series and its corresponding calibration series to be the same in each experiment within 0.1 per cent. All experiments were completed very close to 298.15 K (within 0.01 K).

Temperatures were measured by quartz-crystal thermometry.(23,24) 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.(25)

NBS benzoic acid (sample 39i) was used for calibration of the calorimeter; its specific energy of combustion is $-(26434.0 \pm 3.0)$ $\mathrm{J \cdot g^{-1}}$ under certificate conditions. Conversion to standard states(26) gives $-(26413.7 \pm 3.0)$ $\mathrm{J \cdot g^{-1}}$ for $\Delta_c U^\circ_m / M$, 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, ε(calor), was (16747.4 ± 0.4) $\mathrm{J \cdot K^{-1}}$ (mean and standard deviation of the mean) for the 1,2,3,4-tetrahydroquinoline and (16784.3 ± 0.4) $\mathrm{J \cdot K^{-1}}$ for the 5,6,7,8-tetrahydroquinoline measurements.

For the cotton fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta_c U^o_m/M$ was $-16945\ J{\cdot}g^{-1}$. 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,(26) included densities of 1030 $kg{\cdot}m^{-3}$ and 990 $kg{\cdot}m^{-3}$, and estimated values of 1.7 $m^3{\cdot}K^{-1}$ and 1.6 $m^3{\cdot}K^{-1}$ for $(\delta V_m/\delta T)_p$ for 1,2,3,4-tetrahydroquinoline and 5,6,7,8-tetrahydroquinoline, respectively. Values of the molar heat capacities at 298.15 K for the tetrahydroquinolines 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 tetrahydroquinoline combustions was determined by titration with standard sodium hydroxide.(27) Carbon dioxide was also recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as absorbant.(19) 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 tetrahydroquinoline combustions were 100.002±0.005 (mean and standard deviation of the mean) for calibrations, 99.992±0.005 for the corresponding 1,2,3,4-tetrahydroquinoline combustions, 99.995±0.007 for calibrations, and 100.020±0.015 for the corresponding 5,6,7,8-tetrahydroquinoline combustions.

Adiabatic Heat-Capacity Calorimetry. Heat-capacity and enthalpy measurements were made with a calorimetric system similar to that described by Huffman et al. (28-30) The four gold-plated copper adiabatic shields were controlled to within 1 mK by electronic controllers with proportional, derivative, and integral actions responding to imbalance signals from (copper + constantan) difference thermocouples. The calorimetric vessels, the loading, and the sealing procedures have been described.(28,5,6) The outer surfaces of the vessels were plated with a nickel diffusion barrier and a thin layer of gold. The calorimeters were sealed using a gold-gasketed screw-cap closure on the filling tube rather than the solder-seal method described by Huffman.(30) The characteristics of the calorimeters and sealing conditions are given in table 1.¥

The temperature measurement system employed direct-current methods described previously.(28-30) Energy measurement procedures were the same as those described for studies on quinoline.(5,6) Energies were measured to a precision of 0.01

¥ All tables appear at the end of this report.

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 sample. The maximum correction to the measured energy for the helium exchange gas was approximately 0.24 per cent near 4.6 K for 5,6,7,8-tetrahydroquinoline and 0.02 per cent near 11.4 K for 1,2,3,4-tetrahydroquinoline. The sizes of the other two corrections are indicated in table 1.

Ebulliometric Vapor-Pressure Measurements. The essential features of the ebulliometric equipment and procedures are described in the literature.(31,32) 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.(33)

The precision in the temperature measurements for the ebulliometric vapor pressure studies was 0.001 K. This gives a variance of:

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

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(34) to vapor pressures of the reference materials (benzene, decane, and water) reported in reference 33.

Inclined-Piston Vapor-Pressure Measurements. The equipment for these measurements has been described by Douslin and McCullough,(35) and Douslin and Osborn.(36) Recent revisions to the equipment and procedures are given in references 5 and 6. 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:

$$\sigma(p) = 0.00015(p/\mathrm{kPa}) + 0.0002. \qquad (2)$$

The uncertainties in the temperatures are 0.001 K.

3. RESULTS

COMBUSTION CALORIMETRY

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

$$C_9H_{11}N\ (l) + 47/4\ O_2\ (g) = 9\ CO_2\ (g) + 11/2\ H_2O\ (l) + 1/2\ N_2\ (g). \qquad (3)$$

Table 3 also gives derived values of $\Delta_c U^\circ_m$, the standard molar energy of combustion; $\Delta_c H^\circ_m$, the standard molar enthalpy of combustion; and $\Delta_f H^\circ_m$, the standard molar enthalpy of formation for the isomers. Values of $\Delta_c U^\circ_m$ and $\Delta_c H^\circ_m$ refer to reaction **3**. The values of $\Delta_f H^\circ_m$ refer to reaction **4**:

$$9C(\mathrm{cr,\ graphite}) + 11/2H_2\ (g) + 1/2N_2\ (g) = C_9H_{11}N\ (l). \qquad (4)$$

Uncertainties given in table 3 are the "uncertainty interval."(37) The enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ were taken to be $-(393.51 \pm 0.13)$ and $-(285.830 \pm 0.042)$ $\mathrm{kJ \cdot mol^{-1}}$, respectively, as assigned by CODATA.(38)

ADIABATIC HEAT-CAPACITY CALORIMETRY

Crystallization and Melting Studies. Crystallization of 1,2,3,4-tetrahydroquinoline was initiated by slowly cooling (approximately $2\ \mathrm{K \cdot h^{-1}}$) the liquid sample 10 to 15 K below its triple point temperature. Complete crystallization was ensured by reheating and then maintaining the sample under adiabatic conditions in the partially melted state (10 to 20 per cent liquid) until ordering of the crystals was complete, as evidenced by a cessation of spontaneous warming. The time required for warming to cease was approximately 24 h. The sample was then cooled at an effective rate of 1 $K \cdot h^{-1}$ to crystallize the remaining liquid. As a final step, the sample was thermally cycled between less than 100 K and within 2 K of the triple-point temperature to provide additional tempering. All solid-phase measurements on 1,2,3,4-tetrahydroquinoline were completed on crystals pre-treated in this manner.

The 5,6,7,8-tetrahydroquinoline sample always formed a glass on cooling, and only crystallized when reheated above the glass-transition temperature near 160 K. The triple-point temperature of the crystals formed initially was 222.347 K. This was found to be a metastable form. The triple-point temperature of the stable form was roughly 0.3 K higher. Conversion from the metastable to stable crystalline forms occurred three times in the calorimeter; however, only once was conversion allowed to go to completion. In spite of many attempts, a method could not be devised to convert the metastable to the stable form at will. Detection of the crystalline-form conversion was complicated by the presence of a near first-order phase transition near 210 K in the metastable crystalline form. No solid-state phase transformations were found in the stable form. Some evidence was observed for the presence of a phase transition near 110 K in the metastable form, but confirming investigations were not done.

When it did occur, conversion from the metastable to stable crystalline form occurred above 210 K (i.e., from the high-temperature form of the metastable crystals.) Complete conversion to the stable form required approximately one week of annealing in the partially melted state after nucleation. The single set of crystals used for all measurements reported for the stable crystalline form was thoroughly annealed as described above for the 1,2,3,4-tetrahydroquinoline crystals.

The triple-point temperature T_{tp} and sample purity for 1,2,3,4-tetrahydroquinoline and the metastable crystalline form of 5,6,7,8-tetrahydroquinoline were determined from measurements of the equilibrium melting temperatures T(F) as a function of fraction F of the sample in the liquid state. Equilibrium melting temperatures were determined by measuring temperatures at approximately 300 s intervals for 0.75 to 1 h after an energy input. The values were extrapolated to infinite time by assuming an exponential decay towards the equilibrium value. The observed temperatures at 0.75 to 1 h after an energy input were always within 3 mK of the calculated equilibrium temperatures for F values listed in table 4. Standard procedures were used to derive the mole-fractions of impurities and triple-point temperatures. No evidence for solid-soluble impurities was found.

As part of the one enthalpy-of-fusion determination for the fully-annealed stable crystals of 5,6,7,8-tetrahydroquinoline, a single equilibrium temperature and corresponding fraction melted were determined. These results, reported in table 4, were used with the mole-fraction impurity value determined for the metastable crystalline form to estimate the triple-point temperature for the stable form. Triple-point temperatures for both forms are listed in table 4.

Phase Transformations and Enthalpy Measurements. Experimental molar enthalpy results are summarized in table 5. 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 4, 5, and 6 were taken without interruption of adiabatic conditions.

Enthalpy-of-fusion results for 1,2,3,4-tetrahydroquinoline were highly reproducible (within 0.01 per cent). Solid-state phase transformations were detected in the 1,2,3,4-tetrahydroquinoline sample near 232 K, 115 K, and 62 K. The curve of heat capacity against temperature is shown in figure 2.

Both the cr(I)-to-cr(II) and cr(II)-to-cr(III) conversions proceeded readily on cooling. In table 5 it is seen that the transition enthalpies for series 1 are slightly low relative to the others. Prior to series 1 the sample was cooled rapidly from 260 K to near 100 K with the calorimeter in contact with a copper refrigerant tank filled with liquid nitrogen. For all other series the crystals were annealed approximately 3 to 5 K below T_{trs} for approximately 24 h for each transition. No warming was apparent during annealing; however, based on the series 1 results, the annealing was necessary to obtain complete phase conversion.

Conversion of cr(III) to cr(IV) was effected by annealing the crystals near 60 K for approximately 24 h. Phase cr(IV) was not annealed prior to series 9. Approximate annealing times for the other reported series were: series 10 (25 h), series 11 (75 h), and series 13 (150 h). It is seen in table 5 that only the transition enthalpy for series 9 is discordant. Annealing for more than 24 h did not affect the results.

If the existence of two crystalline forms is not recognized, the enthalpy-of-fusion results for 5,6,7,8-tetrahydroquinoline, listed in table 5, seem discordant. For all enthalpy-of-fusion measurements, at least one equilibrium temperature in the partially liquid state and a corresponding fraction melted were determined. In this way the triple-point temperature corresponding to each melting was ascertained. During measurements in the partially melted state for series 13 and 19, the sample warmed

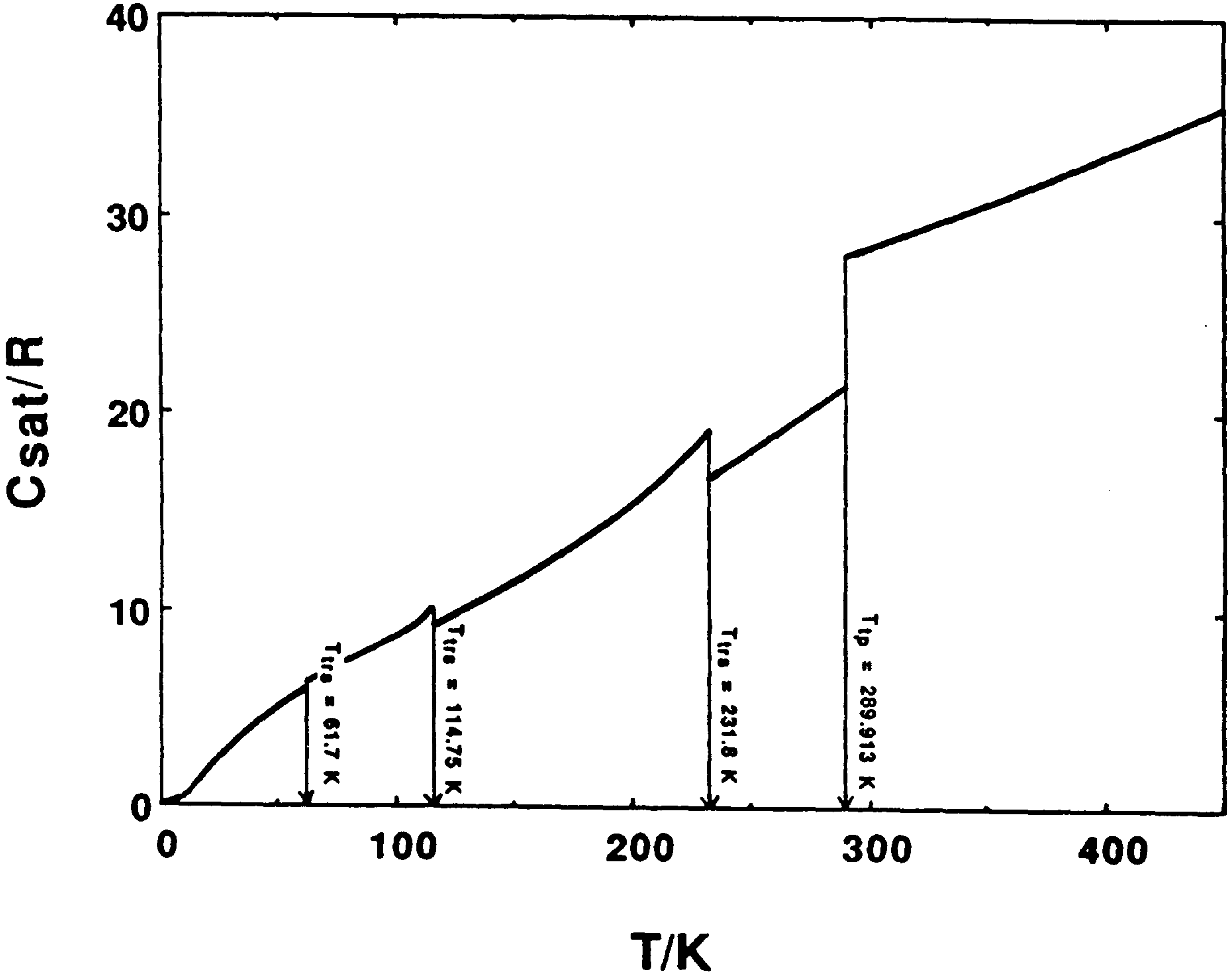


Figure 2. Heat capacity against temperature for 1,2,3,4-tetrahydroquinoline. The vertical lines indicate phase-transition temperatures.

spontaneously, which is indicative of phase transformation. No analogous warming was observed during series 1, 11, or 21. The triple-point temperature for series 1 and 21 was 222.357 K (that of the metastable form), while for series 11, the single measured equilibrium temperature was 222.617 K.

Some insight into the relationship between the stable and metastable forms may be obtained if the difference between their entropies of fusion is considered. The difference (0.67·R) is very near the value expected for two-position disorder, 0.69·R {i.e., (ln 2)·R}. Scenarios involving positional disorder of the nitrogen atom in the crystal can be formulated readily to account for such a disorder. Also, it is important to recall that 5,6,7,8-tetrahydroquinoline always crystallized rapidly from the supercooled liquid near 160 K. At this temperature reorientations, particularly those involving out-of-plane rotations, may not occur. Without experimental structural information additional speculation is not justified.

Included in table 5 are the results of three series of measurements in the temperature range of a phase transition in the metastable crystalline form of 5,6,7,8-tetrahydroquinoline. Transformation from the high- to low-temperature phase of the metastable crystals was apparent near 190 K, as evidenced by spontaneous warming of the sample. Conversion accelerated over a period of several days. Prior to the series 12 measurement, the sample was allowed to warm near 193 K for 2 days. Although it was clear from the continued warming that conversion was incomplete after 2 days, series 12 was completed, and the relatively small transition enthalpy, 12.76·R K, was measured. The crystals were not melted after series 12. Prior to series 13, the crystals were allowed to transform for approximately 10 days. The sample warmed from 192 K to near 200 K during this time period, and a large (172·R K) transition enthalpy was measured. Immediately upon crossing the transition during series 13, the sample began to warm again, which was indicative of conversion to the stable crystalline form. Conversion was not allowed to go to completion as evidenced by the continued warming of the sample through the enthalpy-of-fusion determination. This interpretation is consistent with the measured enthalpy of fusion being intermediate between the stable and metastable crystal values in table 5. Figure 3 shows details of the curve of heat-capacity against temperature for 5,6,7,8-tetrahydroquinoline near the triple-point temperature. Although the sample did not equilibrate during series 13, the results are sufficient to show the general nature of the transition in the metastable crystalline form, and are included in figure 3. The complete experimental curves of heat capacity against temperature for the liquid and stable crystal forms are shown in figure 4.

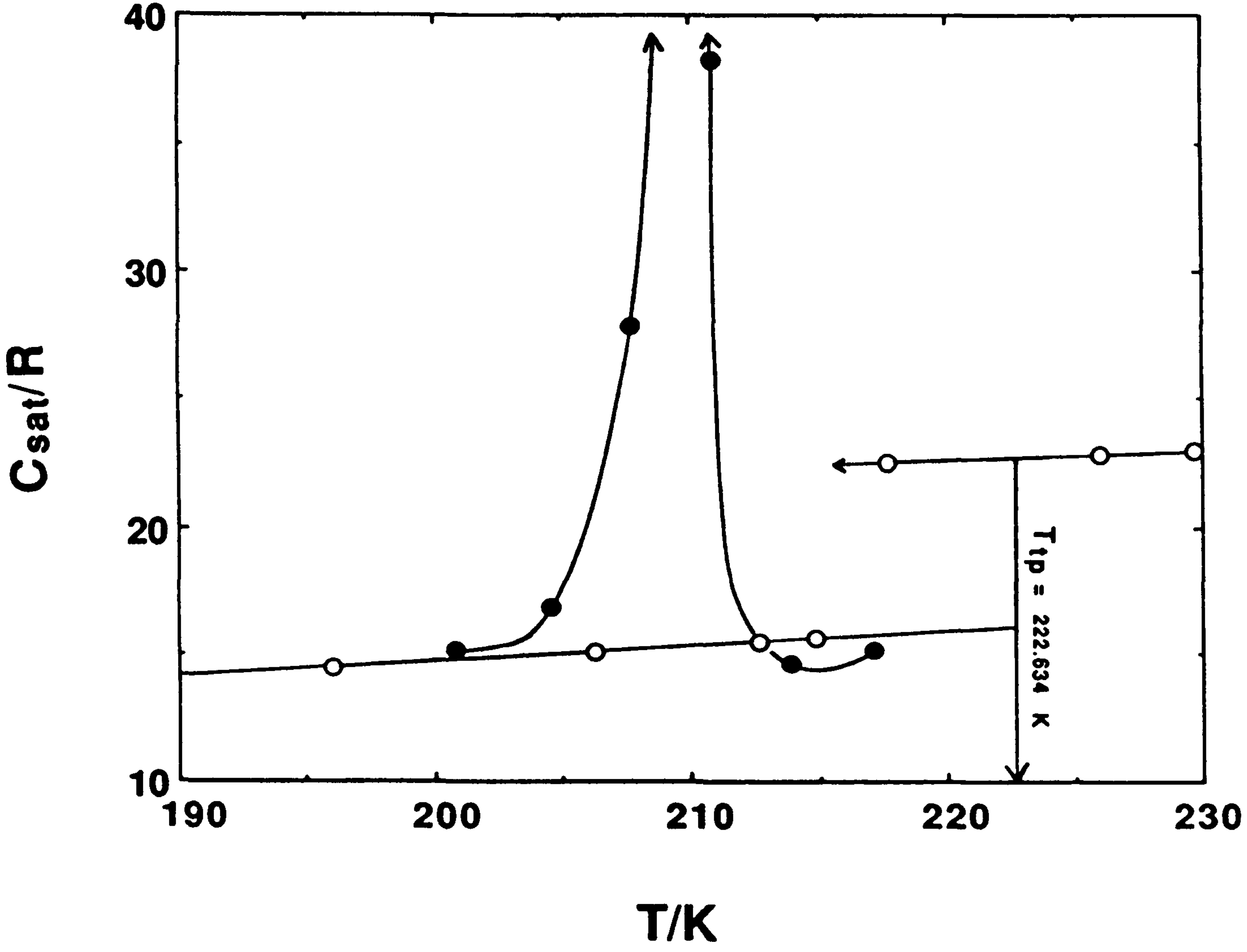


Figure 3. Heat capacity against temperature near the triple-point temperature for 5,6,7,8-tetrahydroquinoline. ○, experimental results for the stable crystal and liquid phases; ●, series 13 results for the metastable crystalline form. The vertical line indicates the triple-point temperature. The curves are guides for the eye.

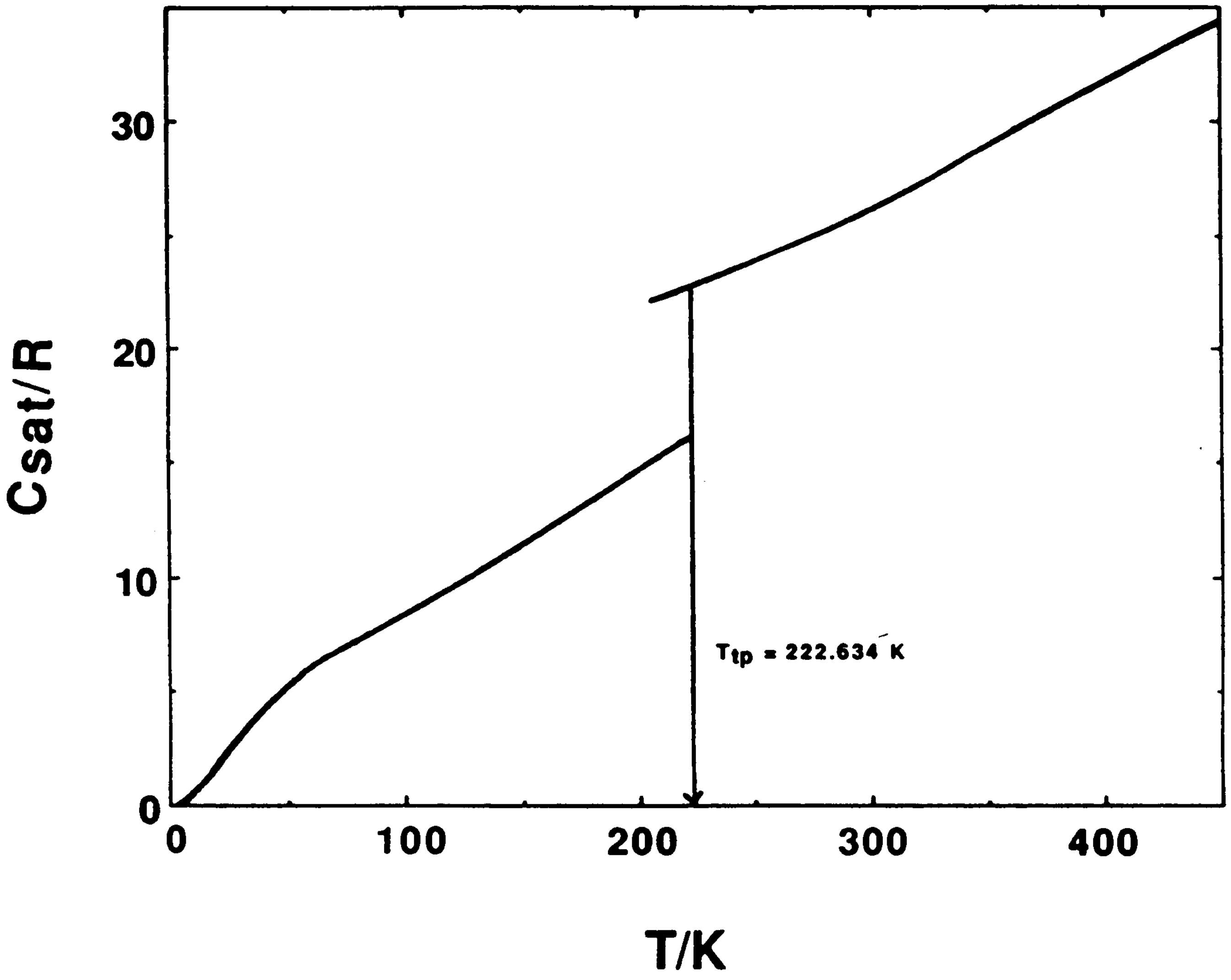


Figure 4. Heat capacity against temperature for 5,6,7,8-tetrahydroquinoline. The vertical line indicates the triple-point temperature.

Prior to attempting to convert the crystals into a low-temperature form before series 19, the sample had partially converted to the higher-melting, more stable form. *In spite of extensive annealing in the 190 to 200 K range, a small transition enthalpy* was measured. The extensive conversion of the crystals to the stable form was evidenced by the series 19 enthalpy-of-fusion value being relatively close to that for the fully-annealed stable crystals as seen in table 5.

Heat-capacity Measurements. The experimental molar heat capacities under vapor saturation pressure $C_{sat,m}$ are listed in table 6. The difference between $C_{p,m}$ and $C_{sat,m}$ is insignificant at all measurement temperatures. Values in table 6 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 $C_{sat,m}$ with temperature, except very near phase-transition temperatures. The precision of the heat-capacity measurements ranged from approximately 2 per cent at 11 K to 0.2 per cent near 20 K and improved gradually to less than 0.1 per cent above 100 K, except near phase transitions where long equilibration times necessitated long temperature extrapolations. The heat capacities in table 6 have not been corrected for pre-melting, but the temperature increments are provided so that an independent calculation can be made.

Heat-capacity measurements for both compounds were routine in the liquid phase with equilibrium being reached in less than 1 h after each energy input. For 1,2,3,4-tetrahydroquinoline, equilibrium was achieved within 1 h for all measurements in phases cr(II) and cr(III), below 60 K in phase cr(IV), and below 250 K in phase cr(I). In phase cr(I) above 250 K, equilibration times increased to 2 h near 265 K, 5 h near 275 K, and to 10 h near 285 K. No attempt was made to equilibrate the sample between 60 K and 67 K, (i.e., in the cr(IV)-to-cr(III) transition region). Details of measurements in the cr(IV)-to-cr(III) transition region are shown in figure 5. During series 9 measurements, equilibrium was not reached within 24 h in this region. Results of this series are included in figure 5 and table 6; however, these results were not considered in the calculation of derived thermodynamic functions. For clarity, the results from series 10 and 13 are not shown in the figure. They are nearly coincident with the series 11 results. Heat capacities used to define the uninterrupted curve in this figure, as well as those in figures 6 and 7, are included in table 6.

Details of heat-capacity measurements in the cr(II)-to-cr(I) and cr(III)-to-cr(II) transition regions are shown in figures 6 and 7. The results for both transitions

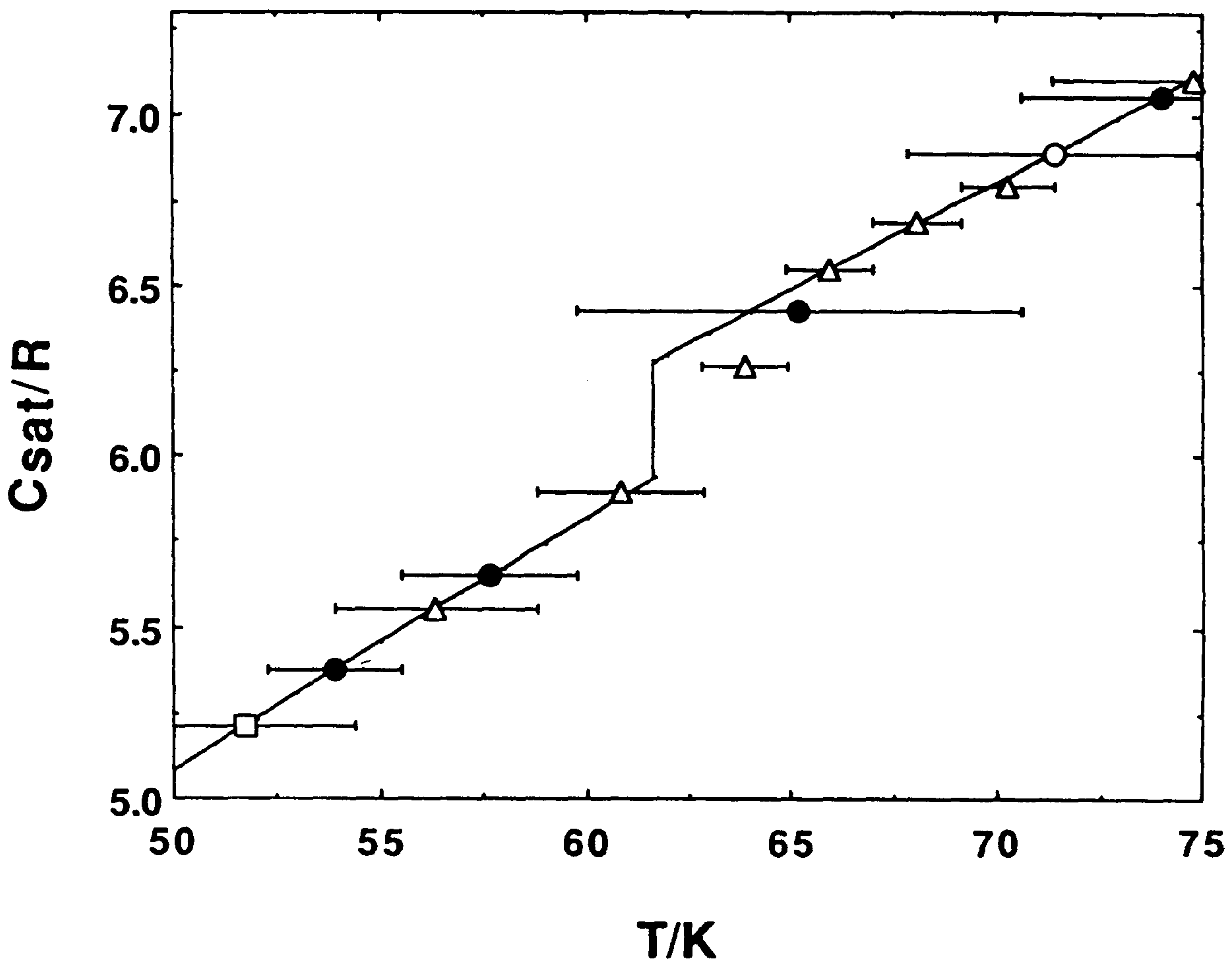


Figure 5. Experimental average heat capacities in the cr(IV)-to-cr(III) transition region for 1,2,3,4-tetrahydroquinoline. O, series 7; Δ, series 9; ●, series 11; □, series 12. The horizontal bars span the temperature increment associated with each average heat-capacity value. The heat-capacity curve is described in the text.

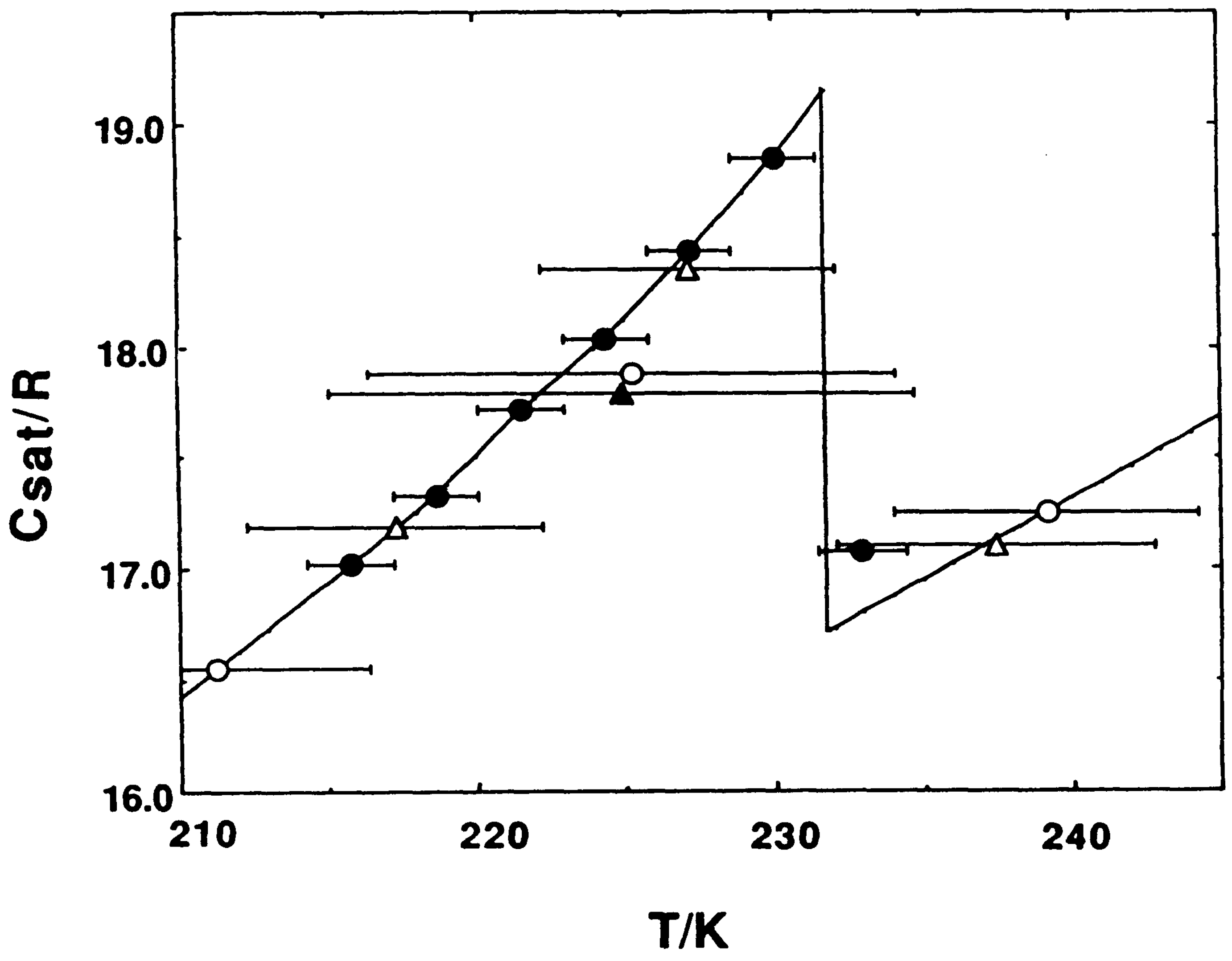


Figure 6. Experimental average heat capacities in the cr(II)-to-cr(I) transition region for 1,2,3,4-tetrahydroquinoline. Δ, series 1; ●, series 5, O, series 6; ▲, series 15. The horizontal bars span the temperature increment associated with each average heat-capacity value. The heat-capacity curve is described in the text.

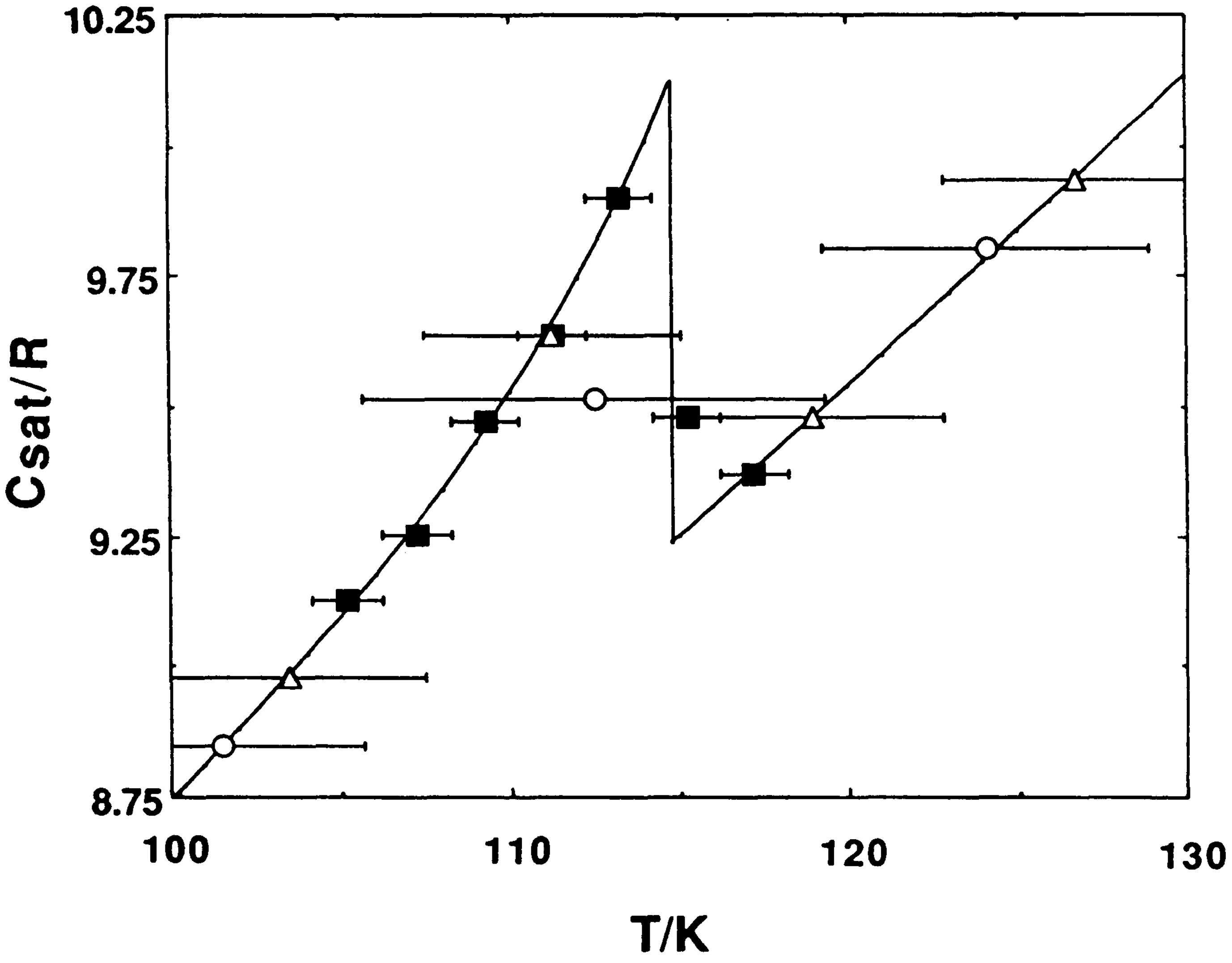


Figure 7. Experimental average heat capacities in the cr(III)-to-cr(II) transition region for 1,2,3,4-tetrahydroquinoline. Δ, series 7; O, series 8; ■, series 14. The horizontal bars span the temperature increment associated with each average heat-capacity value. The heat-capacity curve is described in the text.

are consistent with the lambda-shaped heat-capacity curves shown. The horizontal bars on each point indicate the temperature increment for the particular measurement.

Equilibration times for the 5,6,7,8-tetrahydroquinoline measurements in the stable crystalline phase were less than 1 h below 200 K, and increased to roughly 2 h near 210 K and 10 h near 220 K. Equilibration times for measurements completed on the metastable crystals and mixed crystals also were less than 1 h below 200 K. No attempt was made to reach equilibrium in the transition region of the metastable crystalline form.

Extrapolations to T→0 were made using least-squares fits of the Debye heat-capacity equation. Results between 12 and 18 K, and below 10 K were used in the fit for the 1,2,3,4-, and 5,6,7,8-isomers, respectively. The corresponding Debye characteristic temperatures were Θ = 89.8 K with 4.01 degrees of freedom and Θ = 70.0 K with 2.19 degrees of freedom, respectively.

THERMODYNAMIC PROPERTIES IN THE CONDENSED STATE

Condensed-phase entropies and enthalpies relative to that of the crystals at T→0 for the solid and liquid phases under vapor saturation pressure are listed in table 7. 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 table 6 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 a solid-insoluble impurity and the mole-fraction impurity value shown in table 1.

VAPOR-PRESSURE MEASUREMENTS

Vapor pressures for 1,2,3,4- and 5,6,7,8-tetrahydroquinolines are reported in table 8. Following previous practice,(32) 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 indicated correct operation of the equipment and the high purity of the samples.

Cox Equation Fits to Vapor Pressures. Previous studies by Scott and Osborn(39) have shown that the Cox equation(40) 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.(39)

The Cox equation in the form:

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

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:

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

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:

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

Parameters derived from the fits are given in table 9. Details of the Cox equation fits are given in table 8.

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

$$dp/dT = \Delta_l^g H_m\ /\ (\ T\ \Delta_l^g V_m)\ , \qquad (9)$$

where $\Delta_l^g V_m$ is the increase in molar volume from the liquid to the real vapor. In the calculation of $\Delta_l^g V_m$, estimates of the second virial coefficients were made using the correlation of Scott et al.,(41) and liquid-phase densities at 298.15 K of 1030 $kg{\cdot}m^{-3}$

and 990 kg·m^{-3} for 1,2,3,4- and 5,6,7,8-tetrahydroquinolines, respectively. The liquid-phase densities were measured during loading of the heat-capacity calorimeters. Generally, we have found these density estimates to be within 3 per cent of precisely determined values. Derived enthalpies of vaporization and the corresponding entropies of compression are reported in table 10.

THERMODYNAMIC PROPERTIES IN THE IDEAL-GAS STATE

Enthalpies and entropies at selected temperatures for the ideal gas were calculated using values in tables 7 and 10 and are listed in columns 2 and 4 of table 11. The derived ideal-gas enthalpies and entropies were combined with the condensed-phase enthalpy 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 11. Enthalpies and entropies for equilibrium hydrogen and graphite were determined from JANAF tables.(42) All uncertainties in table 11 represent one standard deviation.

4. DISCUSSION

A search of the literature failed to find any experimental thermodynamic property measurements for either of the two tetrahydroquinoline isomers. Cocchetto and Satterfield(10) estimated the equilibrium constants for the hydrogenation reactions of quinoline using the group-additivity schemes of Benson(11) and van Krevelen and Chermin.(12) Cocchetto and Satterfield(10) state that the estimated free energies of formation, and hence the equilibrium constants, "could be in error by one order of magnitude at 1000 K and two orders of magnitude at 500 K." In a subsequent paper, Cocchetto and Satterfield(13) compared experimental equilibria results (at hydrogen pressures of 3.55 MPa and 7.0 MPa and temperatures of 603 K, 648 K, and 693 K) with those estimates and showed that the estimates were crude, and were indeed probably in error by at least two orders of magnitude for the quinoline/1,2,3,4-tetrahydroquinoline equilibrium. In figure 8 the experimental and estimated equilibrium constants for the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline, as given by Cocchetto and Satterfield in figure 6 of reference 13, are compared with values of the equilibrium constant obtained using the calorimetric measurements reported here. The methodology used to calculate the equilibrium constants from the calorimetric measurements and the extrapolation to processing temperatures has been outlined in reference 24. Also plotted in figure 8 is the equilibrium constant obtained by Shih et al.(43) who approached the equilibrium from both the quinoline and the 1,2,3,4-tetra-

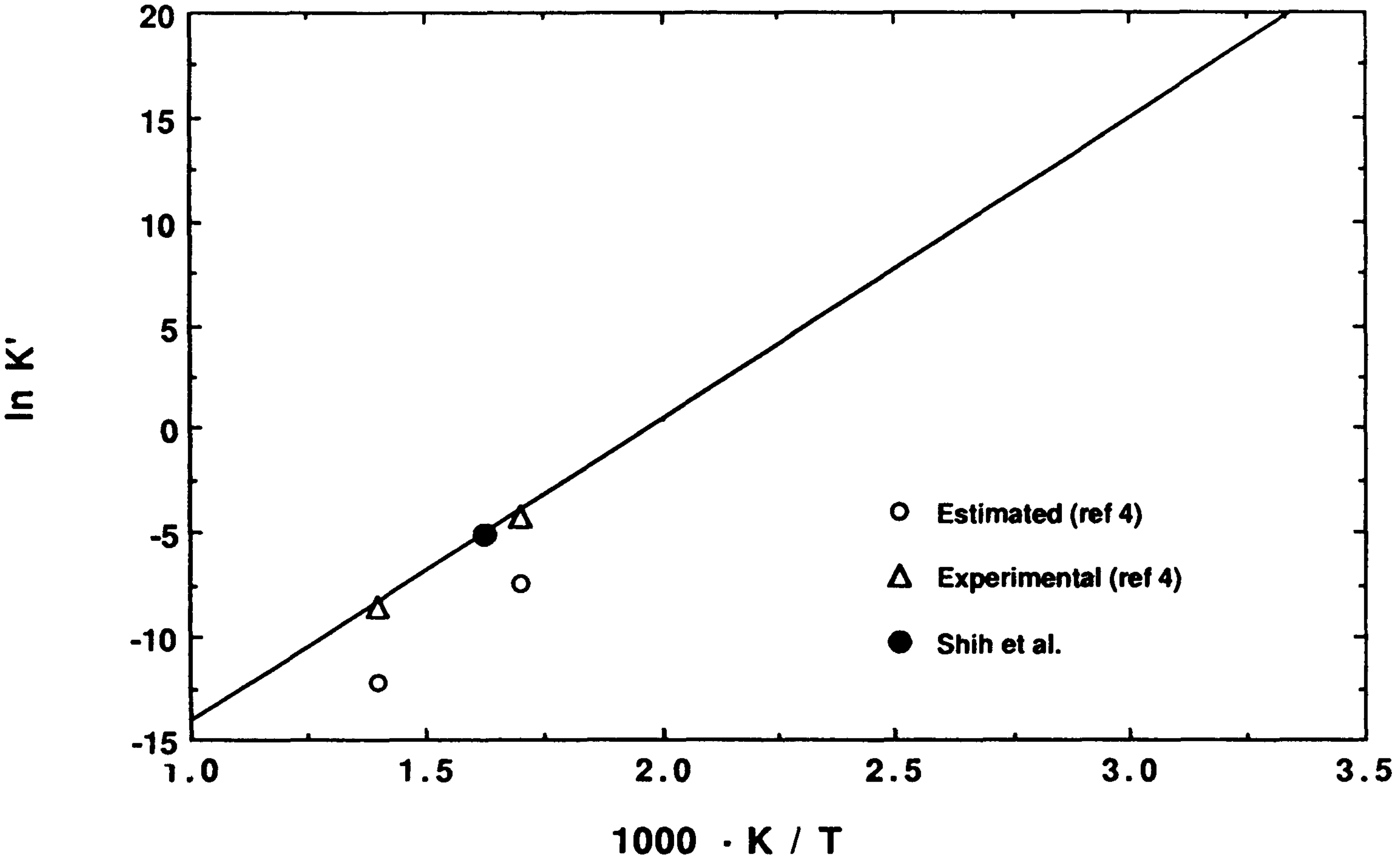


Figure 8. Ln K' as a function of inverse temperature for the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline. The solid line represents the function calculated from the calorimetric data. The line is an extrapolation in the region 1.0 to 2.0 on the x-axis. See text for explanation of the legend.

hydroquinoline sides of the reaction at 615 K and 3.55 MPa hydrogen pressure. The agreement between the experimentally measured values and those determined from the calorimetric measurements is excellent. The equation of the line representing the variation of the equilibrium constant versus temperature derived from the calorimetric measurements is:

$$\ln K' = (14530/T{\cdot}K) - 28.635. \qquad (10)$$

In figure 9 the experimental and estimated equilibrium constants for the hydrogenation of quinoline to 5,6,7,8-tetrahydroquinoline, as given by Cocchetto and Satterfield in figure 6 of reference 13, are compared with values of the equilibrium constant obtained using the calorimetric measurements reported here. In this case the agreement between the experimentally measured values and those determined from the calorimetric measurements is not as good (ln K' is 1.2 units different at the mid temperature of the experimental measurements in reference 13). The equation of the line representing variation of the equilibrium constant versus temperature derived from the calorimetric measurements is:

$$\ln K' = (15887/T{\cdot}K) - 29.119. \qquad (11)$$

In later work on the kinetics of the HDN of quinoline on a sulfided NiMo/Al_2O_3 catalyst Satterfield and Cocchetto(44) and Satterfield and Yang(14) derived kinetic models for the overall reaction scheme. Models were derived for both the vapor- and liquid-phase reaction. In the models, the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline was assumed to be much faster than the subsequent hydrogenolysis of 1,2,3,4-tetrahydroquinoline to o-propylaniline and the hydrogenation of 1,2,3,4-tetrahydroquinoline to decahydroquinoline. As a result 1,2,3,4-tetrahydroquinoline/quinoline will readily reach a pseudoequilibrium. Using the data given in table 3 of reference 14, equilibrium constants were calculated for the quinoline/1,2,3,4-tetrahydroquinoline liquid-phase equilibrium. These are reported in table 12 along with values derived from equation **10** above. The agreement between the modelling equilibrium constants and those derived here is excellent. Similar calculations for the quinoline/5,6,7,8-tetrahydroquinoline equilibria are also reported in table 12. In that case the modelling equilibrium constants are over twice as small as those calculated from equation **11**. Satterfield and Yang state that the "rate constants k_{10}" (k_{10} applies to the dehydrogenation of 5,6,7,8-tetrahydroquinoline to quinoline) "and k_{11}" (k_{11} applies to the dehydrogenation of decahydroquinoline) "are an order of magnitude smaller than the

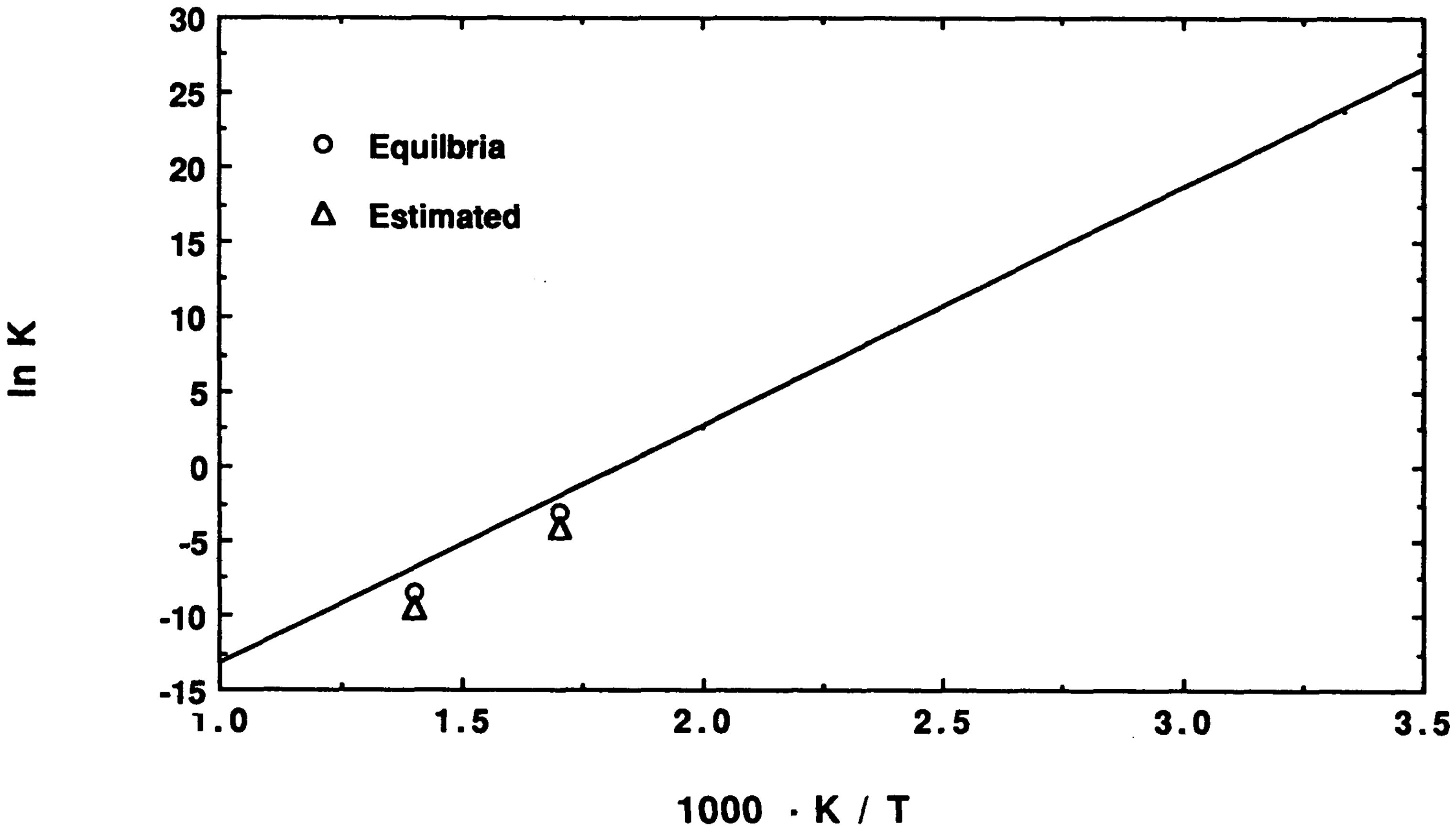


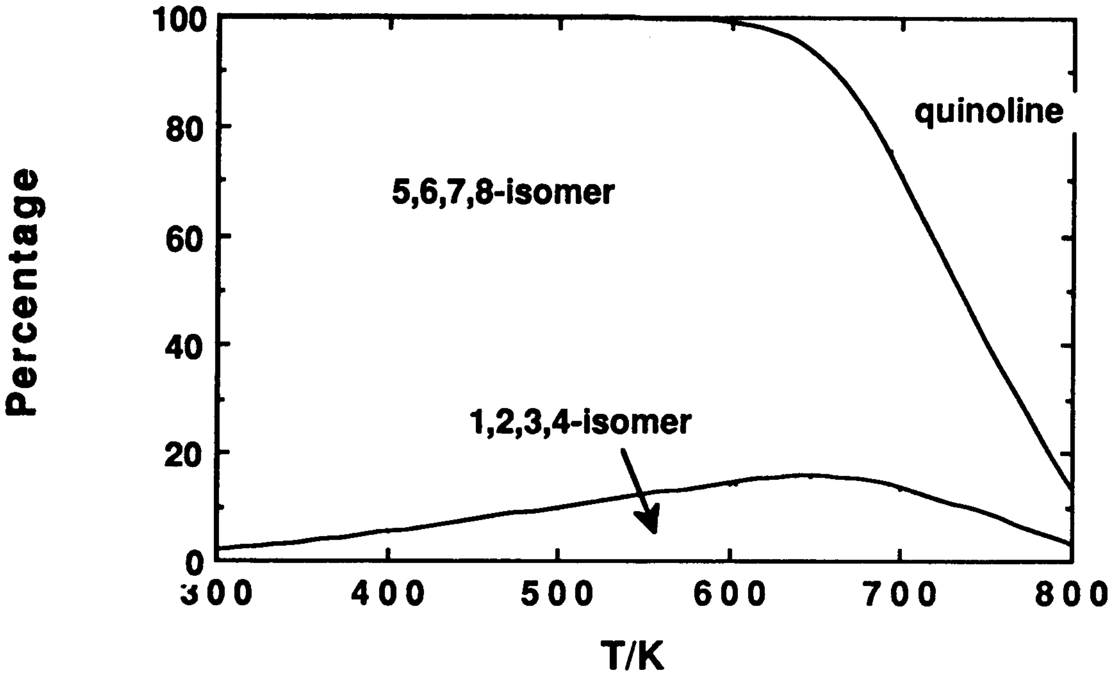
Figure 9. Ln K' as a function of inverse temperature for the hydrogenation of quinoline to 5,6,7,8-tetrahydroquinoline. The solid line represents the function calculated from the calorimetric data. The line is an extrapolation in the region 1.0 to 2.0 on the x-axis. See text for explanation of the legend.

other rate constants and the inherent errors are quite large." Therefore, the lack of agreement in this case may be due to the value allocated to k_{10} in their kinetic modelling. A value 50 per cent smaller than that given for k_{10} would bring both sets of results into near perfect agreement.

Giola and Lee(45) have also proposed a model for the kinetics of the HDN of quinoline. While their results do not list an equilibrium constant, K, for the quinoline/5,6,7,8-tetrahydroquinoline equilibrium they give a value of 0.0056 for K for the quinoline/1,2,3,4-tetrahydroquinoline equilibrium at 623 K. This is in excellent agreement with the value, 0.0049, obtained using equation 10 above.

Figure 10 is a chart showing the relative amounts of quinoline and both tetrahydroquinolines at thermodynamic equilibrium in the gas phase at different temperatures. The upper chart denotes equilibria under 3.55 MPa hydrogen pressure whereas the lower chart applies under 7.0 MPa hydrogen pressure. Note that the percentage of the 1,2,3,4-tetrahydroquinoline passes through a maximum in both charts and the percentage of quinoline decreases with increasing hydrogen pressure. However, in the latter case at 800 K and a hydrogen pressure even as high as 7.0 MPa, there is still over 60 per cent quinoline present at equilibrium.

Figure 11 is a chart showing the relative amounts of quinoline and 1,2,3,4-tetrahydroquinoline at thermodynamic equilibrium in the gas phase at different temperatures. The upper chart denotes equilibria under 3.55 MPa hydrogen pressure, whereas the lower chart applies under 7.0 MPa hydrogen pressure. In this case, again at 800 K at 7.0 MPa hydrogen pressure, approximately 90 per cent of the equilibrium mixture is quinoline. For this equilibrium doubling the hydrogen pressure has made changes in the equilibrium distribution which are barely perceptible in the charts. Obviously, HDN reactions to remove nitrogen efficiently from polycyclic aromatic compounds need a catalyst which will function efficiently at relatively low temperatures (below 750 K). Further discussion of the reaction schemes and equilibria in the quinoline HDN reaction is reserved for a future topical report in this series detailing the thermodynamic properties of 2-methylaniline (from which the thermodynamic properties of 2-propylaniline can be derived).



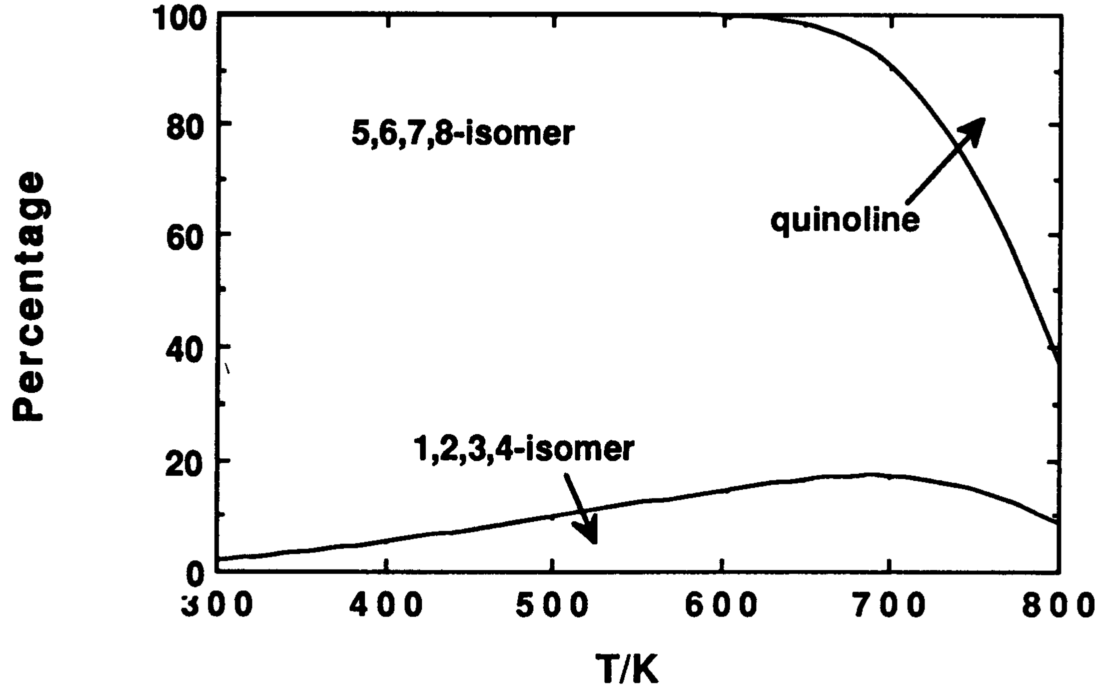


Figure 10. Relative percentages of quinoline and its tetrahydro-isomers at thermodynamic equilibrium in the gas phase at different temperatures. The upper chart is under a hydrogen pressure of 3.55 MPa, and the lower chart is for 7.0 MPa hydrogen pressure.

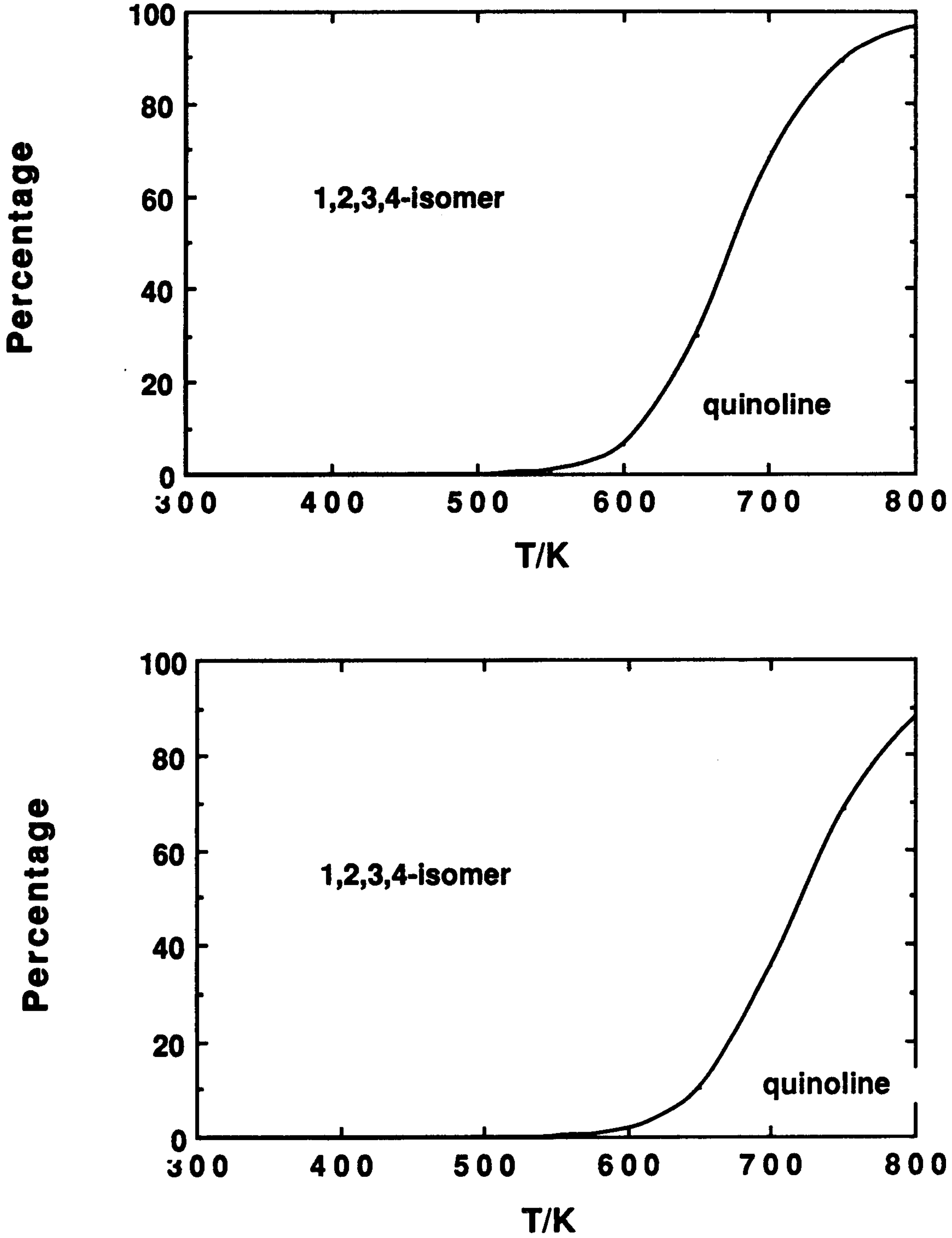


Figure 11. Relative percentages of quinoline and 1,2,3,4-tetrahydroquinoline at thermodynamic equilibrium in the gas phase at different temperatures. The upper chart is under a hydrogen pressure of 3.55 MPa, and the lower chart is for 7.0 MPa hydrogen pressure.

5. CONCLUSIONS

The results of the thermodynamic property measurements reported in this report have been used to determine equilibrium constants, and hence equilibrium concentrations, for the quinoline/hydrogen/tetrahydroquinoline system at temperatures of interest in the processing of fuels from crudes with a high nitrogen content. The results prove that, under typical processing conditions (650 K and 7.0 MPa hydrogen pressure), there is thermodynamic equilibrium between quinoline and 1,2,3,4-tetra-hydroquinoline. The proof that equilibrium conditions exist between quinoline and 5,6,7,8-tetrahydroquinoline in processing is not as unequivocal as in the former case, but there is strong evidence of such an equilibrium. Kinetic modelling of the HDN reaction for quinoline should be repeated using the results from the thermodynamic studies reported here. Using the results from this report to define the ratios of the rate constants for the equilibria, the remaining rate constants could be determined with greater precision and further insights gained into their relative importance.

6. REFERENCES

1. Steele, W. V.; Chirico, R. D.; Collier, W. B.; Harrison, R. H.; Gammon, B. E. *Assessment of Thermodynamic Data and Needs, Including Their Economic Impact, for Development of New Fossil Fuel Refining Processes.* NIPER-159. Published by DOE Fossil Energy, Bartlesville Project Office. Available from NTIS Report No. DE-86000298, June **1986**.
2. Katzer, J. R.; Sivasubramanian, R. *Catal. Rev.-Sci. Eng.* **1979**, 20, 155.
3. Ledorix, M. J. *Catalysis (London)* **1985**, 7, 125.
4. Ho, T. C. *Catal. Rev.-Sci. Eng.* **1988**, 30, 117.
5. Steele, W. V.; Archer, D. G.; Chirico, R. D.; Collier, W. B.; Gammon, B. E.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K. *The Thermodynamic Properties of Quinoline and Isoquinoline.* NIPER-301. Published by DOE Fossil Energy, Bartlesville Project Office. Available from NTIS Report No. DE-88001218, March **1988**.
6. Steele, W. V.; Archer, D. G.; Chirico, R. D.; Collier, W. B.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Gammon, B. E. *J. Chem. Thermodynamics* **1988**, 20, 1233.
7. Steele, W. V.; Chirico, R. D.; Hossenlopp, I. A.; Nguyen, A. *The Thermodynamic Properties of the Five Benzoquinolines.* NIPER-337. April **1988**.
8. Steele, W. V.; Chirico, R. D.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Gammon, B. E. Accepted for publication in The Journal of Chemical Thermodynamics.
9. Satterfield, C. N.; Modeil, M.; Hites, R. A.; Declerck, C. J. *Ind Eng. Chem. Process Des. Dev.* **1976**, 17, 141.
10. Cocchetto, J. F.; Satterfield, C. N. *Ind Eng. Chem. Process Des. Dev.* **1975**, 15, 272.
11. Benson, S. W. *Thermochemical Kinetics.* 2nd edition. Wiley: New York. **1976**.
12. van Krevelen, D. W.; Chermin, H. A. G. *Chem. Eng. Sci.* **1951**, 1, 66.
13. Cocchetto, J. F.; Satterfield, C. N. *Ind Eng. Chem. Process Des. Dev.* **1981**, 20, 49.
14. Satterfield, C. N.; Yang, S. H. *Ind Eng. Chem. Process Des. Dev.* **1984**, 23, 11.
15. Commission on Atomic Weights. *Pure Appl. Chem.* **1970**, 21, 93.
16. *CODATA Bulletin No. 63,* November **1986**. International Council of Scientific Unions, Committee on Data for Science Technology.
17. Comitie International des Poids et Measures. *Metrologia* **1969**, 5, 35.

18. Good, W. D.; Moore, R. T. *J. Chem. Eng. Data* **1970**, 15, 150.

19. Good, W. D.; Smith, N. K. *J. Chem. Eng. Data* **1969**, 14, 102.

20. Good, W. D. *J. Chem. Eng. Data* **1969**, 14, 231.

21. Good, W. D.; Scott, D. W.; Waddington, G. *J. Phys. Chem.* **1956**, 60, 1080.

22. Good, W. D.; Douslin, D. R.; Scott, D. W.; George, A.; Lacina, J. L.; M^{c}Cullough, J. P.; Waddington, G. *J. Phys. Chem.* **1959**, 63, 1133.

23. Smith, N. K.; Stewart, R. C. Jr.; Osborn, A. G.; Scott, D. W. *J. Chem. Thermodynamics* **1980**, 12, 919.

24. Chirico, R. D.; Hossenlopp, I. A.; Nguyen, A.; Strube, M. M.; Steele, W. V. *Thermodynamic Studies Related to the Hydrogenation of Phenanthrene.* NIPER-247. Published by DOE Fossil Energy, Bartlesville Project Office. Available from NTIS Report No. DE-8687001252, April **1987.**

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

26. Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry* editor Rossini, F. D. Interscience Publishers Inc., New York, **1956**, Chapt. 5, pp. 75-128.

27. Smith, N. K.; Good, W. D. *J. Chem. Eng. Data* **1967**, 12, 572.

28. Huffman, H. M. *Chem Rev.* **1947**, 40, 1.

29. Ruehwein, R. A.; Huffman, H. M. *J. Am. Chem. Soc.* **1943**, 65, 1620.

30. Scott, D. W.; Douslin, D. R.; Gross, M. E.; Oliver, G. D.; Huffman, H. M. *J. Am. Chem. Soc.* **1952**, 74, 883.

31. Swietoslawski, W. *Ebulliometric Measurements.* Reinhold Publishing Corp., New York, **1945.**

32. Osborn A. G.; Douslin, D. R. *J. Chem. Eng. Data* **1966**, 11, 502.

33. Chirico, R. D.; Nguyen, A.; Steele, W. V.; Strube, M. M.; Tsonopoulos, C. Accepted for publication *J. Chem. Eng. Data*, **1988.**

34. Antoine, C. C. R. *Acad. Sci.* **1888**, 107, 681.

35. Douslin, D. R.; M^{c}Cullough, J. P. *BuMines RI* 6149, **1963**, pp. 11.

36. Douslin, D. R.; Osborn A. G. *J. Sci. Instrum.* **1965**, 42, 369.

37. Rossini, F. D. *Experimental Thermochemistry,* editor Rossini, F. D. Interscience Publishers Inc., New York, **1956**, Chapt. 14, pp. 297-320.

38. CODATA Recommended Key Values for Thermodynamics 1977. See *J. Chem. Thermodynamics* **1978**, 10, 903.

39 Scott, D. W.; Osborn, A. G. *J. Phys. Chem.* **1979**, 83, 2714.

40. Cox, E. R. *Ind. Eng. Chem.* **1936**, 28, 613.

41. Scott, D. W.; Finke, H. L.; Gross, M. E.; Guthrie, G. B.; Huffman, H. M. *J. Am. Chem. Soc.* **1950**, 72, 2424.

42. Chase, M. W., Jr.; Davies, C. A.; Cowney, J. R.; Frurip, D. J.; M^{c}Donald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables Third edition. J. Phys. Chem. Ref. Data* **1985**, 14, supplement No. 1, 2 volumes.

43. Shih S. S.; Katzer, J. R.; Kwart, H.; Stiles, A. B. *Am. Chem. Soc. Div. Pet. Chem. Prepr.* **1977**, 22, 219.

44. Satterfield, C. N.; Cocchetto, J. F. *Ind Eng. Chem. Process Des. Dev.* **1981**, 20, 53.

45. Giola, F.; Lee, V. *Ind Eng. Chem. Process Des. Dev.* **1986**, 25, 918.

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 premelting corrections.

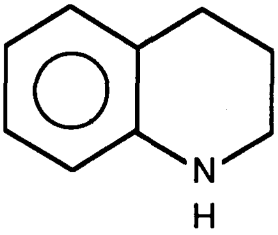
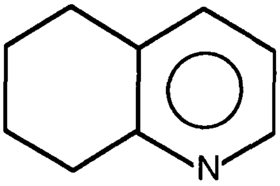
	1,2,3,4-Tetrahydroquinoline	**5,6,7,8-Tetrahydroquinoline**
		
m/g	50.757	46.948
V_i(298.15 K)/cm^3	62.47	59.06
T_{cal}/K	298.4	296.6
p_{cal}/kPa	6.32	7.44
$r(T_{max})$	3.75	3.36
r_{min}	2.00	1.85
$10^2(\delta C/C)_{max}$	0.020	0.030
x_{pre}	0.00040	0.00057

TABLE 2. Typical combustion experiment for the tetrahydroquinolines at 298.15 K. (p° = 101.325 kPa)[a]

	1,2,3,4-isomer	**5,6,7,8-isomer**
m'(compound)/g	0.903870	0.820575
m''(oil)/g	0.048053	0.040980
m'''(fuse)/g	0.001367	0.001647
$n_i(H_2O)$/mol	0.05535	0.05535
m(Pt)/g	32.720	32.863
$\Delta T=(t_i - t_f + \Delta t_{corr})$/K	2.20605	2.00045
ε(calor)(ΔT)/J	−37027.0	−33502.3
ε(cont)(ΔT)/J [b]	−46.5	−39.9
ΔU_{ign}/J	0.7_5	0.7_5
$\Delta U_{dec}(HNO_3)$/J	41.8	58.0
ΔU(corr. to std. states)/J [c]	17.7	16.7
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	2212.5	1886.8
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	23.2	27.9
$m'(\Delta_c U^\circ_m/M)$(compound)/J	−34777.5	−31552.0
$(\Delta_c U^\circ_m/M)$(compound)/$J \cdot g^{-1}$	−38476.2	−38451.1

[a] The symbols and abbreviations of this table are those of reference 26 except as noted.

[b] $\varepsilon_i(\text{cont})(t_i - 298.15\ \text{K}) + \varepsilon_f(\text{cont})(298.15\ \text{K} - t_f + \Delta t_{corr})$

[c] Items 81 to 85, 87 to 90, 93, and 94 of the computational form of reference 26.

TABLE 3. Summary of experimental energies of combustion and molar thermochemical functions for the tetrahydroquinolines at $T = 298.15$ K and $p^\circ = 101.325$ kPa.

1,2,3,4-tetrahydroquinoline

$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$

−38476.2	−38479.0	−38475.1	−38475.0	−38475.4	−38475.4

$<\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})>$	−38476.0±0.6
$(\Delta_c U^\circ_m)(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$	−5124.76±0.66
$(\Delta_c H^\circ_m/M)(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$	−5130.34±0.66
$(\Delta_f H^\circ_m/M)(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$	16.69±0.80

5,6,7,8-tetrahydroquinoline

$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$

−38451.1	−38448.1	−38452.7	−38450.4	−38448.0	−38456.1

$<\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})>$	−38451.1±1.5
$(\Delta_c U^\circ_m)(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$	−5121.44±1.16
$(\Delta_c H^\circ_m/M)(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$	−5127.04±1.16
$(\Delta_f H^\circ_m/M)(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$	13.39±1.24

TABLE 4. Melting-study summary; F is the fraction melted at observed temperature T(F), T_{tp} is the triple-point temperature, and x is the mole-fraction impurity

N[a]	F	T(F)/K	N[a]	F	T(F)/K
	1,2,3,4-Tetrahydroquinoline			**5,6,7,8-Tetrahydroquinoline**	
2	0.208	289.7885	21[b]	0.361	222.3100
2	0.407	289.8480	21	0.593	222.3245
2	0.559	289.8670	21	0.823	222.3310
2	0.706	289.8760			
2	0.855	289.8825	11[c]	0.693	222.6170
T_{tp}/K	289.913			222.347[b] (222.634)[d]	
x	0.00044			0.00026[b]	

---

[a] Adiabatic series number.

[b] These results from series 21 were obtained on the metastable crystal form.

[c] Series 11 was completed on the stable crystal form. See text.

[d] Estimated triple point temperature of the stable crystal form as described in the text.

TABLE 5. Experimental enthalpy measurements $(R=8.31441\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}})$

N[a]	h[b]	T_i/K	T_f/K	T_{trs}/K	$\Delta_{tot}H_m/R{\cdot}K$[c]	$\Delta_{trs}H_m/R{\cdot}K$[d]
			1,2,3,4-Tetrahydroquinoline			
			cr(IV) to cr(III)			
9	2	58.831	64.907	61.700	36.69	−0.49 [e]
10	1	59.714	70.532		69.61	0.07
11	1	59.773	70.594		69.53	−0.10
13	1	59.780	70.591		69.60	0.03
					Average:	0.00
			single-phase measurements in cr(III)			
13	1	70.599	105.644		278.96	−0.27
			cr(III) to cr(II)			
1	1	112.249	122.211	114.750	95.10	−0.28 [e]
7	1	107.462	115.053		73.15	−0.06
8	1	105.676	119.285		129.50	0.13
13	1	105.645	119.266		129.42	−0.04
14	1	114.225	116.216		18.88	−0.02
					Average:	0.00
			single-phase measurements in cr(II)			
14	1	118.228	169.166		562.70	0.57
14	1	169.163	216.143		696.56	0.68
			cr(II) to cr(I)			
1	1	222.245	232.097	231.800	180.75	−0.22 [e]
5	1	231.447	234.443		51.17	−0.02
6	1	216.407	234.084		316.12	0.03
15	1	215.043	234.749		350.51	−0.03
					Average:	0.00

TABLE 5. Continued

N[a]	h[b]	$\frac{T_i}{K}$	$\frac{T_f}{K}$	$\frac{T_{trs}}{K}$	$\frac{\Delta_{tot}H_m}{R\cdot K}$[c]	$\frac{\Delta_{trs}H_m}{R\cdot K}$[d]
		1,2,3,4-Tetrahydroquinoline continued				
		single-phase measurements in cr(I)				
3	1	239.356	282.622		822.17	0.14
4	1	238.000	283.331		860.98	0.80
15	1	234.747	282.403		897.92	1.63
		cr(I) to liquid				
1	2	283.373	298.259	289.913	1794.77	1420.70
2	6	281.633	294.231		1717.19	1420.88
15	2	281.895	293.361		1687.23	1420.87
					Average:	1420.82
		liquid to liquid				
17	1	338.286	409.292		2267.67	0.64
17	1	409.251	443.081		1165.17	−0.37
		5,6,7,8-Tetrahydroquinoline				
		single-phase measurements in cr				
11	1	62.165	100.303		279.18	−0.20
11	1	100.304	161.857		632.12	−0.08
11	1	161.857	209.697		657.10	−0.15
		cr to liquid				
1	3	210.136	226.911	222.634	1237.83	944.25[f]
11	2	215.641	228.956		1346.58	1091.41
13	4	218.415	234.451		1375.53	1037.52[g]
19	2	217.174	234.095		1425.83	1076.44[g]
21	4	216.382	230.854		1229.15	942.03[f]
					Selected:	1091.41

TABLE 5. Continued

N^a	h^b	$\frac{T_i}{K}$	$\frac{T_f}{K}$	$\frac{T_{trs}}{K}$	$\frac{\Delta_{tot}H_m}{R \cdot K}$ [c]	$\frac{\Delta_{trs}H_m}{R \cdot K}$ [d]
		5,6,7,8-Tetrahydroquinoline continued				
		liquid to liquid				
24	1	240.733	304.168		1577.11	-0.02
27	1	330.208	406.726		2295.55	-0.18
27	1	406.725	442.730		1191.08	-0.14
		cr(meta,II) to cr(meta,I) [f]				
12	1	192.305	216.594	210.0	375.90	12.76
13	6	198.899	215.823		428.69	172.59
19	1	194.942	214.468		331.75	39.52

[a] Adiabatic series number

[b] Number of heating increments

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

[d] $\Delta_{trs}H_m$ is the net molar enthalpy of transition at the transition temperature T_{trs}.

[e] This value was not included in the average.

[f] This result was obtained for the metastable crystal form. See text.

[g] This result was obtained for a mixture of stable and metastable crytals. See text.

[h] This phase transition was present only in the metastable crystal form. See text.

TABLE 6. Experimental molar heat capacities at vapor saturation pressure
(R = 8.31441 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)

N^a	$\langle T\rangle/\mathrm{K}$	$\Delta T/\mathrm{K}$	$C_{\mathrm{sat,m}}{}^{b}/R$	N^a	$\langle T\rangle/\mathrm{K}$	$\Delta T/\mathrm{K}$	$C_{\mathrm{sat,m}}{}^{b}/R$
			1,2,3,4-Tetrahydroquinoline				
			cr(IV)				
13	11.448	0.7624	0.597	12	34.211	3.6776	3.617
13	12.431	1.1516	0.715	12	37.965	3.8229	4.003
13	13.689	1.3328	0.885	12	42.028	4.3049	4.398
13	15.098	1.4623	1.083	12	46.615	4.8526	4.802
13	16.667	1.6480	1.306	12	51.714	5.3354	5.210
13	18.388	1.7910	1.556	11	53.886	3.2138	5.374
13	20.300	2.0237	1.834	10	55.163	3.1412	5.478
13	22.475	2.3268	2.142	9	56.347	4.9413	5.551
13	24.906	2.5332	2.479	13	57.497	4.5523	5.637
13	27.632	2.9155	2.834	11	57.636	4.2547	5.650
12	30.732	3.2764	3.214	10	58.221	2.9795	5.686
			cr(III)				
9	65.947	2.1184	6.548	9	90.522	9.8799	8.103
9	68.065	2.1275	6.688	8	93.002	8.6020	8.274
9	70.255	2.2541	6.797	7	95.219	8.4709	8.408
7	71.392	7.0513	6.892	8	101.489	8.3728	8.847
10	73.963	6.8596	7.057	7	103.458	8.0060	8.978
11	74.027	6.8571	7.057	14	105.174	2.0734	9.128
9	74.783	6.8031	7.107	14	107.237	2.0462	9.254
7	78.725	7.6123	7.362	14	109.270	2.0162	9.471
9	81.883	7.3979	7.560	14	111.274	1.9869	9.639
8	84.686	8.0300	7.741	14	113.247	1.9520	9.902
7	86.757	8.4527	7.866				
			cr(II)				
14	117.216	1.9930	9.372	1	197.180	10.0378	15.170
7	118.948	7.7886	9.479	6	200.976	10.2441	15.526
13	124.096	9.6591	9.794	1	207.238	10.0131	16.129

TABLE 6. Continued

N[a]	<T>/K	ΔT/K	$C_{\mathrm{sat},m}/R$[b]	N[a]	<T>/K	ΔT/K	$C_{\mathrm{sat},m}/R$[b]
1,2,3,4-Tetrahydroquinoline							
cr(II) (continued)							
8	124.107	9.6547	9.802	6	211.255	10.3125	16.554
7	126.719	7.7573	9.937	5	215.759	2.9023	17.047
1	127.178	9.9036	9.949	1	217.273	9.9176	17.196
1	137.143	9.7752	10.572	5	218.656	2.8913	17.392
1	146.945	9.8050	11.211	5	221.536	2.8692	17.742
1	156.834	9.9457	11.886	5	224.395	2.8496	18.092
1	166.857	10.0759	12.622	5	227.232	2.8249	18.497
1	177.000	10.1904	13.417	5	230.046	2.8023	18.925
1	187.127	10.0513	14.272				
cr(I)							
6	239.138	10.2457	17.266	1	268.678	10.1084	19.707
1	248.009	10.4815	17.925	2	276.930	9.8283	20.574
1	258.451	10.4078	18.796	1	278.584	9.8096	20.820
2	262.235	20.5641	19.140				
liquid							
15	297.956	9.2056	28.405	16	360.197	12.5873	31.291
2	298.026	7.6232	28.383	16	372.655	12.4404	31.864
1	302.552	8.6236	28.584	16	384.986	12.2988	32.454
15	307.107	9.1207	28.817	16	397.205	12.1600	33.032
16	315.191	9.3995	29.192	16	409.281	12.0265	33.616
16	325.005	10.2412	29.631	16	420.789	11.0439	34.198
16	336.111	11.9690	30.150	16	431.739	10.9362	34.729
16	348.003	11.8268	30.713	16	441.322	8.3373	35.186

TABLE 6. Continued

N^a	$\frac{\langle T \rangle}{K}$	$\frac{\Delta T}{K}$	$\frac{C_{sat,m}}{R}^b$	N^a	$\frac{\langle T \rangle}{K}$	$\frac{\Delta T}{K}$	$\frac{C_{sat,m}}{R}^b$
5,6,7,8-Tetrahydroquinoline							
cr							
10	4.651	0.7858	0.048	8	55.918	4.1232	5.655
10	5.483	0.7168	0.085	8	60.895	5.7750	6.034
10	6.336	0.8213	0.125	8	66.949	6.2881	6.464
10	7.281	0.9153	0.184	8	73.569	6.9139	6.876
10	8.277	0.9683	0.263	8	80.955	7.8258	7.318
10	9.331	1.1134	0.355	8	89.287	8.4076	7.829
10	10.481	1.1867	0.473	9	96.163	9.3840	8.197
10	11.721	1.2938	0.617	9	105.843	9.9125	8.761
10	13.025	1.3141	0.778	9	115.835	10.0671	9.344
10	14.441	1.5226	0.967	9	125.912	10.0789	9.941
10	16.002	1.6038	1.187	9	135.967	10.0283	10.552
10	17.684	1.7659	1.423	9	145.992	10.0144	11.172
10	19.558	1.9886	1.692	9	156.055	10.0321	11.801
10	21.654	2.2175	1.994	9	166.078	10.0091	12.448
10	24.030	2.5394	2.331	19	174.776	20.3837	13.020
10	26.713	2.8272	2.697	9	176.089	10.0102	13.107
10	29.699	3.1672	3.079	7	185.843	10.3561	13.773
10	33.066	3.5717	3.493	9	186.290	10.3445	13.794
10	36.750	3.7987	3.911	7	196.075	10.0566	14.458
10	40.773	4.2473	4.330	7	206.288	10.2743	15.134
10	45.231	4.6741	4.772	11	212.644	6.1907	15.654
10	50.157	5.1805	5.211	7	214.838	6.7704	15.934
10	55.670	5.8507	5.635				
liquid							
23	165.365 [c]	5.9745	20.830	20	310.423	10.0411	26.797
24	211.150	5.6655	22.323	25	316.337	9.2016	27.125
24	217.658	7.3542	22.514	20	320.437	10.0054	27.345

TABLE 6. Continued

5,6,7,8-Tetrahydroquinoline

liquid (continued)

N[a]	$\langle T\rangle$/K	ΔT/K	$C_{\mathrm{sat},m}$/R [b]	N[a]	$\langle T\rangle$/K	ΔT/K	$C_{\mathrm{sat},m}$/R [b]
24	225.946	9.2298	22.809	25	325.890	9.8768	27.644
1	229.670	5.5181	22.948	25	336.209	10.7290	28.213
11	233.033	8.1681	23.085	26	343.430	11.6019	28.614
1	235.171	5.4829	23.155	26	355.068	11.6522	29.260
24	235.648	10.1793	23.170	26	366.651	11.4962	29.904
20	236.718	5.5138	23.220	26	378.081	11.3470	30.537
20	242.322	5.6999	23.444	26	389.362	11.2054	31.160
20	250.175	10.0114	23.781	26	400.538	11.0710	31.777
20	260.240	10.1296	24.249	26	411.544	10.9433	32.381
20	270.291	9.9817	24.722	26	422.422	10.8228	32.963
20	280.319	10.0842	25.228	26	433.165	10.7071	33.538
20	290.344	9.9798	25.739	26	442.042	7.0771	34.005
20	300.327	10.1692	26.265				

---

[a] Adiabatic series number.

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

[c] Obtained immediately after crossing the glass transition. This series was terminated after this measurement because the sample crystallized.

TABLE 7. Molar thermodynamic functions at vapor saturation (R = 8.31441 J·K^{-1}·mol^{-1})

$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m^o}{R}$	$\frac{\Delta_0^T H_m^o}{RT}$	$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m^o}{R}$	$\frac{\Delta_0^T H_m^o}{RT}$
1,2,3,4-Tetrahydroquinoline							
cr(IV)							
10.000	0.410	0.142	0.106	35.000	3.701	2.347	1.535
12.000	0.656	0.238	0.176	40.000	4.204	2.874	1.838
14.000	0.928	0.359	0.264	45.000	4.664	3.396	2.127
16.000	1.211	0.501	0.365	50.000	5.077	3.909	2.401
18.000	1.500	0.660	0.475	55.000	5.455	4.411	2.662
20.000	1.790	0.834	0.592	60.000 [a]	5.811	4.901	2.910
25.000	2.491	1.309	0.902	61.700 [a]	5.934	5.065	2.991
30.000	3.127	1.820	1.221				
cr(III)							
61.700 [a]	6.276	5.065	2.991	104.000	9.021	8.986	4.877
70.000	6.803	5.890	3.412	106.000	9.173	9.160	4.957
80.000	7.441	6.840	3.876	108.000	9.340	9.333	5.036
90.000	8.070	7.753	4.307	110.000	9.527	9.506	5.116
95.000	8.408	8.198	4.514	112.000	9.742	9.679	5.197
100.000	8.742	8.638	4.717	114.000 [a]	10.005	9.854	5.279
102.000	8.879	8.813	4.797	114.750 [a]	10.120	9.920	5.310
cr(II)							
114.750 [a]	9.235	9.920	5.310	205.000	15.905	16.854	8.372
120.000	9.541	10.340	5.489	210.000	16.415	17.243	8.557
130.000	10.134	11.127	5.823	215.000	16.938	17.635	8.746
140.000	10.755	11.900	6.153	220.000	17.505	18.031	8.938
150.000	11.415	12.665	6.481	222.000	17.759	18.191	9.016
160.000	12.113	13.423	6.811	224.000	17.993	18.351	9.096
170.000	12.862	14.180	7.145	226.000	18.254	18.512	9.175
180.000	13.665	14.937	7.485	228.000	18.539	18.674	9.256
190.000	14.523	15.699	7.832	230.000	18.842	18.837	9.338
200.000	15.433	16.467	8.189	231.800 [a]	19.147	18.985	9.413

TABLE 7. Continued

T/K	$C_{\mathrm{sat},m}/R$	$\Delta_0^T S_m^{\circ}/R$	$\Delta_0^T H_m^{\circ}/RT$	T/K	$C_{\mathrm{sat},m}/R$	$\Delta_0^T S_m^{\circ}/R$	$\Delta_0^T H_m^{\circ}/RT$
1,2,3,4-Tetrahydroquinoline continued							
cr(I)							
231.800 [a]	16.717	18.985	9.413	270.000	19.744	21.752	10.653
240.000	17.313	19.577	9.673	280.000 [a]	20.622	22.486	10.993
250.000	18.065	20.298	9.993	289.913 [a]	21.470	23.218	11.337
260.000	18.889	21.023	10.320				
liquid							
289.913 [a]	28.034	28.119	16.238	390.000	32.690	37.082	19.857
290.000 [a]	28.038	28.127	16.241	400.000	33.165	37.916	20.184
298.150	28.389	28.909	16.569	410.000	33.654	38.741	20.506
300.000	28.470	29.085	16.642	420.000	34.157	39.558	20.825
310.000	28.939	30.026	17.031	430.000	34.645	40.367	21.141
320.000	29.407	30.952	17.410	440.000	35.123	41.169	21.453
330.000	29.863	31.864	17.781	450.000 [a]	35.608	41.964	21.762
340.000	30.334	32.763	18.143	460.000 [a]	36.100	42.752	22.069
350.000	30.808	33.649	18.498	470.000 [a]	36.592	43.534	22.373
360.000	31.280	34.523	18.847	480.000 [a]	37.082	44.309	22.674
370.000	31.743	35.387	19.189	490.000 [a]	37.571	45.079	22.973
380.000	32.214	36.239	19.525	500.000 [a]	38.059	45.843	23.270

TABLE 7. Continued

$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m^o}{R}$	$\frac{\Delta_0^T H_m^o}{RT}$	$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m^o}{R}$	$\frac{\Delta_0^T H_m^o}{RT}$
			5,6,7,8-Tetrahydroquinoline				
			cr				
5.000	0.062	0.021	0.016	70.000	6.659	5.915	3.426
6.000	0.107	0.036	0.027	80.000	7.263	6.843	3.868
7.000	0.165	0.057	0.042	90.000	7.865	7.734	4.279
8.000	0.240	0.083	0.062	100.000	8.417	8.591	4.665
9.000	0.325	0.116	0.087	110.000	9.003	9.421	5.033
10.000	0.422	0.155	0.115	120.000	9.589	10.229	5.388
12.000	0.650	0.252	0.185	130.000	10.187	11.020	5.734
14.000	0.907	0.371	0.269	140.000	10.800	11.798	6.074
16.000	1.186	0.510	0.366	150.000	11.420	12.564	6.410
18.000	1.468	0.666	0.473	160.000	12.049	13.321	6.743
20.000	1.756	0.836	0.587	170.000	12.698	14.071	7.074
25.000	2.465	1.305	0.892	180.000	13.360	14.815	7.405
30.000	3.118	1.813	1.210	190.000	14.031	15.555	7.736
35.000	3.717	2.339	1.526	200.000	14.675	16.292	8.067
40.000	4.252	2.871	1.834	210.000	15.295	17.023	8.396
45.000	4.750	3.401	2.130	220.000 [a]	15.932	17.749	8.724
50.000	5.196	3.925	2.415	222.634 [a]	16.100	17.940	8.810
60.000	5.967	4.941	2.944				
			liquid				
210.000	22.246	21.530	13.186	350.000	28.979	34.328	18.048
220.000	22.584	22.572	13.606	360.000	29.534	35.152	18.360
222.634	22.675	22.842	13.713	370.000	30.089	35.969	18.669
230.000	22.961	23.585	14.004	380.000	30.643	36.778	18.977
240.000	23.350	24.570	14.386	390.000	31.195	37.581	19.283
250.000	23.774	25.532	14.752	400.000	31.747	38.378	19.588
260.000	24.236	26.473	15.108	410.000	32.296	39.169	19.891
270.000	24.710	27.396	15.455	420.000	32.834	39.954	20.193
280.000	25.211	28.304	15.794	430.000	33.369	40.733	20.493

TABLE 7. Continued

T/K	$C_{sat,m}/R$	$\Delta_0^T S_m^o/R$	$\Delta_0^T H_m^o/RT$	T/K	$C_{sat,m}/R$	$\Delta_0^T S_m^o/R$	$\Delta_0^T H_m^o/RT$
5,6,7,8-Tetrahydroquinoline							
liquid (continued)							
290.000	25.722	29.198	16.128	440.000	33.898	41.506	20.792
298.150	26.149	29.916	16.396	450.000 [a]	34.429	42.273	21.089
300.000	26.247	30.078	16.456	460.000 [a]	34.963	43.036	21.385
310.000	26.775	30.948	16.781	470.000 [a]	35.495	43.794	21.679
320.000	27.324	31.806	17.102	480.000 [a]	36.026	44.546	21.973
330.000	27.870	32.656	17.420	490.000 [a]	36.556	45.295	22.265
340.000	28.423	33.496	17.735	500.000 [a]	37.088	46.039	22.556

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

TABLE 8. Summary of vapor-pressure results; IP refers to measurements performed with the inclined-piston gauge, water,decane or benzene refers to which material was used as the standard in the reference ebulliometer, the pressure p for ebulliometric measurements was calculated from the condensation temperature of the reference substance, T is the temperature of the experimental inclined-piston pressure gauge measurements or for ebulliometric measurements of the condensation temperature of the sample, ΔT is the difference between the boiling and condensation temperatures $(T_{boil} - T_{cond})$ for the sample in the ebulliometer, Δp is the difference of the calculated value of pressure from the observed value of pressure, $\sigma(p)$ is the propagated error calculated from equations (1) and (2).

Method	T/K	p/kPa	Δp/kPa	$\sigma(p)$/kPa	ΔT/K
1,2,3,4-Tetrahydroquinoline					
IP	323.151	0.0273	−0.0001	0.0002	
IP	333.149	0.0553	0.0000	0.0002	
IP	343.150	0.1066	0.0001	0.0002	
IP	353.149	0.1960	−0.0002	0.0002	
IP	363.150	0.3471	0.0000	0.0003	
IP	373.149	0.5916	0.0001	0.0003	
IP	383.150	0.9752	0.0004	0.0003	
IP	388.150	1.2369	0.0004	0.0004	
IP	393.150	1.5574	0.0002	0.0004	
IP	398.151	1.9475	0.0003	0.0005	
IP	403.151	2.4184	0.0001	0.0006	
IP	408.150	2.9840	0.0004	0.0007	
benzene	439.015	9.5897	−0.0021	0.0006	0.007
benzene	442.740	10.8926	−0.0027	0.0006	0.007
benzene	446.470	12.3446	−0.0006	0.0007	0.006
benzene	450.216	13.9602	0.0005	0.0008	0.005
benzene	453.972	15.7520	0.0013	0.0009	0.005
benzene	457.742	17.7372	0.0018	0.0009	0.005
water [a]	461.524	19.9330	0.0030	0.0011	0.004
benzene	461.525	19.9330	0.0027	0.0010	0.004
water	469.123	25.0230	0.0048	0.0013	0.003

Table 8. Continued

Method	T/K	p/kPa	Δp/kPa	$\sigma(p)$/kPa	ΔT/K
	1,2,3,4-Tetrahydroquinoline continued				
water	476.777	31.1770	0.0026	0.0016	0.003
water	484.479	38.5650	0.0010	0.0019	0.001
water	492.230	47.3750	−0.0027	0.0023	0.001
water	500.029	57.8170	−0.0028	0.0027	0.000
water	507.880	70.1200	−0.0049	0.0032	0.001
water	515.781	84.5330	−0.0076	0.0037	0.000
water	523.731	101.3250	−0.0055	0.0043	0.000
water	531.731	120.7901	−0.0017	0.0049	0.000
water	539.785	143.2499	−0.0005	0.0057	0.000
water	547.882	169.0200	0.0062	0.0065	0.000
water	556.035	198.4899	0.0100	0.0074	0.003
water	564.236	232.0200	0.0043	0.0084	0.002
water	572.486	270.0200	−0.0096	0.0094	0.004
	5,6,7,8-Tetrahydroquinoline				
IP	303.151	0.0303	0.0001	0.0002	
IP	313.150	0.0623	0.0002	0.0002	
IP	323.151	0.1213	0.0000	0.0002	
IP	333.154	0.2258	−0.0001	0.0002	
IP	343.154	0.4031	0.0001	0.0003	
IP	353.152	0.6916	0.0000	0.0003	
IP	363.149	1.1453	0.0000	0.0004	
IP	368.149	1.4558	−0.0001	0.0004	
IP	373.149	1.8369	0.0002	0.0005	
decane [a]	375.022	2.0000	0.0001	0.0001	0.051
IP	378.147	2.2997	0.0000	0.0006	
decane [a]	381.522	2.6660	0.0000	0.0002	0.037
IP	383.151	2.8599	−0.0001	0.0006	
IP	388.154	3.5327	0.0001	0.0007	
decane	398.380	5.3330	0.0000	0.0003	0.023

Table 8. Continued

Method	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma(p)}{kPa}$	$\frac{\Delta T}{K}$
	5,6,7,8-Tetrahydroquinoline continued				
decane	409.108	7.9989	-0.0001	0.0004	0.019
decane	417.161	10.6661	-0.0007	0.0006	0.016
decane	423.672	13.3320	0.0002	0.0007	0.017
decane	430.440	16.6650	0.0002	0.0008	0.014
water [a]	436.055	19.9330	0.0056	0.0011	0.010
decane	436.062	19.9330	0.0007	0.0009	0.011
water [a]	443.463	25.0230	0.0045	0.0013	0.007
decane	443.468	25.0230	0.0006	0.0011	0.009
water	450.923	31.1770	0.0019	0.0016	0.007
water	458.432	38.5650	0.0002	0.0019	0.006
water	465.991	47.3750	-0.0009	0.0023	0.005
water	473.601	57.8170	-0.0026	0.0027	0.003
water	481.263	70.1200	-0.0033	0.0032	0.002
water	488.976	84.5330	-0.0014	0.0037	0.002
water	496.741	101.3250	-0.0019	0.0043	0.002
water	504.557	120.7901	0.0013	0.0050	0.002
water	512.429	143.2499	0.0010	0.0057	0.003
water	520.347	169.0200	0.0029	0.0065	0.002
water	528.320	198.4899	0.0037	0.0074	0.003
water	536.342	232.0200	0.0037	0.0084	0.003
water	544.414	270.0200	-0.0076	0.0095	0.004

[a] This value was not included in the fit.

TABLE 9. Cox equation coefficients

	1,2,3,4-Tetrahydro quinoline	**5,6,7,8-Tetrahydro quinoline**
T_{ref}/K	523.728	496.740
P_{ref}/kPa	101.325	101.325
A	2.94663	2.86473
10^3B	−1.44316	−1.36067
10^6C	0.98459	0.98307
T/K [a]	323 to 572	303 to 544

[a] Temperature range of the vapor pressures used in the fit.

TABLE 10. Enthalpies of vaporization and entropies of compression obtained from the Cox and Clapeyron equations [a] ($R=8.31441$ J·K^{-1}mol^{-1} and $p°=101.325$ kPa)

T/K	$\Delta_l^g H_m/RK$	$\Delta S_{comp,m}/R$	T/K	$\Delta_l^g H_m/RK$	$\Delta S_{comp,m}/R$
		1,2,3,4-Tetrahydroquinoline			
298.15 [b]	7857±18	−10.226±0.002	460.00	6442±14	−1.673±0.000
300.00 [b]	7839±17	−10.064±0.002	480.00	6275±20	−1.089±0.000
320.00 [b]	7654±11	−8.449±0.001	500.00	6107±29	−0.562±0.000
340.00	7471±6	−7.059±0.001	520.00	5936±40	−0.084±0.000
360.00	7292±4	−5.852±0.000	540.00	5762±53	0.351±0.000
380.00	7117±2	−4.798±0.000	560.00	5581±69	0.749±0.000
400.00	6945±3	−3.871±0.000	580.00 [b]	5394±89	1.114±0.000
420.00	6775±5	−3.052±0.000	600.00 [b]	5198±112	1.451±0.000
440.00	6608±9	−2.323±0.000	620.00 [b]	4991±139	1.764±0.000
		5,6,7,8-Tetrahydroquinoline			
260.00 [b]	7227±8	−11.985±0.001	440.00	5857±15	−1.504±0.000
280.00 [b]	7067±5	−10.021±0.001	460.00	5706±22	−0.923±0.000
298.15 [b]	6924±3	−8.500±0.000	480.00	5553±32	−0.399±0.000
300.00 [b]	6909±3	−8.357±0.000	500.00	5394±44	0.074±0.000
320.00	6753±2	−6.933±0.000	520.00	5230±58	0.505±0.000
340.00	6600±1	−5.705±0.000	540.00	5058±76	0.898±0.000
360.00	6449±2	−4.638±0.000	560.00 [b]	4876±97	1.259±0.000
380.00	6300±3	−3.704±0.000	580.00 [b]	4683±123	1.592±0.000
400.00	6152±6	−2.882±0.000	600.00 [b]	4475±152	1.901±0.000
420.00	6005±10	−2.153±0.000			

---

[a] $\Delta S_{comp}/R = \ln(p/p°)$

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

TABLE 11. Thermodynamic properties in the ideal-gas state (R = 8.31441 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ and p° = 101.325 kPa)

$\frac{T}{K}$	$\frac{\Delta_0^T H_m^\circ}{RT}$	$\frac{\Delta_{imp} H_m^\circ}{RT}$ [a]	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_{imp} S_m^\circ}{R}$ [b]	$\frac{\Delta_f H_m^\circ}{RT}$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_f G_m^\circ}{RT}$
			1,2,3,4-Tetrahydroquinoline				
290.00 [c,d]	43.597±0.074	0.000	44.513±0.078	0.000	34.32±0.18	−58.76±0.23	93.08±0.27
298.15 [d]	42.921±0.063	0.000	45.035±0.066	0.000	33.09±0.17	−59.07±0.23	92.15±0.28
300.00 [d]	42.772±0.059	0.000	45.152±0.064	0.000	32.81±0.17	−59.14±0.24	91.95±0.28
320.00 [d]	41.330±0.039	0.001	46.421±0.045	0.000	30.08±0.16	−59.84±0.25	89.92±0.29
340.00	40.118±0.025	0.001	47.679±0.037	0.001	27.69±0.15	−60.48±0.28	88.17±0.31
360.00	39.105±0.022	0.003	48.929±0.036	0.002	25.59±0.15	−61.06±0.30	86.65±0.33
380.00	38.260±0.020	0.006	50.174±0.037	0.005	23.73±0.15	−61.59±0.32	85.32±0.35
400.00	37.557±0.022	0.011	51.416±0.039	0.009	22.07±0.16	−62.07±0.34	84.14±0.38
420.00	36.974±0.024	0.018	52.652±0.042	0.014	20.60±0.17	−62.50±0.37	83.10±0.40
440.00	36.500±0.030	0.028	53.886±0.046	0.022	19.29±0.18	−62.89±0.39	82.17±0.43
460.00 [c]	36.115±0.038	0.042	55.115±0.052	0.032	18.11±0.19	−63.23±0.41	81.34±0.45
480.00 [c]	35.807±0.047	0.060	56.338±0.061	0.045	17.05±0.20	−63.55±0.44	80.59±0.48
500.00 [c]	35.567±0.062	0.083	57.555±0.073	0.060	16.09±0.22	−63.83±0.46	79.92±0.50

TABLE 11. Continued

$\frac{T}{K}$	$\frac{\Delta_0^T H_m^\circ}{RT}$	$\frac{\Delta_{imp} H_m^\circ}{RT}$ [a]	$\frac{\Delta_0^T S_m^\circ}{R}$	$\frac{\Delta_{imp} S_m^\circ}{R}$ [b]	$\frac{\Delta_f H_m^\circ}{RT}$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_f G_m^\circ}{RT}$
5,6,7,8-Tetrahydroquinoline							
260.00 [d]	42.904±0.031	0.000	42.283±0.038	0.000	34.58±0.29	−57.82±0.19	92.41±0.34
280.00 [d]	41.034±0.024	0.000	43.523±0.033	0.000	31.25±0.27	−58.72±0.21	89.97±0.34
298.15 [d]	39.620±0.019	0.001	44.638±0.032	0.000	28.63±0.25	−59.46±0.23	88.09±0.34
300.00 [d]	39.487±0.019	0.001	44.753±0.032	0.001	28.37±0.25	−59.54±0.23	87.91±0.34
320.00	38.206±0.018	0.002	45.978±0.032	0.001	25.88±0.23	−60.28±0.25	86.16±0.34
340.00	37.150±0.018	0.003	47.205±0.034	0.003	23.71±0.22	−60.95±0.27	84.66±0.35
360.00	36.281±0.019	0.007	48.433±0.036	0.006	21.80±0.22	−61.56±0.30	83.36±0.37
380.00	35.569±0.021	0.013	49.663±0.038	0.010	20.13±0.21	−62.10±0.32	82.23±0.38
400.00	34.989±0.025	0.021	50.893±0.041	0.016	18.64±0.21	−62.59±0.34	81.23±0.40
420.00	34.524±0.031	0.033	52.123±0.046	0.025	17.33±0.22	−63.03±0.37	80.35±0.42
440.00	34.153±0.040	0.050	53.350±0.054	0.037	16.15±0.22	−63.42±0.39	79.58±0.45
460.00 [c]	33.860±0.052	0.070	54.569±0.064	0.051	15.10±0.23	−63.78±0.42	78.88±0.47
480.00 [c]	33.638±0.070	0.096	55.784±0.080	0.069	14.16±0.24	−64.10±0.44	78.26±0.49
500.00 [c]	33.472±0.091	0.128	56.991±0.098	0.089	13.30±0.25	−64.39±0.47	77.69±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 graphically extrapolated values of the liquid-phase heat capacities.

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

TABLE 12. Comparison of equilbrium constants for the quinoline/tetrahydroquinoline systems. The kinetic modelling values reported are those of reference 14.

Quinoline/5,6,7,8-tetrahydroquinoline

T/K	623		648		663	
Kinetic modelling	0.0046	0.0051	0.0016	0.0019	0.00092	0.0011
Equation 10 [a]	0.0049		0.0020		0.0012	

Quinoline/5,6,7,8-tetrahydroquinoline

T/K	623		648		663	
Kinetic modelling	0.014	0.013	0.0048	0.0045	0.0025	0.0025
Equation 11 [a]	0.027		0.010		0.0058	

[a] See text.

☆U.S. GOVERNMENT PRINTING OFFICE: 1989-661-023/00010