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The thermodynamic properties of 1,2,3,4- and 5,6,7,8-tetrahydroquinolines[a, b]

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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 standard 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 were used to determine equilibrium constants, and hence, equilibrium molalities, for the quinoline/hydrogen/tetrahydroquinoline reaction network at temperatures of interest in the processing of fossil-fuel feedstocks with a high nitrogen content. The results show 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. That equilibrium conditions exist between quinoline and 5,6,7,8-tetrahydroquinoline in processing is more equivocal; however, there is strong evidence for such an equilibrium.

1. Introduction

This laboratory has a research program, funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Extraction & Process Technology (AEPT), in

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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(5) and the five benzoquinolines(6) were the subject of earlier publications from this group. This paper provides 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 in which 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 information, 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 equilibrium 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.(7) Cocchetto and Satterfield(8) estimated the equilibrium constants for the hydrogenation reactions of quinoline using the group-additivity schemes of Benson(9) and van Krevelen and Chermin.(10) In a subsequent paper, Cocchetto and Satterfield(11) compared experimental equilibrium results with the estimated equilibrium constants; they showed that the estimates were crude, and were probably in error by at least two powers of ten for the quinoline + 1,2,3,4-tetrahydroquinoline) equilibrium.

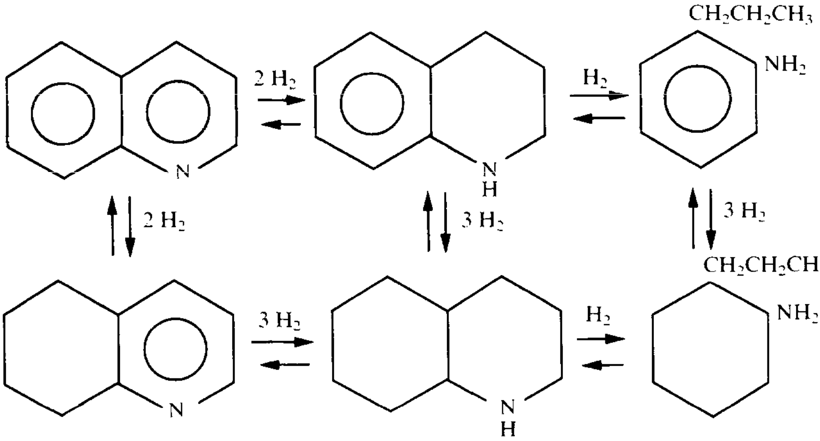

FIGURE 1. Initial steps in the hydrodenitrogenation of quinoline.

In this paper, equilibrium constants are derived and compared with the values determined experimentally by Satterfield and co-workers. In a later paper, Satterfield and Yang(12) developed a kinetic model for the HDN of quinoline using a modular approach. In the present paper, the ratios of their rate constants for the forward and reverse reactions between quinoline and the tetrahydroquinolines are compared with equilibrium constants determined from this research.

2. Experimental

Commercial samples of both tetrahydroquinolines were purified by Professor E. J. Eisenbraun and his research group at Oklahoma State University in the following manner. The original 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 $2\,\mathrm{mol\cdot dm^{-3}}$ KOH(aq). The liberated tetrahydroquinoline was extracted with ether, dried (Na_2CO_3), filtered, and concentrated. For the 1,2,3,4-isomer, the final purification step was double distillation at 328 K and 13 Pa. The corresponding conditions used in the final 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, followed by 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 vapor transfer through Linde 3A molecular sieves.

Molar values are reported in terms of $M = 133.1937\,\mathrm{g\cdot mol^{-1}}$ for the compounds, based on the relative atomic masses of 1969(13)† and the gas constant: $R = 8.31441\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, adopted by CODATA.(14) The platinum resistance thermometers used in these measurements were calibrated by comparison with standard thermometers whose constants were determined at the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards. All temperatures are reported in terms of the IPTS-68.(15) The platinum resistance thermometer used in the adiabatic heat-capacity studies was calibrated below 13.81 K using the method of McCrackin and Chang.(16) Measurements of mass, time, electric resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

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

The apparatus and experimental procedures used in the combustion calorimetry of organic nitrogen compounds at the National Institute for Petroleum and Energy Research (NIPER) have been described.(17–19) A rotating-bomb calorimeter (laboratory designation BMR II)(20) and platinum-lined bombs (laboratory designations Pt-3b and Pt-5)(21) with internal volumes of 0.393_4 and $0.393_0\ \mathrm{dm^3}$, respectively, were used without bomb 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, $1.0\ \mathrm{cm^3}$ of water was added to the bomb, and the bomb was flushed and charged to 3.04 MPa with pure oxygen. The sample and auxiliary masses were chosen to give the same temperature rise in each tetrahydroquinoline combustion series and corresponding calibration series to within 0.1 per cent. All experiments were completed within 0.01 K of 298.15 K.

Temperatures were measured by quartz-crystal thermometry.(22,23) 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.(24)

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(25) 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 did not form in the calibration experiments because high-purity oxygen was used in the preliminary bomb flushing and in charging the bomb. The energy equivalent of the calorimeter obtained for each calibration series ε(calor) was $(16747.4 \pm 0.4)\ \mathrm{J \cdot K^{-1}}$ (mean and standard deviation of the mean) for 1,2,3,4-tetrahydroquinoline and $(16784.3 \pm 0.4)\ \mathrm{J \cdot K^{-1}}$ for 5,6,7,8-tetrahydroquinoline measurements, respectively.

For the cotton fuse, empirical formula $\mathrm{CH_{1.774}O_{0.887}}$, $\Delta_c U^\circ_m/M$ was $-16945\ \mathrm{J \cdot g^{-1}}$. Auxiliary information necessary for reducing apparent mass to mass, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states,(25) included densities of $1030\ \mathrm{kg \cdot m^{-3}}$ and $990\ \mathrm{kg \cdot m^{-3}}$, and estimated values of $1.7\ \mathrm{m^3 \cdot K^{-1}}$ and $1.6\ \mathrm{m^3 \cdot K^{-1}}$ for $(\partial V_m/\partial T)_p$ for 1,2,3,4-tetrahydroquinoline and 5,6,7,8-tetrahydroquinoline at 298.15 K, 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 paper.

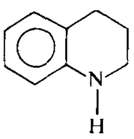
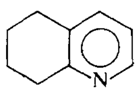
Nitric acid formed during the tetrahydroquinoline combustions was determined by titration with standard sodium hydroxide.(26) Carbon dioxide was also recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as absorbent.(19) The combustion products were checked for unburnt carbon and other products of incomplete combustion, but none was 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.

Heat-capacity and enthalpy measurements were made with a calorimetric system similar to that described by Huffman and his colleagues.(27–29) 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 platinum calorimetric vessels have been described.(30) The loading and the sealing procedures were the same as described for quinoline.(5) The calorimeters were sealed using a gold-gasketed screw-cap closure on the filling tube rather than the solder-seal method described by Huffman.(27) The characteristics of the calorimeters and sealing conditions are given in table 1.

The temperature-measurement system employed direct-current methods described previously.(27–29) Energy-measurement procedures were the same as those described for studies on quinoline.(5) Energies were measured to a precision of 0.01 per cent, and temperatures were measured to a precision of 0.0001 K. The energy increments to the filled calorimeters were corrected for enthalpy changes in the empty calorimeter, for the helium exchange gas, and for vaporization of the 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.

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

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 to that of the empty calorimeter, T_{max} is the highest temperature of the measurements, $(\delta C/C)_{max}$ is the maximum fractional 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

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 studied was 0.001 K. Uncertainties in the pressures were described adequately by the expression:

$$\sigma(p) = (0.001\ \mathrm{K})\{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_{\mathrm{x}}/\mathrm{d}T)^2\}^{1/2}, \qquad (1)$$

where p_{ref} is the vapor pressure of the reference substance and p_{x} is the vapor pressure of the sample under study. Values of $\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T$ for the reference substances were calculated from fits of the Antoine equation(34) to vapor pressures of the reference materials (benzene, decane, and water) listed in reference 33.

The equipment for the inclined-piston measurements was described by Douslin and McCollough,(35) and Douslin and Osborn.(36) Recent revisions to the equipment and procedures are given in reference 5. The low-pressure range of the inclined-piston measurements, 10 to 3500 Pa, necessitated diligent outgassing of the sample prior to its 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 ($< 1.0 \times 10^{-4}$ 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, were adequately described by the expression:

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

The uncertainties in the temperatures were 0.001 K.

3. Results

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 $\Delta_c U_m^\circ/M$ for all the experiments are reported in table 3. All values of $\Delta_c U_m^\circ/M$ in table 3 refer to the reaction:

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

Table 3 also gives derived values of the standard molar energy of combustion $\Delta_c U_m^\circ$, the standard molar enthalpy of combustion $\Delta_c H_m^\circ$, and the standard molar enthalpy of formation $\Delta_f H_m^\circ$ for the isomers. Values of $\Delta_c U_m^\circ$ and $\Delta_c H_m^\circ$ refer to reaction (3). The values of $\Delta_f H_m^\circ$ refer to reaction:

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

TABLE 2. Typical combustion experiment for the tetrahydroquinolines at 298.15 K ($p^\circ = 101.325$ 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
m(glass)/g	0.038524	0.031467
$\Delta T = (t_i - t_f + \Delta t_{\text{corr}})/\text{K}$	2.20605	2.00045
$\varepsilon(\text{calor})(\Delta T)/\text{J}$	−37027.0	−33502.3
$\varepsilon(\text{cont})(\Delta T)/\text{J}$[b]	−46.5	−39.9
$\Delta U_{\text{ign}}/\text{J}$	0.7_5	0.7_5
$\Delta U_{\text{dec}}(\text{HNO}_3)/\text{J}$	41.8	58.0
ΔU(corr. to std. states)/J[c]	17.7	16.7
$-m''(\Delta_c U_m^\circ/M)(\text{oil})/\text{J}$	2212.5	1886.8
$-m'''(\Delta_c U_m^\circ/M)(\text{fuse})/\text{J}$	23.2	27.9
$m'(\Delta_c U_m^\circ/M)(\text{compound})/\text{J}$	−34777.5	−31552.0
$(\Delta_c U_m^\circ/M)(\text{compound})/(\text{J}\cdot\text{g}^{-1})$	−38476.2	−38451.1

[a] The symbols and abbreviations of this table are those of reference 25 except as noted.

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

[c] Items 81 to 85, 87 to 90, 93, and 94 of the computational form of reference 25.

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

For the adiabatic heat-capacity studies, crystallization of 1,2,3,4-tetrahydroquinoline was initiated by slowly cooling (approximately 0.6 $\text{mK}\cdot\text{s}^{-1}$) the liquid sample 10 to 15 K below its triple-point temperature. Complete crystallization was

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					
$\{(\Delta_c U_m^\circ/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$					
−38476.2	−38479.0	−38475.1	−38475.0	−38475.4	−38475.4
$\langle\{(\Delta_c U_m^\circ/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})\rangle$	−38476.0 ± 0.6				
$\Delta_c U_m^\circ(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$	−5124.76 ± 0.66				
$\Delta_c H_m^\circ(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$	−5130.34 ± 0.66				
$\Delta_f H_m^\circ(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$	16.69 ± 0.80				
5,6,7,8-tetrahydroquinoline					
$\{(\Delta_c U_m^\circ/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$					
−38451.1	−38448.1	−38452.7	−38450.4	−38448.0	−38456.1
$\langle\{(\Delta_c U_m^\circ/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})\rangle$	−38451.1 ± 1.5				
$\Delta_c U_m^\circ(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$	−5121.44 ± 1.16				
$\Delta_c H_m^\circ(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$	−5127.04 ± 1.16				
$\Delta_f H_m^\circ(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$	13.39 ± 1.24				

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 0.3 $\mathrm{mK \cdot s^{-1}}$ to crystallize the remaining liquid. As a final step, the sample was thermally cycled between $T < 100$ 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 when cooled, and crystallized only when it was reheated above the glass-transition temperature near 160 K. The crystals formed initially were a metastable form with a triple-point temperature of 222.347 K. 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 one conversion was allowed to go to completion. In spite of many attempts, a reproducible method could not be found to convert the metastable to the stable form. Detection of the crystalline-form conversion was complicated by the presence of a nearby first-order phase transition near 210 K in the metastable form. No solid-state phase transformations were found for the stable form. There was evidence for a phase transition near 110 K in the metastable form, but confirming investigations were not attempted.

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 7 d 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 by temperature cycling as described above for the 1,2,3,4-tetrahydroquinoline crystals.

The triple-point temperatures T_{tp} and sample purities for 1,2,3,4-tetrahydroquinoline and the metastable crystalline form of 5,6,7,8-tetrahydroquinoline were

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	$T(F)/\mathrm{K}$	N[a]	F	$T(F)/\mathrm{K}$
	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
$T_{\mathrm{tp}}/\mathrm{K}$	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	$\frac{T_i}{\mathrm{K}}$	$\frac{T_f}{\mathrm{K}}$	$\frac{T_{trs}}{\mathrm{K}}$	$\frac{\Delta_{tot}H_m{}^c}{R \cdot \mathrm{K}}$	$\frac{\Delta_{trs}H_m{}^d}{R \cdot \mathrm{K}}$
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
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

TABLE 5—*continued*

N[a]	h[b]	T_i/K	T_f/K	$T_\mathrm{trs}/\mathrm{K}$	$\Delta_\mathrm{tot}H_\mathrm{m}/R\cdot\mathrm{K}$[c]	$\Delta_\mathrm{trs}H_\mathrm{m}/R\cdot\mathrm{K}$[d]
			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
			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)[h]			
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] $\Delta_\mathrm{tot}H_\mathrm{m}$ is the molar energy input from initial temperature T_i to final temperature T_f.

[d] $\Delta_\mathrm{trs}H_\mathrm{m}$ is the net molar enthalpy of transition at the transition temperature T_trs for phase changes, and is the difference from enthalpies calculated from smoothed heat capacities corrected for premelting for single-phase measurements.

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

[f] This result was obtained for a metastable crystalline form. See text.

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

[h] This phase transition was present only between the metastable crystalline forms. See text.

determined from measurements of the equilibrium melting temperatures $T(F)$ as a function of the 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 for either sample.

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. The triple-point temperature for the stable form is listed in table 4.

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 reproducible to within 0.01 per cent. Solid-state phase transformations were detected in the 1,2,3,4-tetrahydroquinoline sample near 232, 115, 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 rapidly on cooling. The transition enthalpies in table 5 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 the 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 complete 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 series were: series 10 (25 h), series 11 (75 h), and series 13 (150 h). In table 5 only the transition enthalpy for series 9 is discordant. Annealing beyond 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 and a corresponding fraction melted were determined in the partially liquid state. The

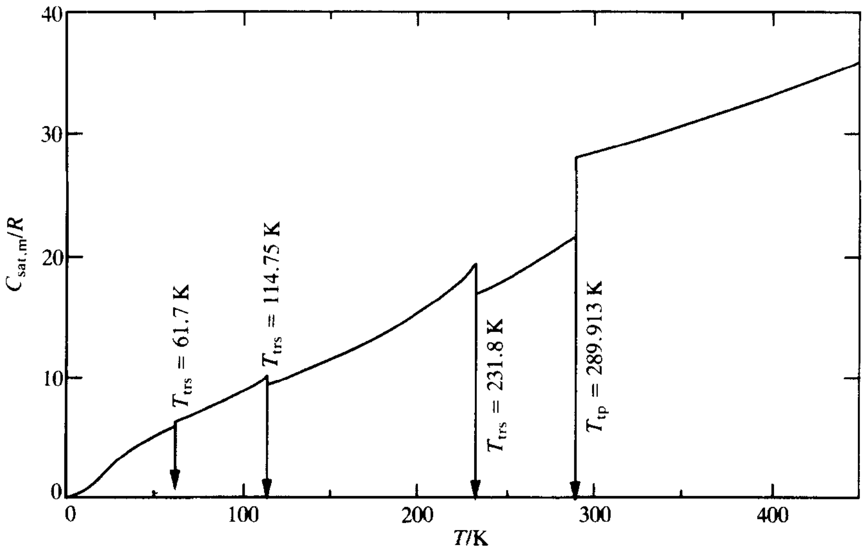


FIGURE 2. Heat capacity against temperature for 1,2,3,4-tetrahydroquinoline. The vertical lines indicate phase-transition temperatures.

triple-point temperature corresponding to each melting was derived. During measurements in the partially melted state for series 13 and 19, the sample warmed spontaneously, which indicated phase transformation. No analogous warming was observed during series 1, 11, or 21. The triple-point temperature for series 1 and 21 was 222.347 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 structures of the stable and metastable forms may be obtained from the difference between their entropies of fusion. The difference ($0.67R$) is near the value expected for two-position disorder, $0.69R$ (*i.e.* $R \cdot \ln 2$). Scenarios involving positional disorder of the nitrogen atom in the crystal can be formulated readily to account for such disorder. The disorder may arise from the 5,6,7,8-tetrahydroquinoline crystallizing only from the supercooled liquid near 160 K. At this temperature, reorientations, particularly those involving out-of-plate rotations, might 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 near 190 K was evidenced by spontaneous warming of the sample. Conversion accelerated over a period of several days. Prior to the series 12 measurements, the sample was tempered under adiabatic conditions near 193 K for 2 d. Although it was clear from the continued warming that conversion was

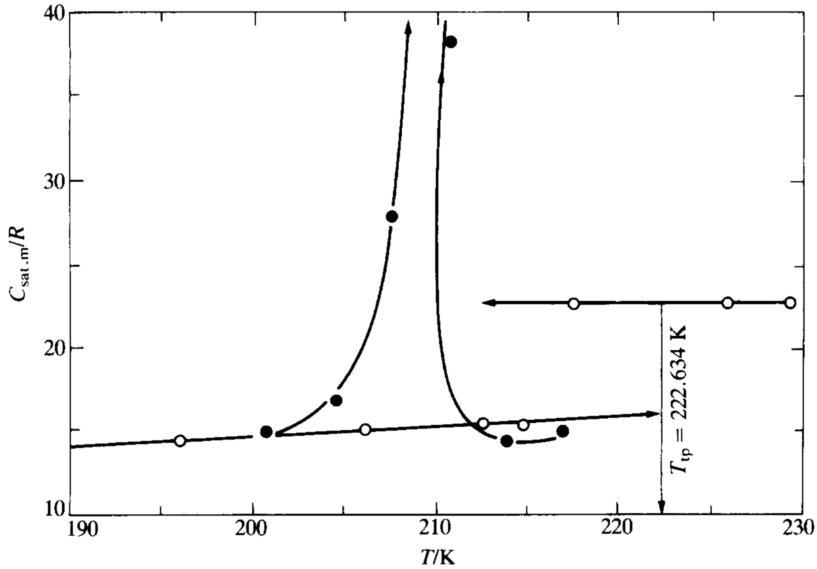


FIGURE 3. Heat capacity against temperature near the triple-point temperature for 5,6,7,8-tetrahydroquinoline. ○, Experimental results for the stable crystal and liquid phases; ●, series 13 results for the metastable crystalline form. The vertical line indicates the triple-point temperature. The curves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

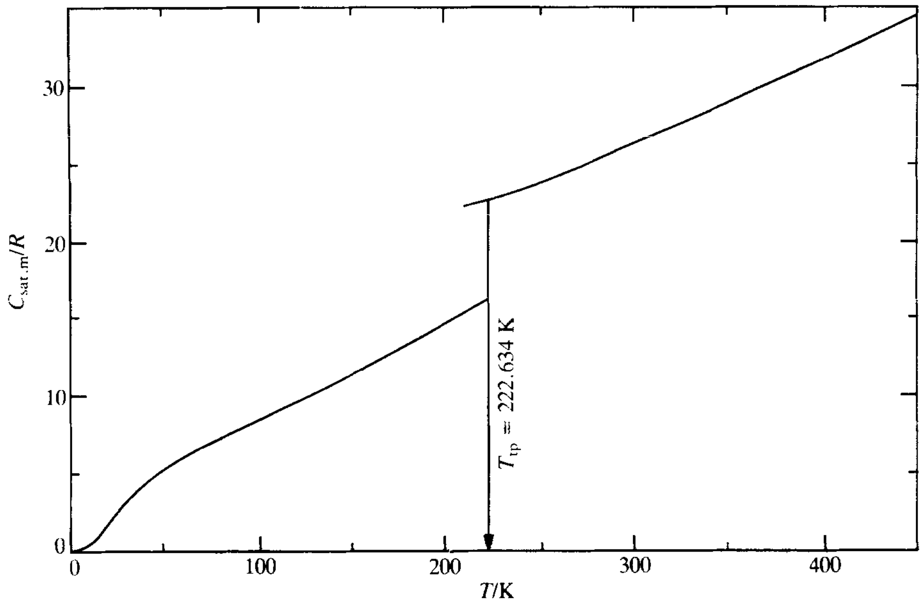


FIGURE 4. Heat capacity against temperature for 5,6,7,8-tetrahydroquinoline. The vertical line indicates the triple-point temperature.

incomplete after 2 d, the series 12 measurements were made, and a relatively small transition enthalpy (12.76 $R \cdot \mathrm{K}$) was measured. The crystals were not melted after series 12. Prior to series 13, the crystals were allowed to transform for approximately 10 d. The sample warmed from 192 to near 200 K during this period, and a large (172 $R \cdot \mathrm{K}$) transition enthalpy was measured subsequently. Immediately upon crossing the transition temperature during series 13, the sample began to warm again, which indicated 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 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 included in figure 3 show the transition between the metastable crystalline forms. The complete experimental curves of heat capacity against temperature for the liquid and stable crystal forms are shown in figure 4.

Prior to the attempt to convert the 5,6,7,8-tetrahydroquinoline crystals to the 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 near 209 K was measured. The extent of conversion of the crystals to the stable form was evidenced by the enthalpy-of-fusion value for series 19 being relatively close to that for the fully annealed stable crystals (see table 5).

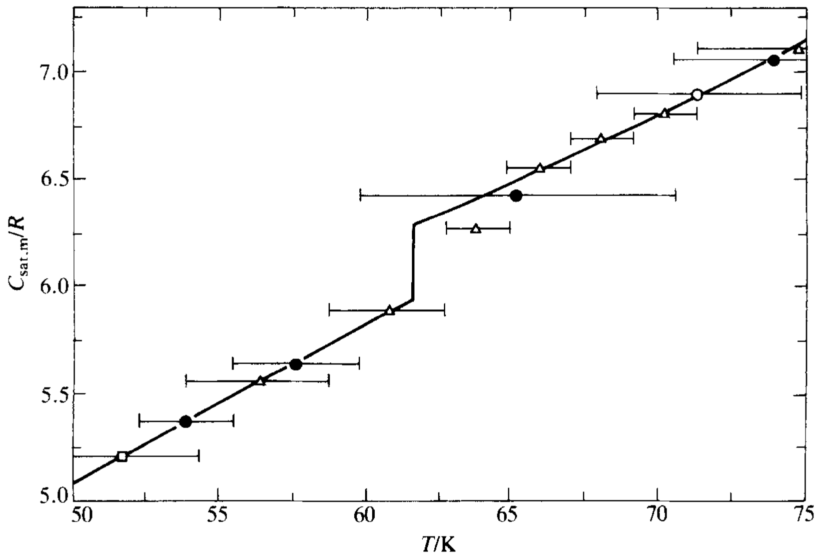


FIGURE 5. Experimental average heat capacities in the cr(IV)-to-cr(III) transition region for 1,2,3,4-tetrahydroquinoline. ○, Series 7; △, series 9; ●, series 11; □, series 12. The horizontal bars span the temperature increment associated with each average heat-capacity value. The heat-capacity curve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

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.

Equilibrium was reached in less than 1 h after each energy input during heat-capacity measurements for the liquid-phase of both compounds. 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 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 those from series 11. 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 are

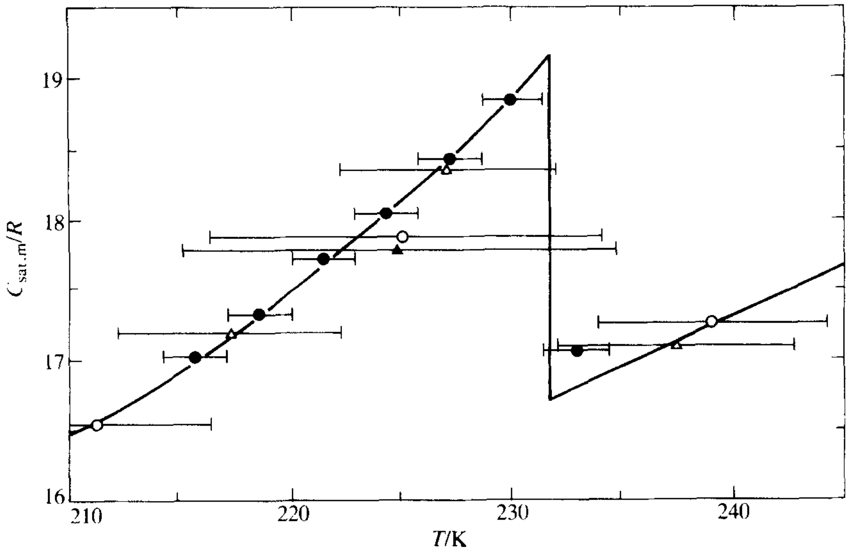


FIGURE 6. Experimental average heat capacities in the cr(II)-to-cr(I) transition region for 1,2,3,4-tetrahydroquinoline. △, Series 1; ●, series 5; ○, series 6; ▲, series 15. The horizontal bars span the temperature increment associated with each average heat-capacity value. The heat-capacity curve is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

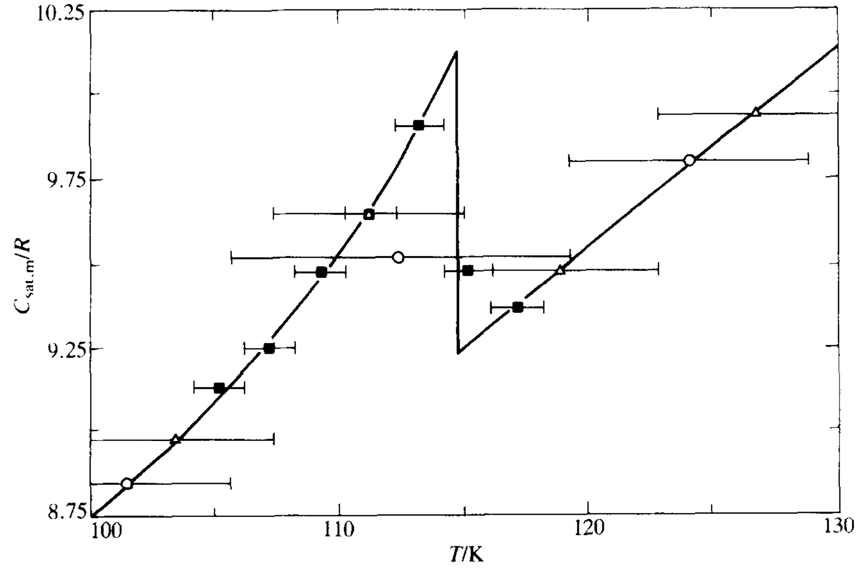


FIGURE 7. Experimental average heat capacities in the cr(III)-to-cr(II) transition region for 1,2,3,4-tetrahydroquinoline. △, Series 7; ○, series 8; ■, series 14. The horizontal bars span the temperature increment associated with each average heat-capacity value. The heat-capacity curve is described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

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

N^a	$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{\Delta T}{\mathrm{K}}$	$\frac{C_{\mathrm{sat,m}}}{R}^b$	N^a	$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{\Delta T}{\mathrm{K}}$	$\frac{C_{\mathrm{sat,m}}}{R}^b$
			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
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	315.191	9.3995	29.192
2	298.026	7.6232	28.383	16	325.005	10.2412	29.631
1	302.552	8.6236	28.584	16	336.111	11.9690	30.150
15	307.107	9.1207	28.817	16	348.003	11.8268	30.713

TABLE 6—*continued*

N^a	$\langle T\rangle/\mathrm{K}$	$\Delta T/\mathrm{K}$	$C_{\mathrm{sat,m}}{}^b/R$	N^a	$\langle T\rangle/\mathrm{K}$	$\Delta T/\mathrm{K}$	$C_{\mathrm{sat,m}}{}^b/R$
16	360.197	12.5873	31.291	16	409.281	12.0265	33.616
16	372.655	12.4404	31.864	16	420.789	11.0439	34.198
16	384.986	12.2988	32.454	16	431.739	10.9362	34.729
16	397.205	12.1600	33.032	16	441.322	8.3373	35.186
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
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				

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[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 ($R = 8.31441\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)

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							
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
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*

$\frac{T}{\mathrm{K}}$	$\frac{C_{\mathrm{sat,m}}}{R}$	$\frac{\Delta_0^T S_{\mathrm{m}}^{\circ}}{R}$	$\frac{\Delta_0^T H_{\mathrm{m}}^{\circ}}{RT}$	$\frac{T}{\mathrm{K}}$	$\frac{C_{\mathrm{sat,m}}}{R}$	$\frac{\Delta_0^T S_{\mathrm{m}}^{\circ}}{R}$	$\frac{\Delta_0^T H_{\mathrm{m}}^{\circ}}{RT}$
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
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.

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

The experimental molar heat capacities under vapor saturation pressure $C_{\mathrm{sat,m}}$ are listed in table 6. The differences between $C_{p,\mathrm{m}}$ and $C_{\mathrm{sat,m}}$ are 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 $C_{\mathrm{sat,m}}$ with temperature, except near phase-transition temperatures. The precision of the heat-capacity measurements ranged from approximately 5 per cent at 5 K to 2 per cent at 10 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 were not corrected for premelting, but the temperature increments are provided so that an independent calculation can be made.

TABLE 8. Summary of vapor-pressure results; IP refers to measurements performed with the inclined-piston gauge and water, decane, or benzene refers to the material 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 ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$) 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	$\frac{T}{\mathrm{K}}$	$\frac{p}{\mathrm{kPa}}$	$\frac{\Delta p}{\mathrm{kPa}}$	$\frac{\sigma(p)}{\mathrm{kPa}}$	$\frac{\Delta T}{\mathrm{K}}$
		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
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

TABLE 8—*continued*

Method	$\frac{T}{\mathrm{K}}$	$\frac{p}{\mathrm{kPa}}$	$\frac{\Delta p}{\mathrm{kPa}}$	$\frac{\sigma(p)}{\mathrm{kPa}}$	$\frac{\Delta T}{\mathrm{K}}$
		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
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.

Extrapolations to $T \rightarrow 0$ 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 fits for the 1,2,3,4- and 5,6,7,8-isomers, respectively. The corresponding Debye characteristic temperatures were $\Theta = 89.8$ K with 4.01 degrees of freedom, and $\Theta = 70.0$ K with 2.19 degrees of freedom, respectively.

Condensed-phase entropies and enthalpies relative to that of the crystals at $T \rightarrow 0$ for the solid and liquid phases under vapor saturation pressure are listed in table 7. These were derived by integration of the smoothed heat capacities corrected for premelting, 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 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.

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:

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

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. The fitting procedure has been described.(5, 33, 41) Parameters derived from the fits are given in table 9. Details of the Cox equation fits are given in table 8.

Enthalpies of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ were derived from the Cox equation fits using the Clapeyron equation:

$$\mathrm{d}p/\mathrm{d}T = \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}/(T\Delta_{\mathrm{l}}^{\mathrm{g}}V_{\mathrm{m}}), \tag{7}$$

TABLE 9. Cox equation coefficients

	1,2,3,4-Tetrahydroquinoline	5,6,7,8-Tetrahydroquinoline
$T_{\mathrm{ref}}/\mathrm{K}$	523.728	496.740
$p_{\mathrm{ref}}/\mathrm{kPa}$	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. Molar enthalpies of vaporization and entropies of compression obtained from the Cox and Clapeyron equations[a]
($R = 8.31441\ \mathrm{J \cdot K^{-1}\ mol^{-1}}$ and $p^\circ = 101.325$ kPa)

T/K	$\Delta_l^g H_m/(R \cdot K)$	$\Delta S_{comp,m}/R$	T/K	$\Delta_l^g H_m/(R \cdot K)$	$\Delta S_{comp,m}/R$
		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] $\Delta S_{comp}/R = \ln(p/p^\circ)$.

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

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.*,(42) and liquid-phase densities at 298.15 K of 1030 kg·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, and are estimated to be accurate to 3 per cent. Derived enthalpies of vaporization and entropies of compression are reported in table 10.

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, nitrogen, and graphite were determined from JANAF tables.(43) All uncertainties in table 11 represent one standard deviation and include the uncertainties for the elements given in the JANAF tables.

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

$\frac{T}{\mathrm{K}}$	$\frac{\Delta_0^T H_\mathrm{m}^\circ}{RT}$	$\frac{\Delta_\mathrm{imp} H_\mathrm{m}^\circ}{RT}$ [a]	$\frac{\Delta_0^T S_\mathrm{m}^\circ}{R}$	$\frac{\Delta_\mathrm{imp} S_\mathrm{m}^\circ}{R}$ [b]	$\frac{\Delta_\mathrm{f} H_\mathrm{m}^\circ}{RT}$	$\frac{\Delta_\mathrm{f} S_\mathrm{m}^\circ}{R}$	$\frac{\Delta_\mathrm{f} G_\mathrm{m}^\circ}{RT}$
			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
			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.

4. Discussion

No other experimental thermodynamic property measurements were found in the literature for either of the two tetrahydroquinoline isomers. Cocchetto and Satterfield(8) estimated the equilibrium constants for the hydrogenation reactions of quinoline using the group-additivity schemes of Benson(9) and van Krevelen and Chermin.(10) Cocchetto and Satterfield(8) stated that the equilibrium constants derived from the estimated standard free energies, "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(11) compared experimental equilibrium results (at hydrogen pressures of 3.55 and 7.0 MPa and temperatures of 603, 648, and 693 K) with those estimates and showed that the estimates were indeed probably in error by at least a factor of 100 for the (quinoline → 1,2,3,4-tetrahydroquinoline) equilibrium.

In figure 8(a), the experimental and estimated equilibrium constants for the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline, as given by Cocchetto and Satterfield (figure 6 of reference 11), are compared with values of the equilibrium constant obtained using the calorimetric measurements reported here. The pseudo-equilibrium constant K' is defined as $K' = K^\circ\{p_{(\mathrm{H_2})}/p^\circ\}$. Also plotted in figure 8(a) is the equilibrium constant obtained by Shih *et al.*(44) who approached the equilibrium from both the quinoline and the 1,2,3,4-tetrahydroquinoline sides of the reaction at

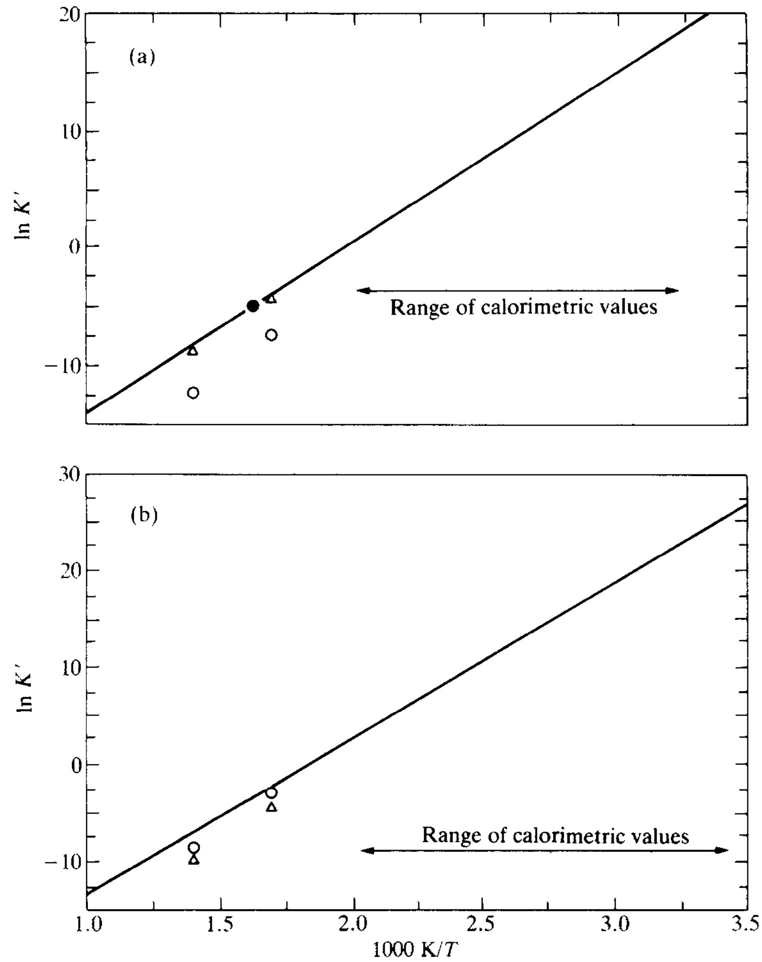

FIGURE 8. Plot of ln K' as a function of inverse temperature for the hydrogenation of quinoline to (a), 1,2,3,4-tetrahydroquinoline and (b), 5,6,7,8-tetrahydroquinoline: △, experimental (reference 11); ○, estimated (reference 11); ●, reference 44. The solid lines represent the functions calculated from the calorimetric results. The lines are an extrapolation in the region 1.0 to 2.0 on the x-axis. See text for definition of K'.

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 with temperature derived from the calorimetric measurements is:

$$\ln K' = 14530(\mathrm{K}/T) - 28.64. \tag{8}$$

In figure 8(b), the experimental and estimated equilibrium constants for the hydrogenation of quinoline to 5,6,7,8-tetrahydroquinoline, as given by Cocchetto and Satterfield (figure 6 of reference 11), are compared with values of the equilibrium constant obtained using the calorimetric measurements reported here. In this case the agreement is not as good; compare figures 8(a) and 8(b). The equation of the line representing the variation of the equilibrium constant with temperature derived from the calorimetric measurements is:

$$\ln K' = 15890(\mathrm{K}/T) - 29.12. \tag{9}$$

In later work on the kinetics of the hydrodenitrogenation of quinoline on a sulfided ($\mathrm{NiMo} + \mathrm{Al_2O_3}$) catalyst, Satterfield and Cocchetto(45) and Satterfield and Yang(12) derived kinetic parameters for models of the overall reaction scheme. Models were developed for both the vapor- and liquid-phase reactions. 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 *ortho*-propylaniline and the hydrogenation of 1,2,3,4-tetrahydroquinoline to decahydroquinoline. This implies that (1,2,3,4-tetrahydroquinoline + quinoline) reaches a pseudoequilibrium.

From the rate constants given in table 3 of reference 12, 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 (8) above. The agreement between the equilibrium constants from the kinetic modelling and those derived here using thermodynamic information is excellent.

TABLE 12. Comparison of equilibrium constants obtained in this research with those from kinetic-modelling studies reported in the literature

T		K°		
K	This research[a]	Satterfield and Yang(12)[b]		Giola and Lee(46)
		Quinoline/1,2,3,4-tetrahydroquinoline		
623	0.0049	0.0046	0.0051	0.0056
648	0.0020	0.0016	0.0019	
663	0.0012	0.00092	0.0011	
		Quinoline/5,6,7,8-tetrahydroquinoline		
623	0.027	0.014	0.013	
648	0.010	0.0048	0.0045	
663	0.0058	0.0025	0.0025	

[a] Calculated using equations (8) and (9).

[b] Satterfield and Yang(12) list two values for the equilibrium constant.

Calculations for the (quinoline → 5,6,7,8-tetrahydroquinoline) equilibria are also reported in table 12. In that case, the equilibrium constants from the kinetic modelling are half those calculated in this research from equation (9). Satterfield and Yang stated 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 tenfold smaller than the other rate constants and the inherent errors are quite large". Therefore, the lack of agreement may arise from an error in the value assigned to k_{10} in their kinetic modelling. Their value would need to be 50 per cent smaller to bring both sets of results into agreement.

Giola and Lee(46) also proposed a model for the kinetics of the HDN of quinoline. While they did not list an equilibrium constant for the (quinoline → 5,6,7,8-tetrahydroquinoline) equilibrium, they gave a value of 0.0056 for K for the (quinoline → 1,2,3,4-tetrahydroquinoline) equilibrium at 623 K. This is in excellent agreement, table 12, with the value obtained using equation (8).

Kinetic modelling of the HDN reaction for quinoline could be improved by using the results from the thermodynamic studies reported here. If the results obtained

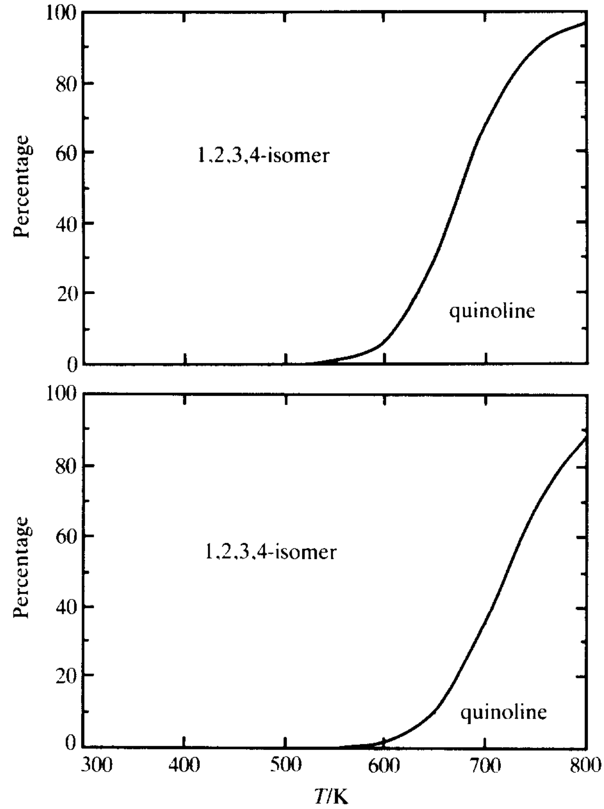

FIGURE 9. Relative percentages of quinoline and 1,2,3,4-tetrahydroquinoline at thermodynamic equilibrium in the gas phase at different temperatures. The upper chart is under a hydrogen pressure of 3.55 MPa, and the lower chart is for 7.0 MPa hydrogen pressure.

here were used to define the ratios of the forward and reverse reaction rate constants for the equilibria, the remaining rate constants could be determined with greater precision to provide further insights into their relative importance.

Figure 9 shows the relative amounts of quinoline and 1,2,3,4-tetrahydroquinoline at thermodynamic equilibrium in the ideal-gas phase as a function of temperature. The upper chart shows equilibrium quantities for 3.55 MPa hydrogen pressure, whereas the lower chart applies to 7.0 MPa hydrogen pressure. At 800 K and 7.0 MPa hydrogen pressure, approximately 90 per cent of the equilibrium mixture is quinoline. At this temperature doubling the hydrogen pressure has made changes in the equilibrium distribution which are barely perceptible in the charts. This shows that to remove nitrogen efficiently from polycyclic aromatic compounds, a catalyst which will function efficiently at relatively low temperatures (below 750 K) is needed.

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