THERMODYNAMIC PROPERTIES OF 9-METHYLCARBAZOLE AND
1,2,3,4-TETRAHYDRO-9-METHYLCARBAZOLE

Topical Report

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EXECUTIVE SUMMARY

Events in the Persian Gulf have highlighted yet again the fragility of the continuity of supplies of Arabian crude oil to U.S. refineries. Successive "oil crunches" have initiated discussion of ways to decrease the U.S.A.'s dependence on so valuable a resource from such a volatile area of the world. Political considerations, such as the possibility of a Americas Free Market encompassing the whole American continent (similar to the European Economic Community), could entail more extensive use of "local" oil supplies. However, much of the "local" supplies are classified as heavy petroleums; e.g., California Wilmington, Mexican Mayan, and Venezuelan Cerro Negro and Boscan. These heavy crudes each contain more heteroatoms (nitrogen in particular), more aromatics and less long-chain saturated hydrocarbons than Arabian light crude.

Even without the political considerations, the picture of crude oil refining in the U.S.A. has changed considerably in the last ten years. The world supply of petroleum crude and light petroleum crude in particular, continues to decline. The density and, hence, complexity of refinery feedstocks have increased markedly in the last decade. The average API gravity of the crude oil run to stills in the United States dropped from approximately 34.2 in 1978 to 32.0 in 1989. That drop in API gravity has been accompanied by an equivalent increase in the amount of petroleum coke exported by the United States. When the cost of the oil imported and the price obtained for the coke are compared, it accounts for approximately **one billion dollars of the trade balance deficit per year**. The need for new technological advances in the processing of heavy petroleum is evident.

Catalytic hydrodesulfurization (HDS) is a key step in upgrading processes for conversion of light petroleum to economically viable products. Due to the increased nitrogen content of heavy petroleums relative to light crudes, catalytic hydrodenitrogenation (HDN) is a key step in their refining. Present HDN technology can be summarized as being HDS technology but with a "much increased severity." Organic nitrogen is commonly removed via reaction at 300 to 400 °C and 50 to 150 atm. of hydrogen. Under these severe conditions, hydrogen is consumed not only in breaking carbon-nitrogen 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 such hydrotreating situations, while the amount theoretically required for selective heteroatom removal is only about 600 scf/bbl. Hence, the saving in expensive hydrogen could be enormous if a process for denitrogenation without saturation of the aromatic rings in the feedstock could be developed.

This research program, funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Extraction and Process Technology (AEPT), provides accurate experimental thermochemical and thermophysical properties for "key" organic nitrogen-containing compounds present in heavy petroleum feedstocks, and applies the experimental information to thermodynamic analyses of key HDN reaction networks

(e.g., quinoline/hydrogen, indole/hydrogen, and in this case carbazole/hydrogen). Thermodynamic analyses, based on accurate information, provide insights for the design of cost-effective methods of nitrogen removal.

Removal of carbazole and its derivatives from heavy petroleum has proved to be particularly difficult using present technology. Studies have shown carbazole and its alkyl-homologs are the dominant nitrogen-containing components in clarified slurry oils, thereby indicating their low reactivity and/or formation during cat-cracking processes. According to the results of some studies, carbazoles survive the various refining processes and end up in the finished products, which leads to gum formation and low thermal stability. The results reported here, and in a companion report to be completed in April 1991, will point the way to the development of new methods of nitrogen removal from carbazole and its derivatives.

This report details the thermodynamic properties of 9-methylcarbazole and 1,2,3,4-tetrahydro-9-methylcarbazole. The thermodynamic properties were measured using adiabatic heat-capacity calorimetry, differential-scanning calorimetry (d.s.c.), comparative ebulliometry, inclined-piston gauge manometry, and combustion calorimetry. Critical properties were estimated from thermodynamic principles. All measured properties were combined to derive Gibbs energies of formation for a range of temperatures. With these Gibbs energies, sufficient information is now available for a comprehensive thermodynamic analysis of the carbazole/hydrogen reaction network. This analysis will be published as the next topical report within this research program.

In addition to providing the concrete base for the upcoming thermodynamic analysis, the properties reported here are particularly useful to the process-design engineer. These results, in conjunction with values for other major nitrogen-containing compound types studied in this project, form a sound base for the development of process design correlations. Such correlations are necessary for the cost-effective, energy-efficient design of process equipment such as distillation towers, heat-exchangers, and gas-liquid reactors. A major risk associated with the lack of thermodynamic data is possible extensive derating of a plant because of undersized equipment. For example, if heat duties or vapor flow rates are underestimated during design, the installed equipment will be unable to accommodate the process streams at design flow rates resulting in less than economic operation of the plant.

ABSTRACT

Measurements leading to the calculation of the ideal-gas thermodynamic properties are reported for 9-methylcarbazole and 1,2,3,4-tetrahydro-9-methylcarbazole. For studies on 1,2,3,4-tetrahydro-9-methylcarbazole experimental methods included combustion calorimetry, adiabatic heat-capacity calorimetry, vibrating-tube densitometry, comparative ebulliometry, inclined-piston gauge manometry, and differential-scanning calorimetry (d.s.c.). Adiabatic heat-capacity and combustion calorimetric studies were reported previously for 9-methylcarbazole. Vapor pressures by comparative ebulliometry and inclined-piston gauge manometry, and heat-capacities for the liquid phase by d.s.c. are reported here. Entropies, enthalpies, and Gibbs energies of formation were derived for the ideal gas for both compounds for selected temperatures between 298.15 K and near 700 K. The Gibbs energies of formation will be used in a subsequent report in thermodynamic calculations to study the reaction pathway of the initial hydrogenation step in the carbazole/H₂ hydrodenitrogenation network.

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GLOSSARY

This report is written with close adherence to the style adopted by The Journal of Chemical Thermodynamics. A complete description of the style can be found in the January 1991 issue of the journal. This glossary summarizes the main points with respect to the symbol usage.

Throughout this report only SI units are used in reporting thermodynamic values. All values are given in dimensionless units i.e., physical quantity = number X unit; for example $\rho/(\text{kg}\cdot\text{m}^{-3})$ rather than " ρ (kg/m^3)" or " ρ kg/m^3 ". Molar values, i.e., intensive functions, are denoted by the subscript "m", e.g., $C_{\text{sat},m}$, whereas extensive functions do not have the subscript. In addition, since thermodynamic values are pressure dependent, they are reported in terms of a standard pressure p° , which in this report is 101.325 kPa (one atmosphere).

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

T = temperature in Kelvin

p = pressure in Pascals (Pa)

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

$\Delta_c U_m^\circ$ = molar energy of combustion

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

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

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

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

$\Delta_l^g V_m$ = change in molar volume from the liquid to the real vapor

$C_{v,m}$ = molar heat capacity at constant volume

$C_{p,m}$ = molar heat capacity at constant pressure

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

μ = chemical potential

n = number of moles of substance

V_x = volume of d.s.c. cell at a temperature T/K .

C_x^{II} = two-phase heat capacity at cell volume V_x

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

$C_v^{\text{II}}(p = p_{\text{sat}})$ = two-phase heat capacity along the saturation line

V_l = molar volume of the liquid

T_c = critical temperature

p_c = critical pressure

p_c = critical density

T_r = reduced temperature = T/T_c

p_r = reduced pressure = p/p_c

ρ_r = reduced density = ρ/p_c

$\lg$ = $\log_{10}$

ω = acentric factor = $[-\lg (p_x/p_c) - 1]$; p_x is the vapor pressure at $T_r = 0.7$

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

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

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

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

$T \rightarrow 0$ = Zero Kelvin

To avoid listing units in tables, entropies are reported as divided by the gas constant R , and enthalpies and Gibbs energies are generally reported divided by the product of the gas constant and temperature, $R \cdot T$. Units of time are s (seconds) or h (hours).

1. INTRODUCTION

In this research program, funded by the Department of Energy (DOE) Office of Fossil Energy, Advanced Extraction and Process Technology (AEPT), thermochemical and thermophysical properties are determined for "key" organic nitrogen-containing compounds present in heavy petroleum, shale oil, tar sands, and the products of the liquefaction of coal. Catalytic hydrodenitrogenation (HDN) is a key step in the upgrading of these feedstocks.⁽¹⁻⁴⁾§ They are typically rich in nitrogen, and their fractionation produces distillates that are also rich in nitrogen, thus giving poor-quality distillate fuels without denitrogenation.

Hydrodenitrogenation (HDN) reaction systems for aromatic compounds contain steps where the aromatic ring structures are hydrogenated. These reaction steps are all reversible within the temperature and pressure ranges of hydrogenation reactors used commercially. Therefore, a knowledge of the thermodynamic equilibria among the species is necessary for the proper interpretation of reaction data, for comparing different catalysts, and for accurate modelling of the overall reaction. In addition a knowledge of the thermophysical properties (vapor pressures, heat capacities, densities, etc.) is necessary for process-design engineering.

Oversaturation of rings is a common problem in the HDN of aromatic compounds. Therefore, to minimize consumption of expensive hydrogen in processing, the HDN pathway involving the most efficient use of hydrogen is sought. The problem of oversaturation in the HDN of aromatics is exacerbated as the number of rings increases. This research group has reported thermodynamic analyses of the indole/hydrogen⁽⁵⁾ and quinoline/hydrogen⁽⁶⁾ networks. This report is the second in a series that will lead to an analysis of a three-ring system; the carbazole/hydrogen HDN network. The thermodynamic properties of 2-aminobiphenyl were reported previously in NIPER-482.⁽⁷⁾

2-Aminobiphenyl is the first feasible hydrogenolysis (i.e., ring opened) product in the HDN network for carbazole. In NIPER-482 thermodynamic equilibria calculations showed that carbazole was less reactive for direct hydrogenolysis than either fluorene or dibenzofuran, two similarly structured compounds. That report also concluded that for the HDN of carbazole, the reaction pathway using the minimum of hydrogen (carbazole → 2-aminobiphenyl → biphenyl) probably cannot be realized.

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

However, the pathway (carbazole $\rightarrow$ 2-aminobiphenyl $\rightarrow$ 2-phenylcyclohexylamine $\rightarrow$ cyclohexylbenzene) should be possible with proper catalyst selection.

If hydrogenolysis is preceded by ring saturation, the initial stable compound formed in the HDN of carbazole is 1,2,3,4-tetrahydrocarbazole, which may then undergo further hydrogenation and hydrogenolysis to form 2-cyclohexylaniline. This HDN reaction pathway consumes **four moles** of hydrogen to reach the same stage on the pathway to nitrogen removal (i.e., one of the two C-N bonds broken) as that reached using the **one mole** to form 2-aminobiphenyl. Figure 1 shows the initial steps in the two pathways.

FIGURE 1. Initial pathways in the hydrodenitrogenation of carbazole.

Calculations of the thermodynamic equilibria obtained as the HDN reaction follows the ring saturation/hydrogenolysis pathway require a knowledge of the Gibbs energies of formation of carbazole and its hydrogenation products. Due to its high melting point (521 K), direct thermodynamic-property measurements on carbazole are not possible using the available equipment at NIPER. However, with measurements on a suitably chosen substituted carbazole derivative, the necessary properties for the parent compound can be estimated *reliably* with the methods of group additivity.⁽⁸⁾ Substitution of a methyl group on the 9 position (i.e., the nitrogen atom) provides an ideal derivative for both measurements and subsequent reliable group-additivity estimates on the parent compound. In this report, measurements leading to the thermodynamic properties of 9-methylcarbazole and its initial stable hydrogenation

product, 1,2,3,4-tetrahydro-9-methylcarbazole, are described. The compounds are shown in figure 2.

FIGURE 2. Compounds studied in this research.

2. EXPERIMENTAL

MATERIALS

The synthesis route for 1,2,3,4-tetrahydro-9-methylcarbazole is shown in figure 3. A mixture of 1.1 mol of cyclohexanone and 6.6 mol of acetic acid contained in a 2 dm³, three-necked flask equipped with a reflux condenser, magnetic stirrer, and addition funnel was stirred and heated under reflux. To this hot solution, 1.1 mol of 1-methyl-1-phenylhydrazine was added during 1 h. The mixture was refluxed for an additional hour and then poured into an ice-water mixture. The precipitated solid was filtered and washed with water. The crude dark-brown solid was air dried to give 198 g (97 per cent yield). It was Soxhlet-extracted through a bed of neutral and basic alumina with petroleum ether to give 152 g of 1,2,3,4-tetrahydro-9-methylcarbazole (76 per cent yield). Purification was accomplished through formation of the picrate derivative, its recrystallization from methanol, and subsequent cleavage by extraction through basic alumina using *n*-hexane.

FIGURE 3. Synthesis route to 1,2,3,4-tetrahydro-9-methylcarbazole;

^a Acetic acid, Δ .

The mole-fraction impurities for 1,2,3,4-tetrahydro-9-methylcarbazole were estimated by g.l.c. to be 0.0007. The mole-fraction impurities of the calorimetric sample were found to be slightly higher in fractional-melting studies completed as part of the adiabatic heat-capacity studies. The mole-fraction of impurities determined in the fractional-melting studies was 0.0015. This higher impurity value is believed to be more reliable than the g.l.c. result.

Previously reported calorimetric studies on 9-methylcarbazole performed at this laboratory^(9,10) were completed on samples prepared as part of American Petroleum Institute (API) Project 52. The 9-methylcarbazole samples used in the research reported here were synthesized by the route shown in figure 4. For step "a," cyclohexanone (1.5 mol) and acetic acid (9 mol) were combined and heated to reflux as described above. Phenylhydrazine (1.5 mol) was added dropwise to this hot solution. After 1 h of additional reflux, the product was allowed to crystallize and was filtered. The solid product was washed with water and ethanol. The crude 1,2,3,4-tetrahydrocarbazole was recrystallized from methanol, and a total of 173 g was recovered (67 per cent yield).

Step "b" in figure 4 was accomplished by treating the purified 1,2,3,4-tetrahydrocarbazole with 10 g of 5 per cent Pd/C catalyst in 0.5 dm³ of refluxing 1,2,4-trimethylbenzene. After 3 h, 2 g of catalyst were added and reflux was continued for four additional hours. The reaction was cooled and 1.5 dm³ of acetone was added to dissolve carbazole, and the catalyst was removed by filtration. Acetone was distilled, petroleum ether (boiling range 311 K to 316 K) was added, and solid carbazole was filtered as a colorless solid.

Step "c" of figure 4 was performed by dissolution of the carbazole (1.08 mol) in 0.9 dm³ acetone and dimethylsulfate (1.92 mol) was added in one portion. A solution of sodium hydroxide (4.5 mol) in water (0.12 dm³) was added dropwise over 0.3 h to the stirred mixture. After 2 h of stirring, the reflux product mixture was cooled and poured into an ice-water mixture. Crude 9-methylcarbazole precipitated (1.08 mol). Purification was accomplished by Soxhlet extraction through basic alumina with petroleum ether (boiling range 318 K to 323 K). Crystallization from petroleum ether gave 0.8 mol of 9-methylcarbazole. Analysis of the purified 9-methylcarbazole by g.l.c. showed the mole fraction impurities to be less than 0.0001. The high purity of the sample was corroborated by the small differences between the boiling and condensation temperatures observed in the ebulliometric vapor-pressure studies.

FIGURE 4. Synthesis route to 9-methylcarbazole:

^a Acetic acid, Δ ; ^b Pd/C, 1,2,4-trimethylbenzene, Δ ; ^c Dimethylsulfate, aq. NaOH, acetone, Δ .

The water used as a reference material in the ebulliometric vapor-pressure measurements was deionized and distilled from potassium permanganate. The decane used as a reference material for the ebulliometric measurements was purified by urea complexation, two recrystallizations of the complex, its decomposition with water, extraction with ether, drying with MgSO_4 , and distillation at 337 K and 1 kPa pressure.

PHYSICAL CONSTANTS AND STANDARDS

Molar values are reported in terms of $M = 185.269 \text{ g}\cdot\text{mol}^{-1}$ and $181.237 \text{ g}\cdot\text{mol}^{-1}$ for 1,2,3,4-tetrahydro-9-methylcarbazole and 9-methylcarbazole, respectively, based on the relative atomic masses of 1981⁽¹¹⁾† and the gas constant $R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ adopted by CODATA.⁽¹²⁾ The platinum resistance thermometers used in these measurements were calibrated by comparison with standard thermometers whose constants were determined at the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS). All temperatures reported are in terms of the IPTS-68.⁽¹³⁾ The platinum resistance thermometer used in the adiabatic heat-capacity studies was calibrated below 13.81 K with the method of

† The 1981 relative atomic masses were used because the CODATA Recommended Key Values for Thermodynamics (reference 36) are based on them.

McCrackin and Chang.⁽¹⁴⁾ Measurements of mass, time, electrical resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

APPARATUS AND PROCEDURES

Combustion Calorimetry. The experimental procedures used in the combustion calorimetry of organic nitrogen compounds at the National Institute for Petroleum and Energy Research have been described.⁽¹⁵⁻¹⁷⁾ A rotating-bomb calorimeter (laboratory designation BMR II)⁽¹⁸⁾ and platinum-lined bomb (laboratory designation Pt-3b)⁽¹⁹⁾ with an internal volume of 0.3934 dm³ were used without rotation.

Temperatures were measured by quartz-crystal thermometry.^(20,21) 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.⁽²²⁾

Densitometry. The densitometry apparatus and measurement procedures employed have been described.⁽²³⁾

Ebulliometric Vapor-Pressure Measurements. The essential features of the ebulliometric equipment and procedures are described in the literature.^(24,25) 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 with the condensation temperature of the standard.⁽²⁶⁾

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

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

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 dp_{ref}/dT for the reference substances were calculated from fits of the Antoine equation⁽²⁷⁾ to vapor pressures of the reference materials (decane and water) reported in reference 26.

Inclined-Piston Vapor-Pressure Measurements. The equipment for the inclined-piston vapor-pressure measurements has been described by Douslin and McCullough,⁽²⁸⁾ and Douslin and Osborn.⁽²⁹⁾ Recent revisions to the equipment and procedures have been

reported.⁽²³⁾ Uncertainties in the pressures determined with the inclined-piston apparatus, on the basis of estimated precision of measuring the mass, area, and angle of inclination of the piston, are adequately described by the expression:

$$\sigma(p) = 1.5 \times 10^{-4} p + 0.2 \text{ Pa.} \quad (2)$$

The uncertainties in the temperatures are 0.001 K.

Adiabatic Heat-Capacity Calorimetry. Adiabatic heat-capacity and enthalpy measurements were made with a calorimetric system described previously.⁽²³⁾ The calorimeter characteristics and sealing conditions are given in table 1.[†] Energy measurement procedures were the same as those described for studies on quinoline.⁽²³⁾ Thermometer resistances were measured with self-balancing, alternating-current resistance bridges (H. Tinsley & Co. Ltd.; Models 5840C and 5840D). Energies were measured to a precision of 0.01 per cent, and temperatures were measured to a precision of 0.0001 K. The energy increments to the filled platinum calorimeter 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 0.1 per cent near 5 K. The sizes of the other two corrections are indicated in table 1.

Differential-Scanning Calorimetry (d.s.c.). Differential-scanning calorimetric measurements were made with a Perkin-Elmer DSC-2. Experimental methods were described previously.⁽³⁰⁻³²⁾

3. RESULTS

COMBUSTION CALORIMETRY

NBS benzoic acid (sample 39i) was used for calibration of the combustion bomb calorimeter; its specific energy of combustion is $-(26434.0 \pm 3.0) \text{ J} \cdot \text{g}^{-1}$ under certificate conditions. Conversion to standard states⁽³³⁾ gives $-(26413.7 \pm 3.0) \text{ J} \cdot \text{g}^{-1}$ for $\Delta_c U_m^0/M$, the specific energy of the idealized combustion reaction. Calibration experiments were interspersed with the 1,2,3,4-tetrahydro-9-methylcarbazole 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 the calibration series, $\epsilon(\text{calor})$, was

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

(16641.6±0.7) J·K⁻¹ (mean and standard deviation of the mean). For the cotton fuse, empirical formula CH_{1.774}O_{0.887}, $\Delta_c U_m^0/M$ was -16945 J·g⁻¹.

1,2,3,4-Tetrahydro-9-methylcarbazole was burned in the form of pellets. For each experiment 1.0 x 10⁻³ dm³ of water was added to the bomb, and the bomb was flushed and charged to 3.04 MPa with pure oxygen. Judicious choice of sample and auxiliary masses allowed the temperature rise in each combustion series and its corresponding calibration series to be the same within 0.1 per cent. All experiments were completed within 0.01 K of 298.15 K.

Auxiliary information, necessary for reducing apparent masses to masses, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states,⁽³³⁾ included a density at 298.15 K of 1120 kg·m⁻³ and an estimated value of 5 x 10⁻⁷ m³·K⁻¹ for ($\partial V_m/\partial T$)_p for 1,2,3,4-tetrahydro-9-methylcarbazole. The density was obtained by weighing a pellet of known volume. The molar heat capacity at 298.15 K for 1,2,3,4-tetrahydro-9-methylcarbazole used in the corrections to standard states is given as part of the heat-capacity study results later in this report.

Nitric acid formed during the 1,2,3,4-tetrahydro-9-methylcarbazole combustions was determined by titration with standard sodium hydroxide.⁽³⁴⁾ Carbon dioxide was also recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as absorbent.⁽¹⁶⁾ The combustion products were checked for unburned carbon and other products of incomplete combustion, but none were detected. Carbon dioxide percentage recoveries were 100.001±0.009 (mean and standard deviation of the mean) for the calibrations and 99.995±0.015 for the corresponding 1,2,3,4-tetrahydro-9-methylcarbazole combustions.

A typical combustion experiment for 1,2,3,4-tetrahydro-9-methylcarbazole is summarized in table 2. It is impractical to list summaries for each combustion, but values of $\Delta_c U_m^0/M$ for all the experiments are reported in table 3. All values of $\Delta_c U_m^0/M$ in table 3 refer to the reaction:

Table 3 also gives derived values of the standard molar energy of combustion $\Delta_c U_m^0$, the standard molar enthalpy of combustion $\Delta_c H_m^0$, and the standard molar enthalpy of formation $\Delta_f H_m^0$ for 1,2,3,4-tetrahydro-9-methylcarbazole. Values of $\Delta_c U_m^0$ and $\Delta_c H_m^0$ refer to reaction 3. The values of $\Delta_f H_m^0$ refer to reaction 4:

Uncertainties given in table 3 are the "uncertainty interval" defined in reference 35. The enthalpies of formation of CO₂(g) and H₂O(l) were taken to be $-(393.51 \pm 0.13)$ and $-(285.830 \pm 0.042)$ kJ·mol⁻¹, respectively, as assigned by CODATA.⁽³⁶⁾

DENSITY MEASUREMENTS

Measured densities for 1,2,3,4-tetrahydro-9-methylcarbazole in the liquid phase (temperature range 348 K to 424 K) are listed in table 4. The temperatures are accurate to 0.001 K. The densitometer cell manufacturer claims that the accuracy of densities measured with the cell ranges from 0.1 kg·m⁻³ for densities within ± 500 kg·m⁻³ of the standard to 0.01 kg·m⁻³ for densities within ± 100 kg·m⁻³ of the standard. With the exception of H₂O and possibly D₂O, densities of fluids are not known with sufficient accuracy above 373 K to justify the claimed uncertainties. Water was used as the standard for all measurements. The difference in density between water and 1,2,3,4-tetrahydro-9-methylcarbazole ranged from 61 kg·m⁻³ at 347.9 K to 66 kg·m⁻³ at 423.7 K. Therefore, the expected accuracy of the 1,2,3,4-tetrahydro-9-methylcarbazole densities is 0.01 kg·m⁻³.

VAPOR-PRESSURE MEASUREMENTS

Vapor pressures for 9-methylcarbazole and 1,2,3,4-tetrahydro-9-methylcarbazole are reported in table 5. Following previous practice,⁽²⁵⁾ 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 ΔT for the samples are reported. For both 9-methylcarbazole and 1,2,3,4-tetrahydro-9-methylcarbazole the small differences between the boiling and condensation temperatures (column 6 table 5) indicated correct operation of the equipment and the high purity of the samples. At the highest temperatures measured for each sample, the large increase in ΔT relative to that for the previous temperature is indicative of sample decomposition.

Cox Equation Fits to Vapor Pressures. The Cox equation⁽³⁷⁾ in the form:

$$\ln(p/p_{\text{ref}}) = \{1 - (T_{\text{ref}}/T)\} \exp\{A + B(T/K) + C(T/K)^2\}, \quad (5)$$

was fitted to the experimental vapor pressures with fixed p_{ref} and T_{ref} values listed in table 6. The values of p_{ref} and T_{ref} used were the respective p_c and T_c obtained in the simultaneous fittings of the vapor pressures and the d.s.c. two-phase heat capacities discussed later in this report. The vapor-pressure fitting procedure has been

described.^(23,26) Parameters derived from the fits are given in table 6. Details of the Cox equation fits are given in table 5.

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

$$dp/dT = \Delta_l^g H_m / (T \Delta_l^g V_m). \quad (6)$$

$\Delta_l^g V_m$ is the increase in molar volume from the liquid to the real vapor. The Cox equation fits were employed to derive dp/dT . Estimates of liquid-phase volumes were made with the extended corresponding-states equation of Riedel,⁽³⁸⁾ as formulated by Hales and Townsend:⁽³⁹⁾

$$(\rho/\rho_c) = 1.0 + 0.85\{1.0 - (T/T_c)\} + (1.692 + 0.986\omega)\{1.0 - (T/T_c)\}^{1/3}, \quad (7)$$

with $\rho_c = 317 \text{ kg}\cdot\text{m}^{-3}$, $T_c = 890 \text{ K}$, and an acentric factor $\omega = 0.473$ for 9-methylcarbazole. For 1,2,3,4-tetrahydro-9-methylcarbazole, values of $\rho_c = 309 \text{ kg}\cdot\text{m}^{-3}$, $T_c = 854 \text{ K}$, and an acentric factor $\omega = 0.521$ were used. [The acentric factor is defined as $\{-\lg(p/p_c) - 1\}$, where p is the vapor pressure at $T_r = 0.7$ and p_c is the critical pressure.] The Cox equation coefficients given in table 6 were used to calculate p . The critical densities were estimates. The uncertainty in the liquid-phase volumes was estimated to be 3 per cent. [For 1,2,3,4-tetrahydro-9-methylcarbazole in the temperature range 347 K to 424 K, a comparison of values calculated using equation (7) with the densities measured experimentally is given in column 3 of table 4. The agreement is excellent.] Vapor-phase volumes were calculated with the virial equation of state truncated at the third virial coefficient. Second virial coefficients were estimated with the corresponding-states equation of Pitzer and Curl,⁽⁴⁰⁾ and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera.⁽⁴¹⁾ This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene, toluene, and decane.⁽⁴²⁾ Third virial coefficients are required for accurate calculation of the gas volume for pressures greater than 1 bar. Uncertainties in the virial coefficients are assumed to be 10 per cent. Derived enthalpies of vaporization are reported in table 6. For $p > 1$ bar the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived enthalpies of vaporization.

ADIABATIC HEAT-CAPACITY CALORIMETRY

Crystallization and Melting Studies. Crystallization of 1,2,3,4-tetrahydro-9-methylcarbazole was initiated by slowly cooling (approximately $2.5 \text{ mK}\cdot\text{s}^{-1}$) the liquid sample roughly 5 K below the triple-point temperature. Complete crystallization was ensured by maintaining the sample under adiabatic conditions in the partially melted state (10 to 20 per cent liquid) for approximately 8 h. No spontaneous warming, which would indicate incomplete crystallization, was observed in this time period. The sample was cooled at an effective rate of $2 \text{ mK}\cdot\text{s}^{-1}$ to crystallize the remaining liquid. Finally, the sample was thermally cycled from $<100 \text{ K}$ to within 2 K of the triple-point temperature, where it was held for a minimum of 6 h to provide further tempering. All of the solid-phase measurements were performed upon crystals pre-treated in this manner.

The triple-point temperature T_{tp} and sample purity were determined by measurement of the equilibrium melting temperatures $T(F)$ as a function of fraction F of the sample in the liquid state.⁽⁴³⁾ Equilibrium melting temperatures were determined by measuring temperatures at approximately 300-s intervals for 0.8 to 1.2 h after an energy input and extrapolating to infinite time by assuming an exponential decay toward the equilibrium value. The observed temperatures at 1 h after an energy input were invariably within 3 mK of the calculated equilibrium temperatures for F values listed in table 8. The results indicated the presence of solid-soluble impurities, and published procedures⁽⁴⁴⁾ were used to derive the apparent mole fraction of impurities, triple-point temperature, and effective distribution coefficient for the impurities between the two phases. The results are summarized in table 8.

Phase Transformations and Enthalpy Measurements. Experimental molar enthalpy results are summarized in table 9. 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 9 and 10 were taken without interruption of adiabatic conditions.

Excellent reproducibility (within ± 0.02 per cent) was obtained in the enthalpy-of-fusion results. This implies that phase $cr(l)$ was formed reproducibly by means of the tempering methods described above. The sample showed four solid phases with a lambda transition near 210.4 K, a first-order transition near 162.4 K, and a heat-capacity "step" near 103.8 K. The complete heat-capacity curve is shown in figure 5.

Conversion of phase cr(I) to phase cr(II) was achieved easily by cooling. Excellent reproducibility was obtained in the enthalpy-of-transition results. Details of measurements made and subsequently derived heat-capacity for the cr(II)-to-cr(I) phase-change region are shown in figure 6. The heat-capacity curve shown in this and other figures is consistent with the measurement results. The shape of the curve is not defined uniquely very near T_{trs} for each transformation. However, this uncertainty does not have a significant effect on the uncertainty of the derived thermodynamic functions.

Conversion of phase cr(II) to phase cr(III) required approximately 3 d of annealing near 160 K. Prior to measurements of the transition enthalpy, the sample was annealed between 158 K and 162 K for 80, 160, and 240 h for series 8, 9, and 20, respectively. An estimate of T_{trs} was obtained as part of the series-20 measurements by adding sufficient energy to convert 85 per cent of the sample from phase cr(III) to phase cr(II) and allowing the sample to approach equilibrium over a period of 2 days. At the end of this period the sample had not equilibrated completely, but an estimate of T_{trs} , (162.4 ± 0.2) K, could be made. The uncertainty in T_{trs} has no significant effect on the precision of the derived thermodynamic functions. Details of measurements made in the cr(III)-to-cr(II) phase-change region are shown in figure 7.

Conversion of phase cr(III) to phase cr(IV) required approximately 2 d of annealing near 103 K. Prior to measurements of the transition enthalpy, the sample was annealed between 100 K and 103 K for 45, 80, and 60 h for series 14, 19, and 20, respectively. The sample was annealed for 1 h only for series 11 and 12, which accounts for the low transition enthalpies measured for these series. Details of measurements made in the cr(IV)-to-cr(III) phase-change region are shown in figure 8.

Heat Capacity Measurements. The experimental molar heat capacities under vapor saturation pressure $C_{sat,m}$ determined by adiabatic calorimetry are listed in table 10. Values in table 10 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 near the solid-phase transition temperature. The precision of the heat-capacity measurements ranged from approximately 5 per cent at 5 K, to 2 per cent at 11 K, 0.2 per cent near 20 K, and improved gradually to less than 0.1 per cent above 100 K, except in the solid phase near the triple-point and solid-phase transition temperatures where equilibration times were long. The heat capacities for the crystal-phase in table 10 have not been

FIGURE 5. Heat capacity against temperature for 1,2,3,4-tetrahydro-9-methylcarbazole. The vertical lines indicate phase-transition temperatures. The upward-pointing arrows indicate first-order phase transitions.

FIGURE 6. Average heat capacities in the cr(II)-to-cr(I) transition region for 1,2,3,4-tetrahydro-9-methylcarbazole. $\square$, Series 3; $\bullet$, series 6; $\circ$, series 7; $\triangle$, series 20.

FIGURE 7. Average heat capacities in the cr(III)-to-cr(II) transition region for 1,2,3,4-tetrahydro-9-methylcarbazole. $\square$, Series 3; $\blacktriangle$, series 8; $\circ$, series 9; $\triangle$, series 13; $\bullet$, series 20. Results of measurements spanning T_{trs} (series 8, series 9, and series 20) are not shown. These are listed in table 9. The horizontal bars span the temperature increment associated with each average heat-capacity value. The heat-capacity curve is not defined uniquely between 162 K and 167 K. See text.

FIGURE 8. Average heat capacities in the cr(IV)-to-cr(III) transition region for 1,2,3,4-tetrahydro-9-methylcarbazole. $\blacktriangle$, Series 11; $\circ$, series 12; $\triangle$, series 14; $\square$, series 18; $\blacksquare$, series 19; $\bullet$, series 20. Results of measurements spanning T_{trs} for series 11 and series 12 are not shown, but are included in table 10. These were not included in the calculation of the transition enthalpy. The horizontal bars span the temperature increment associated with each average heat-capacity value. The heat-capacity curve is not defined uniquely between 103 K and 105 K. See text.

corrected for pre-melting. Pre-melting corrections⁽⁴³⁾ can be calculated with the temperature increments provided.

For heat-capacity measurements in the liquid phase, equilibrium was reached in less than 1 h. Equilibration times for phase cr(IV) were less than 1 h for all temperatures below 103 K. Equilibration times in the vicinity of the cr(IV)-to-cr(III) transition temperature (roughly 103 K to 106 K) were approximately 12 h. For phase cr(III), equilibration times were less than 1 h between 106 K and 150 K, and increased to 2 h at 155 K, 12 h at 160 K, and >48 h at 164 K. For phase cr(II), equilibration times were less than 1 h for all temperatures. Equilibration times for phase cr(I) were less than 1 h for all temperatures less than 290 K, and increased to 2 h at 300 K, 5 h at 320 K. Extrapolation of the heat-capacity results to $T \rightarrow 0$ was made by linear extrapolation of a plot of $C_{\text{sat},m}/T$ against temperature squared for results below 10 K.

DIFFERENTIAL SCANNING CALORIMETRY

Theoretical Background. The theoretical background for the determination of heat capacities for the liquid phase at vapor-saturation pressure $C_{\text{sat},m}$ with results obtained with a d.s.c. has been described.^(31,45) If two phases are present and the liquid is a pure substance, then the vapor pressure p and the chemical potential μ are independent of the amount of substance n and the cell volume V_x , and are equal to p_{sat} and μ_{sat} . The two-phase heat capacities at cell volume V_x , $C_{x,m}^{\text{II}}$, can be expressed in terms of the temperature derivatives of these quantities:

$$nC_{x,m}^{\text{II}}/T = -n(\partial^2\mu/\partial T^2)_{\text{sat}} + V_x(\partial^2 p/\partial T^2)_{\text{sat}} + (\partial V_x/\partial T)_x(\partial p/\partial T)_{\text{sat}}. \quad (8)$$

The third term on the right-hand side of equation (8) includes the thermal expansion of the cell. In this research the thermal expansion of the cells was expressed as:

$$V_x(T) / V_x(298.15 \text{ K}) = 1 + ay + by^2, \quad (9)$$

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

Values of $(\partial p/\partial T)_{\text{sat}}$ can be calculated based on the vapor pressures measured in this research. Therefore, with a minimum of two different filling levels of the cell, $(\partial^2 p/\partial T^2)_{\text{sat}}$ and $(\partial^2 \mu/\partial T^2)_{\text{sat}}$ can be determined. In this research three fillings were used. To obtain the saturation heat capacity $C_{\text{sat},m}$ at vapor pressures greater than 0.1 MPa, the limit where the cell is full of liquid is required; i.e., $(n/V_x) = \{1/V_m(\text{I})\}$ where $V_m(\text{I})$ is the molar volume of the liquid:

$$\lim_{(n/V_x) \rightarrow \{1/V_m(l)\}} (n C_{v,m}^{II}/T) = V_m(l)(\partial^2 p/\partial T^2)_{\text{sat}} - n(\partial^2 \mu/\partial T^2)_{\text{sat}}. \quad (10)$$

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

$$\lim_{(n/V_x) \rightarrow \{1/V_m(l)\}} (n C_{v,m}^{II}) = n[C_{\text{sat},m} - \{T(\partial p/\partial T)_{\text{sat}} (dV_m(l)/dT)\}]. \quad (11)$$

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

Table 11 lists the experimental two-phase heat capacities $C_{x,m}^{II}$ for 9-methylcarbazole and 1,2,3,4-tetrahydro-9-methylcarbazole obtained for three cell fillings for each compound. Heat capacities were determined at 20-K intervals with a heating rate of $0.083 \text{ K}\cdot\text{s}^{-1}$ and a 120-s equilibration period between heats. Sample decomposition precluded heat-capacity measurements above 760 K for 9-methylcarbazole and 660 K for 1,2,3,4-tetrahydro-9-methylcarbazole.

For other compounds, e.g., 2-aminobiphenyl⁽⁷⁾ and dibenzothiophene,⁽⁴⁶⁾ a rapid heating method was used for critical temperature and critical density determinations. By employing a single continuous heat at a rate of $0.333 \text{ K}\cdot\text{s}^{-1}$, sample decomposition was greatly reduced, and the abrupt decrease in heat capacity associated with the conversion from two phases to one phase was observed. However, this method failed in the present research as there was extensive sample decomposition above the range of the heat-capacity measurements.

For both 9-methylcarbazole and 1,2,3,4-tetrahydro-9-methylcarbazole values for T_c and p_c were estimated by a simultaneous non-linear least-squares fit of the vapor pressures listed in table 5 and the $C_{x,m}^{II}$ values given in table 11. $C_{\text{sat},m}$ values were derived from results of the fit and equation (11). Experimental $C_{x,m}^{II}$ values were converted to $C_{v,m}^{II}$ by means of equation (9) for the cell expansion and the vapor-pressure fit described below for $(\partial p/\partial T)_{\text{sat}}$.

$$C_{v,m}^{II} = C_{x,m}^{II} - T/n \{(\partial V_x/\partial T)_x (\partial p/\partial T)_{\text{sat}}\}. \quad (12)$$

The values of $C_{v,m}^{II}$ were used to derive functions for $(\partial^2 p/\partial T^2)_{\text{sat}}$ and $(\partial^2 \mu/\partial T^2)_{\text{sat}}$. The Cox equation⁽³⁷⁾ was used to represent the vapor pressures in the form:

$$\ln(p/p_c) = (1 - 1/T_r) \exp (A + BT_r + CT_r^2), \quad (13)$$

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

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

$$(\partial^2 \mu / \partial T^2)_{\text{sat}} / (\text{J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1}) = \sum_{i=0}^n b_i (1 - T/T_c)^i \quad (14)$$

{For compounds where sufficient information was available to evaluate reliably $(\partial^2 \mu / \partial T^2)_{\text{sat}}$ (e.g., benzene⁽⁴⁷⁾), four terms (i.e., expansion to $n=3$) were required to represent the function. Thus, four terms were used in this research.} In these fits the sum of the weighted squares in the following function was minimized:

$$\Delta = C_{v,m}^{\text{ll}}/R - \{V_m(l)T/nR\}(\partial^2 p / \partial T^2)_{\text{sat}} + (T/R)(\partial^2 \mu / \partial T^2)_{\text{sat}} \quad (15)$$

For the vapor-pressure fits, the functional forms of the weighting factors used have been reported.^(23,26) Within the heat-capacity results, the weighting factors were proportional to the square of the mass of sample used in the measurements. Table 12 lists the coefficients determined in the non-linear least-squares fit. A weighting factor of 20 was used to increase the relative weights of the vapor-pressure measurements in the fit. The weighting factor reflects the higher precision of the vapor-pressure values relative to the experimental heat capacities.

Values of $C_{\text{sat},m}$ for 9-methylcarbazole and 1,2,3,4-tetrahydro-9-methylcarbazole were derived from $C_{v,m}^{\text{ll}}(p=p_{\text{sat}})$ with densities obtained using equation (7) (see *Derived Enthalpies of Vaporization* section). The results for $C_{v,m}^{\text{ll}}(p=p_{\text{sat}})/R$ and $C_{\text{sat},m}/R$ are reported in table 13. The estimated uncertainty in these values is 1 per cent. Differences between $C_{v,m}^{\text{ll}}(p=p_{\text{sat}})/R$ and $C_{\text{sat},m}/R$ are significant only at the highest temperatures measured. Differences in these quantities can be large as the critical temperature is approached.⁽⁴⁵⁾

THERMODYNAMIC PROPERTIES IN THE CONDENSED STATE

Entropies and enthalpies under vapor saturation pressure relative to that of the crystals at $T \rightarrow 0$ for the solid and liquid phases of 1,2,3,4-tetrahydro-9-methylcarbazole and the liquid phase of 9-methylcarbazole are listed in table 14. (These functions were published previously⁽⁹⁾ for the crystal phase of 9-methylcarbazole.) The tabulated values were derived by integration of the smoothed heat capacities corrected for pre-melting, together with the entropies and enthalpies of transition and fusion. The heat capacities were smoothed with cubic-spline functions by least-squares fits to six points at a time and by requiring continuity in value, slope, and curvature at the junction of

successive cubic functions. Due to limitations in the spline-function procedure, some acceptable values from tables 10 and 13 were not included in the fit, while in other regions graphical values were introduced to ensure that the second derivative of the heat capacity with respect to temperature was a smooth function of temperature. Pre-melting corrections were made for 1,2,3,4-tetrahydro-9-methylcarbazole by means of standard methods⁽⁴³⁾ for solid-insoluble impurities and the mole-fraction impurities value shown in table 1.

THERMODYNAMIC PROPERTIES IN THE IDEAL-GAS STATE

Enthalpies and entropies at selected temperatures for the ideal gas were calculated using values in tables 7 and 14 and are listed in columns 2 and 4 of table 15. Entropies and enthalpies of compression to 101.325 kPa were calculated based on the virial equation truncated after the third virial coefficient.

$$pV_m = RT + Bp + Cp^2 \quad (16)$$

Formulations used to calculate the entropy and enthalpy of compression are:⁽⁴⁸⁾

$$\Delta S_{\text{comp},m} = R \ln(p) + (dB/dT)p + (dC/dT)p^2, \quad (17)$$

$$\Delta H_{\text{comp},m} = \{B - T(dB/dT)\}p + \{C - T(dC/dT)\}(p^2/2). \quad (18)$$

Equations (17) and (18) are derived from equations (16.21) and (16.27), respectively, of reference 48. Temperature derivatives were estimated by numerical differentiation of virial coefficients estimated by the methods of Pitzer and Curl⁽⁴⁰⁾ and Orbey and Vera.⁽⁴¹⁾

The first term in equation (17) is the entropy of compression, if the gas were ideal. The uncertainty in this term is not significant. The sum of the second and third terms of equation (17) is the "gas-imperfection correction" to the entropy of compression. Equation (18) gives the "gas-imperfection correction" to the enthalpy of compression directly, as the ideal-gas value is zero. The gas-imperfection corrections are listed in table 15. Uncertainties in these values is difficult to assess because temperature derivatives of estimated values are involved. An uncertainty of 10 per cent of the calculated correction was assumed.

The derived ideal-gas enthalpies and entropies for 1,2,3,4-tetrahydro-9-methylcarbazole 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 15.

The energy of combustion for the crystal phase of 9-methylcarbazole was reported by Good⁽¹⁰⁾ and Jiménez et al.⁽⁴⁹⁾ The value reported by Good $\Delta_c U_m^0 = -(6787.6 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$ was revised slightly in this research to $\Delta_c U_m^0 = -(6786.6 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$. In the revised calculation, the estimated density for the crystal phase of 9-methylcarbazole employed by Good⁽¹⁰⁾ was replaced by a more reliable value determined by x-ray crystallography.⁽⁵⁰⁾ The value reported by Jiménez et al.⁽⁴⁹⁾ for the molar energy of combustion $-(6785.8 \pm 1.7) \text{ kJ} \cdot \text{mol}^{-1}$ is in excellent agreement with that of Good.⁽¹⁰⁾ The value for the molar enthalpy of formation $\Delta_f H_m^0 = (104.1 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$ employed here for the ideal-gas property calculations is derived from the average of the energy of combustion values.

Enthalpies and entropies for nitrogen and equilibrium hydrogen were determined from JANAF tables.⁽⁵¹⁾ Values for graphite were determined with the polynomial⁽⁵²⁾ used to calculate the values from 298.15 K to 6000 K listed in the JANAF tables. All uncertainties in table 15 represent one standard deviation and do not include uncertainties in the properties of the elements.

CALCULATION OF SUBLIMATION PRESSURES

The "third-law" method was employed to calculate sublimation pressures for 9-methylcarbazole from 298.15 K to the triple-point temperature. The "third-law" values were calculated from the tabulated thermodynamic functions of the ideal gas (table 15) and the crystalline solid (table 14). The method applied here was the same as that used previously for biphenyl.⁽⁴⁵⁾ The sublimation vapor pressures were represented by the equation:

$$\ln(p/p_0) = 31.97 - 1.0424 \times 10^4 (T/K)^{-1} - 1.5082 \times 10^5 (T/K)^{-2}, \quad (19)$$

in the temperature region 298.15 to 362.5 K with $p_0 = 1 \text{ Pa}$.

4. DISCUSSION

COMPARISON OF RESULTS WITH LITERATURE

The property-measurement results reported here for 1,2,3,4-tetrahydro-9-methylcarbazole are the first for this important intermediate in the carbazole/H₂ hydrodenitrogenation reaction network. A search of the literature (Chemical Abstracts; 1907 through 1990) failed to locate any previous thermodynamic-property measurements on this material.

Jiménez et al.⁽⁴⁹⁾ reported sublimation pressures for 9-methylcarbazole determined by the Knudsen-effusion method in addition to the energy of combustion discussed earlier. A comparison with those calculated with equation (19) is shown in figure 9. The values reported by Jiménez et al.⁽⁴⁹⁾ are between 5 per cent and 7 per cent lower than the calculated values. The agreement is excellent when the very low pressure range ($p < 0.5$ Pa) is considered.

5. SUMMARY and HIGHLIGHTS

- Thermochemical and thermophysical properties for 9-methylcarbazole and 1,2,3,4-tetrahydro-9-methylcarbazole are reported. For 1,2,3,4-tetrahydro-9-methylcarbazole, the properties measured included the energy of combustion, and vapor pressures, heat capacities, and densities over a range of temperatures. For 9-methylcarbazole, vapor pressures and heat capacities to high temperatures (to 750 K) are reported.
- Ideal-gas thermodynamic properties for 9-methylcarbazole and 1,2,3,4-tetrahydro-9-methylcarbazole were determined based on the accurate calorimetric measurements. The results for 9-methylcarbazole will be used to accurately estimate the properties of carbazole through the application of the methods of group additivity.
- Gibbs energies of formation for 9-methylcarbazole and 1,2,3,4-tetrahydro-9-methylcarbazole for equilibria calculations were derived. The determination of these is an essential precursor to a thermodynamic analysis of the initial steps of the hydrogenolysis of carbazole, which will be presented in a subsequent topical report.
- Carbazole-type molecules are particularly difficult to remove in the HDN (hydrodenitrogenation) of process fluids derived from heavy petroleum. The results reported here will be used to provide an improved understanding of the underlying reasons for these difficulties, and can provide a guide to the development of more efficient process conditions than used presently.

FIGURE 9. Parity plot comparing sublimation pressures measured by Jiménez et al.⁽⁴⁹⁾ with values calculated using equation (19). The line corresponds to perfect agreement between the measured and calculated values. ●, Jiménez et al.⁽⁴⁹⁾

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., and R. D. Chirico. *Thermodynamics and the Hydrodenitrogenation of Indole. In three parts: Part I. Thermodynamic Properties of Indoline and 2-Methylindole, Part II. Gibbs Energies of Reaction in the Hydrodenitrogenation of Indole, Part III. Thermodynamic Equilibria and Comparison with Literature Kinetic Studies*. NIPER-415. Published by DOE Fossil Energy, Bartlesville Project Office. Available from NTIS, Report No. DE-89000751, June 1989.
6. Steele, W. V.; Chirico, R. D. *Thermodynamics of the Hydrodenitrogenation of Quinoline*. NIPER-468. Published by DOE Fossil Energy, Bartlesville Project Office. Available from NTIS Report No. DE-90000245, June 1990.
7. Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. *The Thermodynamic Properties of 2-Aminobiphenyl. (An Intermediate in the Carbazole/Hydrogen Reaction Network)* NIPER-482, December 1990. Published by DOE Fossil Energy, Bartlesville Project Office. Available from NTIS Report No. DE91002209.
8. Benson, S. W. *Thermochemical Kinetics*. 2nd edition. Wiley: New York, 1976.
9. Messerly, J. F.; Todd, S. S.; Finke, H. L.; Good, W. D.; Gammon, B. E. *J. Chem. Thermodynamics* **1988**, 20, 209.
10. Good, W. D. *J. Chem. Eng. Data* **1972**, 17, 28.
11. Commission on Atomic Weights and Isotopic Abundances. *Pure Appl. Chem.* **1933**, 55, 1101.
12. Cohen, E. R.; Taylor, B. N. *J. Phys. Chem. Ref. Data* **1988**, 17, 1795.
13. *Metrologia* **1969**, 5, 35.
14. McCrackin, F. L.; Chang, S. S. *Rev. Sci. Instrum.* **1975**, 46, 550.
15. Good, W. D.; Moore, R. T. *J. Chem. Eng. Data* **1970**, 15, 150.
16. Good, W. D.; Smith, N. K. *J. Chem. Eng. Data* **1969**, 14, 102.
17. Good, W. D. *J. Chem. Eng. Data* **1969**, 14, 231.
18. Good, W. D.; Scott, D. W.; Waddington, G. *J. Phys. Chem.* **1956**, 60, 1080.
19. Good, W. D.; Douslin, D. R.; Scott, D. W.; George, A.; Lacina, J. L.; McCullough, J. P.; Waddington, G. *J. Phys. Chem.* **1959**, 63, 1133.
20. Smith, N. K.; Stewart, R. C., Jr.; Osborn, A. G.; Scott, D. W. *J. Chem. Thermodynamics* **1980**, 12, 919.
21. 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-87001252, April 1987.
22. 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.
23. 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.
24. Swietoslawski, W. *Ebulliometric Measurements*. Reinhold: New York, 1945.
25. Osborn, A. G.; Douslin, D. R. *J. Chem. Eng. Data* **1966**, 11, 502.
26. Chirico, R. D.; Nguyen, A.; Steele, W. V.; Strube, M. M.; Tsonopoulos, C. *J. Chem. Eng. Data* **1989**, 34, 149.

27. Antoine, C. *C. R. Acad. Sci.* **1888**, 107, 681.
28. Douslin, D. R.; McCullough, J. P. *U. S. Bureau of Mines. Report of Investigation 6149*, **1963**, pp. 11.
29. Douslin, D. R.; Osborn A. G. *J. Sci. Instrum.* **1965**, 42, 369.
30. Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Smith, N. K. *High-Temperature Heat-Capacity Measurements and Critical Property Determinations using a Differential Scanning Calorimeter. (Development of Methodology and Application to Pure Organic Compounds)* NIPER-360, December **1988**. Published by DOE Fossil Energy, Bartlesville Project Office. Available from NTIS Report No. DE89000709.
31. Knipmeyer, S. E.; Archer, D. G.; Chirico, R. D.; Gammon, B. E.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Steele, W. V.; Strube, M. M. *Fluid Phase Equilibria* **1989**, 52, 185.
32. Mraw, S. C.; Naas, D. F. *J. Chem. Thermodynamics* **1979**, 11, 567.
33. Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry*. Rossini, F. D.: editor. Interscience: New York, **1956**, Chapt. 5, pp. 75-128.
34. Smith, N. K.; Good, W. D. *J. Chem. Eng. Data* **1967**, 12, 572.
35. Rossini, F. D. *Experimental Thermochemistry*. Rossini, F. D.: editor. Interscience: New York. **1956**, Chapt. 14, pp. 297-320.
36. Cox, J. D.; Wagman, D. D.; Medvedev, V. A.: editors. *CODATA Key Values for Thermodynamics*. Hemisphere: New York. **1989**.
37. Cox, E. R. *Ind. Eng. Chem.* **1936**, 28, 613.
38. Riedel, L. *Chem.-Ing.-Tech* **1954**, 26, 259.
39. Hales, J. L.; Townsend, R. *J. Chem. Thermodynamics* **1972**, 4, 763.
40. Pitzer, K. S.; Curl, R. F. Jr. *J. Am. Chem. Soc.* **1957**, 79, 2369.
41. Orbey, H.; Vera, J. H. *AIChE Journal*, **1983**, 29, 107.
42. Steele, W. V.; Chirico, R. D. To be submitted to *Ind. Eng. Chem. Res.*
43. Westrum, E. F., Jr.; Furukawa, G. T.; McCullough, J. P. *Experimental Thermodynamics*. Vol. 1. McCullough, J. P.; Scott, D. W.: editors. Butterworths: London. **1968**, Chapt 5.
44. Mastrangelo, S. V. R.; Dornte, R. W. *J. Am. Chem. Soc.* **1955**, 77, 6200.
45. Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Steele, W. V. *J. Chem. Thermodynamics* **1989**, 21, 1307.
46. Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Steele, W. V. *The Thermodynamic Properties of Dibenzothiophene*. *J. Chem. Thermodynamics* In press **1991**.
47. Goodwin, R. D. *J. Phys. Chem. Ref. Data* **1988**, 17, 1541.
48. Lewis, G. N.; Randall, M. *Thermodynamics*. Revised by Pitzer, K. S.; Brewer, L. 2nd edition. McGraw-Hill: New York. **1961**.
49. Jiménez, P.; Roux, M. V.; Turrión, C. *J. Chem. Thermodynamics* **1990**, 22, 721.
50. Popova, E. G.; Chetkina, L. A. *Zh. Strukt. Khim.* **1979**, 20, 665.
51. Chase, M. W., Jr.; Davies, C. A.; Cowney, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables* Third edition. Supplement to *J. Phys. Chem. Ref. Data* **1985**, 14.
52. Chirico, R. D.; Archer, D. G.; Hossenlopp, I. A.; Nguyen, A.; Steele, W. V.; Gammon, B. E. *J. Chem. Thermodynamics* **1990**, 22, 665.

TABLE 1. Calorimeter and sample characteristics for adiabatic heat-capacity calorimetry studies on 1,2,3,4-tetrahydro-9-methylcarbazole: 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; and $\delta C/C$ is the vaporization correction; x_{pre} is the mole-fraction impurity used for pre-melting corrections.

m/g	45.828
$V_i(298.15\text{ K})/\text{cm}^3$	61.78
T_{cal}/K	298.3
p_{cal}/kPa	7.83
$r(T_{max})$	3.3
r_{min}	1.8
$10^2 \cdot (\delta C/C)_{max}$	0.033
x_{pre}	0.00035

TABLE 2. Typical combustion experiment at 298.15 K for
1,2,3,4-tetrahydro-9-methylcarbazole ($p^\circ = 101.325 \text{ kPa}$) ^a

$m'(\text{compound})/\text{g}$	0.910170
$m''(\text{fuse})/\text{g}$	0.001725
$n_i(\text{H}_2\text{O})/\text{mol}$	0.05535
$m(\text{Pt})/\text{g}$	20.810
$\Delta T = (t_i - t_f + \Delta t_{\text{corr}})/\text{K}$	2.14287
$\epsilon(\text{calor})(\Delta T)/\text{J}$	-35660.8
$\epsilon(\text{cont})(\Delta T)/\text{J}$ ^b	-39.3
$\Delta U_{\text{ign}}/\text{J}$	0.8
$\Delta U_{\text{dec}}(\text{HNO}_3)/\text{J}$	35.3
$\Delta U(\text{corr. to std. states})/\text{J}$ ^c	18.7
$-m''(\Delta_c U_m^\circ/M)(\text{fuse})/\text{J}$	29.2
$m'(\Delta_c U_m^\circ/M)(\text{compound})/\text{J}$	-35616.1
$(\Delta_c U_m^\circ/M)(\text{compound})/\text{J}\cdot\text{g}^{-1}$	-39131.3

a The symbols and abbreviations of this table are those of reference 33 except as noted.

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

c Items 81 to 85, 87 to 90, 93, and 94 of the computational form of reference 33.

TABLE 3. Summary of energies of combustion and molar thermochemical functions for
1,2,3,4-tetrahydro-9-methylcarbazole ($T = 298.15 \text{ K}$ and $p^\circ = 101.325 \text{ kPa}$)

$\{(\Delta_c U_m^\circ/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$					
-39131.3	-39137.0	-39131.2	-39133.9	-39133.8	-39134.6
$\langle\{(\Delta_c U_m^\circ/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})\rangle$					-39133.6 ± 0.9
$(\Delta_c U_m^\circ/M)(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$					-7250.28 ± 1.08
$(\Delta_c H_m^\circ/M)(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$					-7258.33 ± 1.08
$(\Delta_f H_m^\circ/M)(\text{compound})/(\text{kJ}\cdot\text{mol}^{-1})$					-1.02 ± 1.26

TABLE 4. Measured and calculated densities of 1,2,3,4-tetrahydro-9-methylcarbazole at saturation pressure ^a

T/K	$\rho/\text{kg}\cdot\text{m}^{-3}$	$10^2(\rho - \rho_{\text{CS}})/\rho$
347.899	1036.30	-0.12
363.675	1025.20	0.10
381.190	1013.40	0.12
382.364	1012.00	0.06
397.850	1001.00	0.03
423.677	983.01	0.05

^a ρ_{CS} = density calculated using corresponding states {equation (7)}.

TABLE 5. Vapor-pressure results: IP refers to measurements performed with the inclined-piston gauge; water or decane refers to which material was used as the standard in the reference ebulliometer; T is the temperature of the experimental inclined-piston pressure gauge measurements or, for ebulliometric measurements, of the condensation temperature of the sample; the pressure p for ebulliometric measurements was calculated from the condensation temperature of the reference substance; Δp is the difference of the calculated value of pressure from the observed value of pressure; $\sigma(p)$ is the propagated error calculated from equations (1) and (2); ΔT is the difference between the boiling and condensation temperature ($T_{\text{boil}} - T_{\text{cond}}$) for the sample in the ebulliometer

Method	T K	p kPa	Δp kPa	$\sigma(p)$ kPa	ΔT K
9-Methylcarbazole					
IP	373.154	0.0163	0.0001	0.0002	
IP	383.152	0.0304	0.0000	0.0002	
IP	393.150	0.0550	0.0000	0.0002	
IP	403.152	0.0964	0.0002	0.0002	
IP	413.150	0.1628	0.0001	0.0002	
IP	423.152	0.2674	0.0001	0.0002	
IP	433.151	0.4271	0.0000	0.0003	
IP	443.151	0.6654	0.0001	0.0003	
IP	453.151	1.0120	0.0000	0.0004	
IP	463.148	1.5059	-0.0002	0.0004	
decane	470.622	2.0000	-0.0003	0.0001	0.096
IP	473.153	2.1964	-0.0002	0.0005	
decane	478.494	2.6660	0.0002	0.0002	0.057
IP	483.146	3.1420	-0.0001	0.0007	
decane	498.901	5.3330	0.0001	0.0003	0.032
decane	511.861	7.9989	0.0001	0.0004	0.027
decane	521.574	10.6661	0.0004	0.0005	0.018
decane	529.426	13.332	0.000	0.001	0.011
decane	537.572	16.665	0.001	0.001	0.009
decane	544.338	19.933	0.000	0.001	0.010
decane	553.236	25.023	0.001	0.001	0.006

TABLE 5. Continued

Method	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma(p)}{kPa}$	$\frac{\Delta T}{K}$
water	553.232	25.023	0.004	0.001	0.005
water	562.186	31.177	0.002	0.002	0.002
water	571.191	38.565	0.001	0.002	0.002
water	580.244	47.375	-0.001	0.002	0.001
water	589.351	57.817	-0.005	0.003	0.001
water	607.712	84.533	-0.005	0.004	-0.001
water	616.968	101.325	-0.006	0.004	-0.002
water	626.274	120.790	-0.004	0.005	-0.002
water	635.632	143.25	0.00	0.01	-0.001
water	645.035	169.02	0.00	0.01	-0.002
water	654.490	198.49	0.01	0.01	0.001
water	663.992	232.02	0.01	0.01	0.002
water	673.539 ^a	270.02	0.01	0.01	0.011

1,2,3,4-Tetrahydro-9-methylcarbazole

IP	370.001	0.0173	-0.0001	0.0002	
IP	380.000	0.0330	0.0000	0.0002	
IP	390.000	0.0598	-0.0002	0.0002	
IP	400.002	0.1052	-0.0001	0.0002	
IP	410.004	0.1790	0.0002	0.0002	
IP	420.006	0.2948	0.0003	0.0002	
IP	430.002	0.4719	0.0002	0.0003	
IP	439.999	0.7365	0.0004	0.0003	
IP	450.000	1.1218	0.0001	0.0004	
IP	460.001	1.6718	0.0003	0.0005	
decane	464.679	2.0000	0.0000	0.0001	0.095
IP	469.999	2.4390	-0.0006	0.0006	
decane	472.428	2.6660	-0.0004	0.0002	0.081
IP	475.003	2.9267	0.0003	0.0006	
decane	492.487	5.3330	-0.0001	0.0003	0.054

TABLE 5. Continued

Method	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma(p)}{kPa}$	$\frac{\Delta T}{K}$
decane	505.226	7.9989	0.0004	0.0004	0.032
decane	514.780	10.666	0.000	0.001	0.019
decane	522.498	13.332	0.000	0.001	0.016
decane	530.509	16.665	0.001	0.001	0.014
decane	537.161	19.933	0.001	0.001	0.011
decane	545.908	25.023	0.004	0.001	0.011
water	554.717	31.177	0.001	0.002	0.011
water	563.573	38.565	-0.001	0.002	0.011
water	572.478	47.375	-0.004	0.002	0.011
water	581.431	57.817	-0.003	0.003	0.014
water	590.433	70.120	0.003	0.003	0.018
water	599.498	84.533	-0.012	0.004	0.012
water	608.604	101.325	-0.012	0.004	0.012
water	617.758	120.790	-0.008	0.005	0.013
water	626.964	143.25	0.00	0.01	0.012
water	636.215	169.02	0.01	0.01	0.015
water	645.516	198.49	0.02	0.01	0.018
water	654.835 ^a	232.02	0.15	0.01	0.036

^a The value at this temperature was not included in the fit.

TABLE 6. Cox equation coefficients

	9-Methylcarbazole	1,2,3,4-Tetrahydro-9-methylcarbazole
T_{ref}/K	890	854
$p_{\text{ref}}/\text{kPa}$	3376	2709
A	2.58573	2.62775
10^3B	-1.47375	-1.51344
10^6C	1.03310	1.05631
T/K^a	373 to 664	370 to 645

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

TABLE 7. Enthalpies of vaporization obtained from the Cox and Clapeyron equations

T/K	$\Delta_l^g H_m/RK$	T/K	$\Delta_l^g H_m/RK$	T/K	$\Delta_l^g H_m/RK$
9-Methylcarbazole					
298.15 ^a	9764±12	460.00	8314±2	620.00	6923±33
300.00 ^a	9746±11	480.00	8146±3	640.00	6724±42
320.00 ^a	9558±8	500.00	7980±4	660.00	6515±52
340.00 ^a	9372±6	520.00	7813±7	680.00 ^a	6293±63
360.00 ^a	9188±4	540.00	7645±10	700.00 ^a	6058±76
380.00	9007±3	560.00	7473±14	720.00 ^a	5806±89
400.00	8829±2	580.00	7296±19	740.00 ^a	5536±105
420.00	8654±1	600.00	7114±25	760.00 ^a	5244±121
440.00	8482±1				
1,2,3,4-Tetrahydro-9-methylcarbazole					
298.15 ^a	9688±18	440.00	8368±2	580.00	7111±25
300.00 ^a	9670±18	460.00	8194±2	600.00	6909±33
320.00 ^a	9475±13	480.00	8020±4	620.00	6696±42
340.00 ^a	9283±9	500.00	7846±6	640.00	6470±53
360.00 ^a	9094±6	520.00	7670±9	660.00 ^a	6230±65
380.00	8907±4	540.00	7490±13	680.00 ^a	5972±79
400.00	8724±3	560.00	7304±18	700.00 ^a	5695±94
420.00	8545±2				

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

TABLE 8. Melting-study summary for 1,2,3,4-tetrahydrocarbazole: F is the fraction melted at observed temperature T(F); T_{tp} is the triple-point temperature; x is the mole-fraction impurity; K_d is the distribution coefficient for the impurity as defined in reference 44.

F	T(F)/K
0.1622	323.371
0.3107	323.504
0.5088	323.574
0.7069	323.611
T_{tp}/K	323.71
x	0.0015
K_d	0.057

TABLE 9. Molar enthalpy measurements for 1,2,3,4-tetrahydro-9-methylcarbazole
($R=8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

N^a	h^b	$\frac{T_i}{K}$	$\frac{T_f}{K}$	$\frac{T_{trs}}{K}$	$\frac{\Delta_{tot}H_m^c}{R\cdot K}$	$\frac{\Delta_{trs}H_m^d}{R\cdot K}$
Single-phase measurements in cr(IV)						
18	1	69.838	92.482		223.99	0.1
cr(IV) to cr(III)						
11	1	104.003	113.447	103.8	117.25	-1.3 ^e
12	1	101.830	111.259		114.95	-1.2 ^e
14	1	102.588	108.565		73.08	-0.1
19	1	99.994	110.886		133.12	0.2
20	1	103.698	105.498		21.77	-0.2
Average:						0.0
Single-phase measurements in cr(III)						
15	1	119.893	156.377		551.70	-0.4
20	1	117.330	156.566		589.72	0.0
cr(III) to cr(II)						
8	4	158.218	167.714	162.4	247.28	81.7
9	1	160.780	167.323		196.07	81.8
20	2	161.989	166.771		164.53	81.3 ^e
Average:						81.7
cr(II) to cr(I)						
3	1	210.106	220.507	210.4	222.16	0.0
6	1	210.186	213.217		64.27	0.1
7	1	204.928	215.197		220.16	0.1
20	1	204.373	214.647		220.16	0.0
Average:						0.0
Single-phase measurements in cr(I)						
20	1	214.631	308.748		2392.40	0.5
5	1	282.419	319.204		1082.95	1.1

TABLE 9. Continued

N^a	h^b	$\frac{T_i}{K}$	$\frac{T_f}{K}$	$\frac{T_{trs}}{K}$	$\frac{\Delta_{tot}H_m^c}{R \cdot K}$	$\frac{\Delta_{trs}H_m^d}{R \cdot K}$
cr(l) to liquid						
4	2	318.867	326.242	323.71	2013.09	1764.4
5	6	319.147	326.341		2007.11	1763.6
22	2	315.938	327.294		2143.91	1764.0
Average:						1764.0
Single-phase measurements in liquid						
22	1	337.324	401.201		2568.93	0.2
23	1	332.654	421.940		3643.95	-0.3
23	1	421.840	503.782		3856.87	-1.0

^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} or the excess enthalpy relative the heat-capacity curve described in the text for single-phase measurements.

^e This value was not included in the average. See text.

TABLE 10. Molar heat capacities at vapor-saturation pressure for 1,2,3,4-tetrahydro-9-methylcarbazole ($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)^a

N ^b	$\frac{\langle T \rangle}{\text{K}}$	$\frac{\Delta T}{\text{K}}$	$\frac{C_{\text{sat},m}^c}{R}$	N ^b	$\frac{\langle T \rangle}{\text{K}}$	$\frac{\Delta T}{\text{K}}$	$\frac{C_{\text{sat},m}^c}{R}$
cr(IV)							
17	4.746	1.0470	0.043	17	50.591	5.2034	6.357
17	5.677	0.9418	0.069	18	55.603	5.8989	7.014
17	6.675	1.0255	0.114	17	56.112	5.8387	7.080
17	7.719	1.0670	0.175	11	58.626	4.1179	7.393
17	8.770	1.0383	0.260	18	61.259	5.3996	7.716
17	9.599	1.1330	0.340	11	63.469	5.5490	7.987
17	9.832	1.0834	0.366	18	66.899	5.8672	8.388
17	10.722	1.1388	0.464	11	69.021	5.5475	8.637
17	11.929	1.2814	0.614	11	75.141	6.6757	9.294
17	13.265	1.3872	0.796	11	82.758	8.4615	10.062
17	14.727	1.5359	1.011	14	85.740	8.4740	10.345
17	16.346	1.7037	1.260	12	88.269	8.3014	10.580
17	18.116	1.8408	1.541	11	91.055	8.1255	10.839
17	20.073	2.0809	1.855	16	91.803	8.2735	10.906
17	22.250	2.2772	2.204	19	92.570	5.1363	10.972
17	24.642	2.5011	2.587	14	94.737	9.5149	11.167
17	27.275	2.7636	2.995	20	96.156	15.0800	11.280
17	30.194	3.0722	3.443	18	96.235	7.4920	11.309
17	33.451	3.4411	3.934	12	97.129	9.3692	11.363
17	37.095	3.8460	4.472	19	97.566	4.8526	11.407
17	41.131	4.2269	5.049	11	99.553	8.8597	11.568
17	45.617	4.7459	5.674	14	101.042	3.0874	11.706

TABLE 10. Continued

N ^a	$\frac{\langle T \rangle}{K}$	$\frac{\Delta T}{K}$	$\frac{C_{sat,m}^b}{R}$	N ^a	$\frac{\langle T \rangle}{K}$	$\frac{\Delta T}{K}$	$\frac{C_{sat,m}^b}{R}$
cr(III)							
20	106.188	1.3829	12.324	11	127.726	9.5790	14.191
20	107.561	1.3721	12.452	13	136.338	14.0675	14.951
20	109.714	2.9426	12.643	11	137.318	9.6027	15.036
14	110.038	2.9164	12.642	9	137.432	8.8487	15.045
19	112.345	2.9034	12.865	9	146.254	8.7994	15.861
14	112.931	2.8718	12.907	13	148.152	9.5421	16.049
20	114.257	6.1492	13.029	9	153.294	5.2872	16.554
14	115.783	2.8295	13.170	13	156.151	6.4405	16.884
19	117.348	7.0825	13.291	8	156.716	3.0104	16.922
11	118.185	9.4715	13.363	9	158.380	4.8908	17.166
14	121.533	8.6651	13.654	20	159.269	5.5128	17.304
13	124.225	10.1390	13.883				
cr(II)							
8	169.303	3.1957	17.635	3	194.854	10.1650	20.090
20	171.326	9.1182	17.817	6	196.527	3.1165	20.243
9	171.868	9.1014	17.874	6	199.620	3.0865	20.622
3	174.924	9.7597	18.134	7	199.934	10.0038	20.651
8	175.763	9.7316	18.224	20	200.284	8.1927	20.692
20	180.922	10.0832	18.700	6	202.680	3.0551	20.960
3	184.788	9.9696	19.060	3	205.029	10.1948	21.307
20	191.088	10.2803	19.702	6	205.706	3.0202	21.397
6	193.405	3.1464	19.910	6	208.700	2.9905	21.794

TABLE 10. Continued

N^a	$\frac{\langle T \rangle}{K}$	$\frac{\Delta T}{K}$	$\frac{C_{\text{sat},m}^b}{R}$	N^a	$\frac{\langle T \rangle}{K}$	$\frac{\Delta T}{K}$	$\frac{C_{\text{sat},m}^b}{R}$
cr(l)							
6	214.583	3.0229	21.279	4	274.561	10.4150	26.560
7	220.408	10.4389	21.654	3	277.568	10.3464	26.868
3	225.726	10.4525	22.050	4	285.126	10.4077	27.640
3	236.179	10.4651	22.914	4	295.629	10.3903	28.787
3	246.579	10.3483	23.848	4	305.986	10.1269	30.084
3	256.920	10.3500	24.821	22	311.057	9.9639	30.927
3	267.259	10.3482	25.834	4	315.002	7.5092	31.737
liquid							
4	330.040	7.5744	37.276	22	408.687	15.0648	43.171
5	331.064	9.4563	37.352	22	423.707	15.7639	44.279
22	332.311	10.0501	37.441	22	439.763	16.4316	45.449
4	338.924	10.1763	37.935	22	456.023	16.1835	46.618
21	346.943	12.0966	38.538	22	472.034	15.9534	47.743
21	359.950	13.9029	39.512	22	488.242	16.6033	48.878
21	374.232	14.6566	40.589	22	504.640	16.3726	50.027
21	389.250	15.3790	41.716	22	517.830	10.1003	50.999
21	404.501	15.1317	42.857				

^a Measurements spanning transition temperatures are not included in this table. These are listed in table 9.

^b Adiabatic series number.

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

TABLE 11. Experimental $C_{x,m}^{II}/R$ values ($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

mass/g	0.010714	0.018054	0.029730	0.009255	0.028222	0.021491
Vol. cell/cm ³ ^a	0.05387	0.05570	0.05409	0.05288	0.05288	0.05288
T/K	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$
1,2,3,4-Tetrahydro-9-methylcarbazole				9-Methylcarbazole		
335.0	37.3	37.5	37.1			
355.0	39.2	38.9	38.9			
375.0	40.5	40.6	40.3	38.5	37.7	37.5
395.0	43.1	42.3	42.1	39.9	39.0	38.8
415.0	43.6	43.8	43.4	41.0	40.2	39.9
435.0	45.1	45.2	44.8	42.2	41.4	41.2
455.0	47.7	46.8	46.5	43.4	42.1	42.3
475.0	48.3	48.1	47.9	44.9	43.5	43.4
495.0	50.5	49.4	49.4	45.6	44.7	44.3
515.0	51.4	50.9	50.6	47.0	45.9	45.8
535.0	53.1	52.2	52.4	48.5	47.0	47.1
555.0	54.9	53.9	53.5	49.7	47.9	48.1
575.0	56.0	55.4	54.6	50.3	49.1	48.8
595.0	57.4	56.6	56.2	51.8	50.4	50.2
615.0	60.0	57.8	57.0	54.0	51.1	51.3
635.0	61.5	59.0	58.6	55.0	51.9	52.4
655.0	63.1	61.0	59.3	57.0	52.9	53.6
675.0				58.3	54.2	54.4
695.0				59.7	55.3	55.2
715.0				60.7	55.9	56.2
735.0				62.9	56.9	57.0
755.0				65.6	57.6	57.8

^a Volume measured at 298.15 K.

TABLE 12. Parameters for equations (13) and (14), estimated critical constants and acentric factor for 9-methylcarbazole and 1,2,3,4-tetrahydro-9-methylcarbazole ^a

9-Methylcarbazole				
A	2.58407	b ₀	-0.45003	
B	-1.30663	b ₁	-1.31438	
C	0.81455	b ₂	2.64332	
		b ₃	-2.65174	
T _c = 890 K	p _c = 3376 kPa	ρ _c = 317 kg·m ⁻³	ω = 0.473	
1,2,3,4-Tetrahydro-9-methylcarbazole				
A	2.62392	b ₀	-0.54101	
B	-1.28111	b ₁	-1.27334	
C	0.76201	b ₂	2.23873	
		b ₃	-1.98844	
T _c = 854 K	p _c = 2709 kPa	ρ _c = 309 kg·m ⁻³	ω = 0.521	

^a Values for the critical constants and acentric factor are estimates derived from the fitting procedures (see text).

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

T/K	$C_{V,m}^{\text{II}}(\rho = \rho_{\text{sat}})/R$	$C_{\text{sat},m}/R$	T/K	$C_{V,m}^{\text{II}}(\rho = \rho_{\text{sat}})/R$	$C_{\text{sat},m}/R$
9-Methylcarbazole					
370.0	37.6	37.6	570.0	48.5	48.5
390.0	38.7	38.7	590.0	49.6	49.6
410.0	39.7	39.7	610.0	50.6	50.7
430.0	40.8	40.8	630.0	51.7	51.7
450.0	41.9	41.9	650.0	52.6	52.7
470.0	43.0	43.0	670.0	53.6	53.6
490.0	44.1	44.1	690.0	54.4	54.5
510.0	45.2	45.2	710.0	55.1	55.3
530.0	46.3	46.3	730.0	55.8	56.0
550.0	47.4	47.4	750.0	56.3	56.7
1,2,3,4-Tetrahydro-9-methylcarbazole					
330.0	37.3	37.3	510.0	50.4	50.4
350.0	38.8	38.8	530.0	51.8	51.8
370.0	40.3	40.3	550.0	53.1	53.1
390.0	41.8	41.8	570.0	54.4	54.5
410.0	43.3	43.3	590.0	55.7	55.7
430.0	44.7	44.7	610.0	56.9	56.9
450.0	46.2	46.2	630.0	58.0	58.1
470.0	47.6	47.6	650.0	59.1	59.1
490.0	49.0	49.0			

TABLE 14. Molar thermodynamic functions at vapor-saturation pressure for 1,2,3,4-tetrahydro-9-methylcarbazole ($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

$\frac{T}{K}$	$\frac{C_{\text{sat,m}}}{R}$	$\frac{\Delta_0^T S_m^0}{R}$	$\frac{\Delta_0^T H_m^0}{RT}$	$\frac{T}{K}$	$\frac{C_{\text{sat,m}}}{R}$	$\frac{\Delta_0^T S_m^0}{R}$	$\frac{\Delta_0^T H_m^0}{RT}$
cr(IV)							
5.000	0.047	0.016	0.012	60.000	7.563	5.547	3.414
10.000	0.384	0.127	0.096	65.000	8.171	6.177	3.757
15.000	1.052	0.402	0.297	70.000	8.745	6.803	4.093
20.000	1.843	0.812	0.584	75.000	9.280	7.425	4.421
25.000	2.643	1.309	0.916	80.000	9.790	8.040	4.741
30.000	3.413	1.859	1.268	85.000	10.277	8.649	5.052
35.000	4.165	2.442	1.628	90.000	10.743	9.249	5.355
40.000	4.889	3.046	1.991	95.000	11.188	9.842	5.651
45.000	5.589	3.662	2.352	100.000	11.612	10.427	5.938
50.000	6.277	4.287	2.710	102.000 a	11.787	10.659	6.051
55.000	6.938	4.916	3.065	103.800 a	11.951	10.866	6.152
cr(III)							
103.800 a	12.119	10.866	6.152	150.000	16.213	16.024	8.610
105.000	12.223	11.006	6.221	153.000	16.514	16.348	8.762
110.000	12.658	11.585	6.504	156.000	16.848	16.672	8.914
120.000	13.523	12.723	7.052	158.000	17.114	16.888	9.016
130.000	14.384	13.840	7.583	160.000 a	17.436	17.105	9.120
140.000	15.278	14.938	8.101	162.000 a	17.814	17.324	9.225
145.000	15.739	15.482	8.356	162.400 a	17.896	17.368	9.246
cr(II)							
162.400 a	17.253	17.871	9.749	195.000	20.080	21.254	11.218
164.000 a	17.340	18.041	9.823	200.000	20.668	21.770	11.447
166.000 a	17.444	18.252	9.914	202.000	20.920	21.977	11.539
168.000	17.558	18.461	10.004	204.000	21.175	22.184	11.632
170.000	17.697	18.670	10.094	206.000	21.433	22.392	11.726
175.000	18.145	19.189	10.317	208.000	21.698	22.600	11.821

TABLE 14. continued

$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m^o}{R}$	$\frac{\Delta_0^T H_m^o}{RT}$	$\frac{T}{K}$	$\frac{C_{sat,m}}{R}$	$\frac{\Delta_0^T S_m^o}{R}$	$\frac{\Delta_0^T H_m^o}{RT}$
cr(II) continued							
180.000	18.615	19.707	10.541	210.000 ^a	21.983	22.809	11.916
185.000	19.095	20.223	10.766	210.400 ^a	22.043	22.851	11.936
190.000	19.585	20.739	10.991				
cr(I)							
210.400 ^a	21.036	22.851	11.936	280.000	27.090	29.618	14.891
215.000	21.305	23.309	12.133	290.000	28.124	30.586	15.329
220.000	21.633	23.802	12.345	298.150	29.027	31.378	15.691
230.000	22.391	24.780	12.765	300.000	29.244	31.558	15.774
240.000	23.251	25.751	13.184	310.000	30.486	32.537	16.228
250.000	24.162	26.719	13.605	320.000 ^a	31.872	33.526	16.695
260.000	25.111	27.685	14.029	323.710 ^a	32.429	33.897	16.872
270.000	26.092	28.651	14.457				
liquid							
298.150 ^a	34.953	36.396	21.159	480.000	48.301	55.987	28.931
300.000 ^a	35.085	36.613	21.245	500.000	49.700	57.987	29.734
320.000 ^a	36.535	38.923	22.155	520.000	51.141	59.965	30.530
323.710 ^a	36.808	39.346	22.321	540.000	52.477	61.920	31.318
340.000	38.016	41.183	23.044	560.000	53.805	63.852	32.097
360.000	39.516	43.398	23.918	580.000	55.091	65.763	32.868
380.000	41.022	45.575	24.778	600.000	56.327	67.652	33.630
400.000	42.521	47.717	25.628	620.000	57.504	69.518	34.381
420.000	44.006	49.828	26.468	640.000	58.610	71.361	35.121
440.000	45.467	51.909	27.298	660.000	59.659	73.181	35.849
460.000	46.898	53.962	28.120				

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

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

$\frac{T}{\text{K}}$	$\frac{\Delta_f H_m^\circ}{R T}$	$\frac{\Delta_{\text{imp}} H_m^\circ}{R T}^a$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_{\text{imp}} S_m^\circ}{R}^b$	$\frac{\Delta_f H_m^\circ}{R T}$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_f G_m^\circ}{R T}$
9-Methylcarbazole							
298.15 ^{a,d}	52.00±0.04	0.00	50.29±0.05	0.00	80.31±0.21	-56.58±0.05	136.89±0.20
300.00 ^{a,d}	51.83±0.04	0.00	50.44±0.05	0.00	79.76±0.20	-56.64±0.05	136.39±0.20
320.00 ^{a,d}	50.15±0.03	0.00	52.05±0.04	0.00	74.16±0.19	-57.28±0.04	131.43±0.19
340.00 ^{a,d}	48.73±0.03	0.00	53.63±0.04	0.00	69.22±0.18	-57.87±0.04	127.09±0.18
360.00 ^{a,d}	47.54±0.02	0.00	55.19±0.04	0.00	64.83±0.17	-58.43±0.04	123.26±0.17
380.00	46.54±0.02	0.00	56.73±0.04	0.00	60.92±0.16	-58.94±0.04	119.86±0.16
400.00	45.71±0.02	0.00	58.26±0.04	0.00	57.41±0.15	-59.42±0.04	116.83±0.16
420.00	45.01±0.03	0.00	59.77±0.05	0.00	54.25±0.15	-59.85±0.05	114.10±0.15
440.00	44.43±0.04	0.01	61.28±0.06	0.00	51.39±0.14	-60.26±0.06	111.64±0.15
460.00	43.96±0.06	0.01	62.77±0.07	0.01	48.80±0.14	-60.62±0.07	109.42±0.16
480.00	43.58±0.07	0.02	64.25±0.09	0.01	46.43±0.14	-60.96±0.09	107.39±0.17
500.00	43.27±0.09	0.02	65.72±0.10	0.02	44.27±0.15	-61.27±0.10	105.54±0.18
520.00	43.04±0.10	0.04	67.18±0.12	0.03	42.29±0.15	-61.55±0.12	103.84±0.19
540.00	42.87±0.11	0.05	68.63±0.14	0.04	40.47±0.16	-61.81±0.14	102.28±0.21
560.00	42.75±0.13	0.07	70.06±0.15	0.06	38.80±0.17	-62.04±0.15	100.84±0.22
580.00	42.67±0.14	0.10	71.49±0.17	0.08	37.25±0.18	-62.25±0.17	99.51±0.24
600.00	42.64±0.16	0.14	72.90±0.19	0.10	35.82±0.18	-62.44±0.19	98.27±0.26
620.00	42.63±0.17	0.18	74.30±0.21	0.13	34.50±0.20	-62.61±0.21	97.11±0.28
640.00	42.66±0.19	0.23	75.68±0.23	0.17	33.27±0.21	-62.77±0.23	96.03±0.29
660.00	42.72±0.20	0.29	77.05±0.25	0.21	32.12±0.22	-62.91±0.25	95.03±0.31
680.00	42.79±0.22	0.36	78.40±0.27	0.27	31.05±0.23	-63.03±0.27	94.08±0.33
700.00	42.88±0.23	0.44	79.74±0.29	0.33	30.04±0.25	-63.15±0.29	93.19±0.35
720.00	42.98±0.25	0.53	81.06±0.31	0.40	29.10±0.27	-63.26±0.31	92.35±0.36
740.00	43.09±0.27	0.64	82.35±0.33	0.47	28.20±0.28	-63.36±0.33	91.56±0.38
760.00	43.19±0.29	0.75	83.61±0.35	0.56	27.34±0.30	-63.47±0.35	90.81±0.40

TABLE 15. Continued

$\frac{T}{K}$	$\frac{\Delta_f H_m^\circ}{R T}$	$\frac{\Delta_{imp} H_m^\circ}{R T}$ ^a	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_{imp} S_m^\circ}{R}$ ^b	$\frac{\Delta_f H_m^\circ}{R T}$	$\frac{\Delta_f S_m^\circ}{R}$	$\frac{\Delta_f G_m^\circ}{R T}$
1,2,3,4-Tetrahydro-9-methylcarbazole							
298.15 ^{c,d}	53.65±0.06	0.00	54.12±0.07	0.00	37.55±0.14	-84.15±0.07	121.70±0.13
300.00 ^{c,d}	53.48±0.06	0.00	54.28±0.07	0.00	37.22±0.14	-84.25±0.07	121.47±0.13
320.00 ^{c,d}	51.76±0.05	0.00	55.96±0.06	0.00	33.91±0.13	-85.26±0.06	119.17±0.12
340.00 ^c	50.35±0.04	0.00	57.64±0.05	0.00	31.02±0.11	-86.18±0.05	117.21±0.12
360.00 ^c	49.18±0.03	0.00	59.31±0.05	0.00	28.48±0.11	-87.02±0.05	115.51±0.11
380.00	48.22±0.03	0.00	60.99±0.05	0.00	26.24±0.10	-87.79±0.05	114.03±0.11
400.00	47.44±0.03	0.00	62.66±0.05	0.00	24.26±0.10	-88.48±0.05	112.73±0.11
420.00	46.82±0.03	0.00	64.34±0.05	0.00	22.50±0.09	-89.09±0.05	111.59±0.10
440.00	46.32±0.03	0.01	66.01±0.05	0.01	20.93±0.09	-89.65±0.05	110.58±0.10
460.00	45.94±0.03	0.01	67.68±0.05	0.01	19.53±0.08	-90.16±0.05	109.69±0.10
480.00	45.66±0.03	0.02	69.34±0.06	0.02	18.27±0.08	-90.61±0.06	108.88±0.10
500.00	45.46±0.03	0.03	71.00±0.06	0.02	17.14±0.08	-91.02±0.06	108.16±0.10
520.00	45.33±0.04	0.05	72.65±0.06	0.04	16.12±0.08	-91.39±0.06	107.51±0.10
540.00	45.26±0.04	0.07	74.29±0.07	0.05	15.20±0.08	-91.72±0.07	106.91±0.10
560.00	45.24±0.06	0.10	75.92±0.08	0.07	14.36±0.09	-92.02±0.08	106.38±0.11
580.00	45.26±0.08	0.13	77.53±0.09	0.10	13.60±0.10	-92.28±0.09	105.88±0.12
600.00	45.32±0.10	0.18	79.13±0.11	0.13	12.91±0.11	-92.52±0.11	105.43±0.14
620.00	45.42±0.12	0.23	80.71±0.13	0.17	12.27±0.13	-92.75±0.13	105.02±0.16
640.00	45.53±0.14	0.30	82.27±0.15	0.22	11.69±0.15	-92.95±0.15	104.64±0.18
660.00	45.67±0.16	0.38	83.81±0.18	0.28	11.15±0.17	-93.13±0.18	104.28±0.20

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

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

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

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

END

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