The thermodynamic properties of 9-methylcarbazole and of 1,2,3,4-tetrahydro-9-methylcarbazole^{*a,b*}

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Measurements leading to the calculation of the standard thermodynamic properties of the gases are reported for 9-methylcarbazole and for 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. Standard molar entropies, enthalpies, and Gibbs energies of formation were derived for the gaseous state for each compound for selected temperatures between 298.15 K and near 700 K.

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 nitrogencontaining compounds present in heavy petroleum, shale oil, tar sands, and the

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products of the liquefaction of coal. Their fractionation produces nitrogen-rich distillates, which are poor-quality fuels. Catalytic hydrodenitrogenation (HDN) is a key step in the upgrading of these feedstocks.⁽¹⁻³⁾

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 modeling 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)⁽⁴⁾ and (quinoline + hydrogen)⁽⁵⁾ networks. This paper 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-amino-biphenyl were reported previously.^(6,7)

2-Aminobiphenyl is the first feasible hydrogenolysis (*i.e.* ring-opened) product in the HDN network for carbazole. Thermodynamic-equilibria calculations⁽⁷⁾ 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 to 2-aminobiphenyl to biphenyl) probably cannot be realized. However, the pathway (carbazole to 2-aminobiphenyl to 2-phenylcyclohexylamine to 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 $4H_2$ to reach the same stage on the pathway to nitrogen removal (*i.e.* one of the two C–N bonds broken) as that reached with $1H_2$ to form 2-aminobiphenyl. Figure 1 shows the initial steps in the two pathways.

Calculations of the thermodynamic equilibria obtained as the HDN reaction follows the ring saturation/hydrogenolysis pathways require a knowledge of the standard molar Gibbs energies of formation of carbazole and its hydrogenation products. Due to its high melting temperature (521 K), direct thermodynamicproperty measurements on carbazole are not possible with 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 both for measurements and subsequent reliable group-additivity estimates on the parent compound. In this paper, measurements leading to the thermodynamic properties of



FIGURE 1. Initial pathways in the hydrodenitrogenation of carbazole.

9-methylcarbazole and its initial stable hydrogenation product: 1,2,3,4-tetrahydro-9-methylcarbazole, are described. The compounds are shown in figure 2.

2. Experimental

The synthesis route for 1,2,3,4-tetrahydro-9-methylcarbazole is shown in figure 3. A mixture of $1.1CH_2 \cdot (CH_2)_4 \cdot CO$ (cyclohexanone) and $6.6CH_3 \cdot CO_2H$ (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, $1.1N(C_6H_5)(CH_3) \cdot NH_2$ (1-methyl-1-phenylhydrazine) was added over a period of 1 h. The mixture was refluxed for an additional 1 h 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.

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.



FIGURE 2. Compounds studied in this research.



FIGURE 3. Synthesis route to 1,2,3,4-tetrahydro-9-methylcarbazole. Conditions given in text.

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", $1.5CH_2 \cdot (CH_2)_4 \cdot CO$ and $9CH_3 \cdot CO_2H$ were combined and heated to reflux as described above. $1.5NH(C_6H_5) \cdot NH_2$ (phenylhydrazine) 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-tetrahydro-carbazole 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 mass per cent Pd/C catalyst in 0.5 dm³ of refluxing 1,2,4trimethylbenzene. After 3 h, 2 g of catalyst was added and reflux was continued for 4 h. The reaction mixture was cooled and 1.5 dm³ of acetone was added to dissolve the 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.

<u>Step "c"</u> of figure <u>4 was</u> performed by dissolution of the carbazole (1.08 $\underline{C} \cdot (\underline{CH})_4 \cdot \underline{C} \cdot \underline{N}(\underline{CH}_3) \cdot \underline{C} \cdot (\underline{CH})_4 \cdot \underline{C}$) (carbazole) in 0.9 dm³ of acetone and 1.92($\underline{CH}_3O_2 \cdot SO_2$ (dimethylsulfate) was added in one portion. A solution of 4.5NaOH in 0.12 dm³ of water was added dropwise over 0.3 h to the stirred mixture. After 2 h of stirring and refluxing, the product mixture was cooled and poured



FIGURE 4. Synthesis route to 9-methylcarbazole. Conditions given in text.

(ice + water) mixture. Crude 9-methylcarbazole precipitated into an $\{1.08C \cdot (CH)_4 \cdot C \cdot N(CH_3) \cdot C \cdot (CH)_4 \cdot C\}$. Purification was accomplished by Soxhlet extraction through basic alumina with petroleum ether (boiling range 318 K Crystallization from petroleum ether 323 K). gave to $0.8\overline{C} \cdot (CH)_4 \cdot \overline{C} \cdot N(CH_3) \cdot \overline{C} \cdot (CH)_4 \cdot \overline{C}$. 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.

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 MgSO₄, and distillation at the temperature 337 K and pressure 1 kPa.

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 elemental molar 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 by the method of McCrackin and Chang.⁽¹⁴⁾ Measurements of mass, time, electic resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

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 0.393_4 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-against-temperature curve is inherent in the quartz-crystal thermometer readings.⁽²²⁾

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

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

 \dagger The 1981 molar masses were used because the CODATA Recommended Key Values for Thermodynamics (reference 36) are based on them.

determined, and the vapor pressure was derived with the condensation temperature of the standard.⁽²⁶⁾

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

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

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:

$$\sigma(p)/Pa = 1.5 \cdot 10^{-4} (p/Pa) + 0.2.$$
 (2)

The uncertainties in the temperatures are 0.001 K.

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.

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
$\overline{r(T_{\max})}$	3.3
r _{min}	1.8
$10^2 \cdot (\delta C/C)_{\rm max}$	0.033
x _{pre}	0.00035

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

3. Results

NBS benzoic acid (sample 39i) was used for calibration of the combustion bomb calorimeter; its specific energy of combustion is $-(26434.0\pm3.0) \, J \cdot g^{-1}$ under certificate conditions. Conversion to standard states⁽³³⁾ gives $-(26413.7\pm3.0) \, J \cdot g^{-1}$ for $\Delta_c U_m^{\circ}/M$, 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 ϵ (calor) of the calorimeter obtained for the calibration series was (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}, ($\Delta_c U_m^{\circ}/M$) was $-16945 \, J \cdot g^{-1}$.⁽¹⁶⁾

1,2,3,4-Tetrahydro-9-methylcarbazole was burnt in the form of pellets. For each experiment $1.0 \cdot 10^{-3}$ dm³ of water was added to the bomb, and the bomb was flushed and charged to the pressure 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 $0.001 \cdot \Delta T$. All final experimental temperatures 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 $5 \cdot 10^{-7}$ m³·K¹⁻¹ 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 paper.

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 unburnt carbon and other products of incomplete combustion, but none was detected. Carbon-dioxide recoveries were (100.001 \pm 0.009) per cent (mean and standard deviation of the mean) for the calibrations and (99.995 \pm 0.015) per cent 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 $\Delta_c U_m^{\circ}/M$ for all the experiments are reported in table 3. All values of $\Delta_c U_m^{\circ}/M$ in table 3 relate to the reaction:

$$C_{13}H_{15}N(cr) + 16.75O_2(g) = 13CO_2(g) + 7.5H_2O(l) + 0.5N_2(g).$$
 (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

m'(compound)/g	0.910170
m"(fuse)/g	0.001725
$n_{\rm i}({\rm H}_2{\rm O})/{\rm mol}$	0.05535
m(Pt)/g	20.810
$\Delta T = (t_i - t_f + \Delta t_{corr})/K$	2.14287
$\epsilon(\text{calor}) \cdot (\Delta T) / J$	35660.8
$\varepsilon(\text{cont}) \cdot (\Delta T) / \mathbf{J}^{b}$	- 39.3
$\Delta U_{ m ign}/ m J$	0.8
$\Delta U_{\rm dec}({\rm HNO_3})/{\rm J}$	35.3
$\Delta U(\text{corr. to std. states})/J^c$	18.7
$-m'' \cdot (\Delta_{\rm s} U_{\rm m}^{\circ}/{\rm M})$ (fuse)/J	29.2
$m' \cdot (\Delta_c U_m^{\circ}/M)$ (compound)/J	-35616.1
$(\Delta_{\rm c} U_{\rm m}^{\circ}/M)$ (compound)/($J \cdot g^{-1}$)	- 39131.3

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

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

^b $\varepsilon_{i}(\text{cont})(t_{i}-298.15 \text{ K}) + \varepsilon_{f}(\text{cont})(298.15 \text{ K} - t_{f} + \Delta t_{corr}).$

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

of formation $\Delta_{\rm f} H_{\rm m}^{\circ}$ for 1,2,3,4-tetrahydro-9-methylcarbazole. Values of $\Delta_{\rm c} U_{\rm m}^{\circ}$ and $\Delta_{\rm c} H_{\rm m}^{\circ}$ refer to reaction (3). The values of $\Delta_{\rm f} H_{\rm m}^{\circ}$ refer to the reaction:

$$13C(cr, graphite) + 7.5H_2(g) + 0.5N_2(g) = C_{13}H_{15}N(cr).$$
 (4)

Uncertainties given in table 3 are the "uncertainty interval" defined in reference 35. The standard molar enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ were taken to be $-(393.51\pm0.13)$ and $-(285.830\pm0.042)$ kJ·mol⁻¹, respectively, as assigned by CODATA.⁽³⁶⁾

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 $0.1 \text{ kg} \cdot \text{m}^{-3}$ for densities within $\pm 500 \text{ kg} \cdot \text{m}^{-3}$ of the standard to 0.01 kg $\cdot \text{m}^{-3}$ for densities within $\pm 100 \text{ kg} \cdot \text{m}^{-3}$ of the standard to 0.01 kg $\cdot \text{m}^{-3}$ for 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 $\cdot \text{m}^{-3}$ at

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

$\{(\Delta_{\rm c} U_{\rm m}^{\circ}/M)({\rm compound})\}/({\rm J}\cdot{\rm g}^{-1})$								
- 39131.3	-39137.0 -39131.2 -39133.9 -39133.8 -39134.6							
	$ \begin{array}{ll} & \langle \{(\Delta_{\rm c} U_{\rm m}^{\circ}/M)({\rm compound})\}/({\bf J} \cdot {\bf g}^{-1}) \rangle & -39133.6 \pm 0.9 \\ & \{(\Delta_{\rm c} U_{\rm m}^{\circ})({\rm compound})\}/({\bf k} {\bf J} \cdot {\bf mol}^{-1}) & -7250.28 \pm 1.08 \\ & \{(\Delta_{\rm c} H_{\rm m}^{\circ}/M)({\rm compound})\}/({\bf k} {\bf J} \cdot {\bf mol}^{-1}) & -7258.33 \pm 1.08 \\ & \{(\Delta_{\rm f} H_{\rm m}^{\circ}/M)({\rm compound})\}/({\bf k} {\bf J} \cdot {\bf mol}^{-1}) & -1.02 \pm 1.26 \end{array} $							

T/K	$ ho/(kg \cdot m^{-3})$	$10^2 \cdot (ho - ho_{ m cs})/ ho$
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

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

^{*a*} ρ_{cs} , Density calculated using corresponding states, equation (7).

347.9 K to 66 kg \cdot m⁻³ at 423.7 K. Therefore, the expected accuracy of the densities of 1,2,3,4-tetrahydro-9-methylcarbazole is 0.01 kg \cdot m⁻³.

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 differences ΔT between condensation and boiling temperatures 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 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.

The Cox equation⁽³⁷⁾ in the form:

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

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 paper. 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.

Molar enthalpies of vaporization $\Delta_1^g H_m$ were derived from the Cox equation fits by means of the Clapeyron equation:

$$\mathrm{d}p/\mathrm{d}T = \Delta_{\mathrm{I}}^{\mathrm{g}} H_{\mathrm{m}} / (T \Delta_{\mathrm{I}}^{\mathrm{g}} V_{\mathrm{m}}). \tag{6}$$

 $\Delta_1^{g} V_m$ 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⁾

$$(\rho/\rho_{\rm c}) = 1.0 + 0.85 \{1.0 - (T/T_{\rm c})\} + (1.692 + 0.986\omega) \{1.0 - (T/T_{\rm c})\}^{1/3},\tag{7}$$

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 $\rho_c = 309$

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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 uncertainties in the pressures calculated from equations (1) and (2); ΔT is the difference between the boiling and condensation temperatures ($T_{boil} - T_{cond}$) for the sample in the ebulliometer

Method	$\frac{T}{K}$	$\frac{p}{\mathbf{kPa}}$	$\frac{\Delta p}{\mathbf{k}\mathbf{Pa}}$	$\frac{\sigma(p)}{kPa}$	$\frac{\Delta T}{K}$	Method	$\frac{T}{K}$	$\frac{p}{\mathbf{kPa}}$	$\frac{\Delta p}{\mathbf{k}\mathbf{P}\mathbf{a}}$	$\frac{\sigma(p)}{\mathbf{kPa}}$	$\frac{\Delta T}{K}$
					9-Metl	nylcarbazole					
IP	373.154	0.0163	0.0001	0.0002		decane	529.426	13.332	0.000	0.001	0.011
IP	383.152	0.0304	0.0000	0.0002		decane	537.572	16.665	0.001	0.001	0.009
IP	393.150	0.0550	0.0000	0.0002		decane	544.338	19.933	0.000	0.001	0.010
IP	403.152	0.0964	0.0002	0.0002		decane	553.236	25.023	0.001	0.001	0.006
IP	413.150	0.1628	0.0001	0.0002		water	553.232	25.023	0.004	0.001	0.005
IP	423.152	0.2674	0.0001	0.0002		water	562.186	31.177	0.002	0.002	0.002
IP	433.151	0.4271	0.0000	0.0003		water	571.191	38.565	0.001	0.002	0.002
IP	443.151	0.6654	0.0001	0.0003		water	580.244	47.375	-0.001	0.002	0.001
IP	453.151	1.0120	0.0000	0.0004		water	589.351	57.817	-0.005	0.003	0.001
IP	463.148	1.5059	-0.0002	0.0004		water	607.712	84.533	-0.005	0.004	-0.001
decane	470.622	2.0000	-0.0003	0.0001	0.096	water	616.968	101.325	-0.006	0.004	-0.002
IP	473.153	2.1964	-0.0002	0.0005		water	626.274	120.790	-0.004	0.005	-0.002
decane	478.494	2.6660	0.0002	0.0002	0.057	water	635.632	143.25	0.00	0.01	-0.001
IP	483.146	3.1420	-0.0001	0.0007		water	645.035	169.02	0.00	0.01	-0.002
decane	498.901	5.3330	0.0001	0.0003	0.032	water	654.490	198.49	0.01	0.01	0.001
decane	511.861	7.9989	0.0001	0.0004	0.027	water	663.992	232.02	0.01	0.01	0.002
decane	521.574	10.6661	0.0004	0.0005	0.018	water	673.539"	270.02	0.01	0.01	0.011
				1,2,3,4-	Tetrahyd	ro-9-methyl	carbazole	:			
IP	370.001	0.0173	-0.0001	0.0002		decane	522.498	13.332	0.000	0.001	0.016
IP	380.000	0.0330	0.0000	0.0002		decane	530.509	16.665	0.001	0.001	0.014
IP	390.000	0.0598	-0.0002	0.0002		decane	537.161	19.933	0.001	0.001	0.011
IP	400.002	0.1052	-0.0001	0.0002		decane	545.908	25.023	0.004	0.001	0.011
IP	410.004	0.1790	0.0002	0.0002		water	554.717	31.177	0.001	0.002	0.011
IP	420.006	0.2948	0.0003	0.0002		water	563.573	38,565	-0.001	0.002	0.011
IP	430.002	0.4719	0.0002	0.0003		water	572.478	47.375	-0.004	0.002	0.011
IP	439,999	0.7365	0.0004	0.0003		water	581.431	57.817	-0.003	0.003	0.014
IP	450.000	1.1218	0.0001	0.0004		water	590.433	70.120	0.003	0.003	0.018
IP	460.001	1.6718	0.0003	0.0005		water	599.498	84.533	-0.012	0.004	0.012
decane	464.679	2.0000	0.0000	0.0001	0.095	water	608.604	101.325	-0.012	0.004	0.012
IP	469,999	2.4390	-0.0006	0.0006		water	617.758	120.790	-0.008	0.005	0.013
decane	472.428	2.6660	-0.0004	0.0002	0.081	water	626.964	143.25	0.00	0.01	0.012
IP	475.003	2.9267	0.0003	0.0006		water	636.215	169.02	0.01	0.01	0.015
decane	492.487	5.3330	-0.0001	0.0003	0.054	water	645.516	198.49	0.02	0.01	0.018
decane	505.226	7.9989	0.0004	0.0004	0.032	water	654.835	232.02	0.15	0.01	0.036
decane	514.780	10.666	0.000	0.001	0.019						

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

kg·m⁻³, $T_c = 854$ 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 parameters given in table 6 were used to calculate p. The critical densities were estimates. The uncertainty in the liquid-phase volumes $V_m(l)$ was estimated to be $0.03 \cdot V_m(l)$. For 1,2,3,4-tetrahydro-9-methyl-

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

TABLE 6. Cox equation parameters

" Temperature range of the vapor pressures used in the fit.

carbazole in the temperature range 347 K to 424 K, a comparison of values calculated with 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 101.325 kPa. Uncertainties in the virial coefficients are reported in table 7. For p > 101.325 kPa the uncertainties in the

T/K	$\Delta_{\rm I}^{\rm g} H_{\rm m}/(R\cdot {\rm K})$	T/K	$\Delta_1^g H_m/(R \cdot K)$	T/K	$\Delta_{\rm I}^{\rm g} H_{\rm m}/(R\cdot{\rm K})$
		9-Meth	ylcarbazole		
298.15 <i>ª</i>	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 "	9188 + 4	540.00	7645 + 10	700.00 "	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	2,3,4-Tetrahydr	o-9-methylcarbazole		
298.15 ^a	9688 ± 18	440.00	8368 ± 2	580.00	7111 + 25
300.00 "	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		-		

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

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

F	T(F)/K	
0.1622	323.371	
0.3107	323.504	
0.5088	323.574	
0.7069	323.611	
$T_{\rm tr}/{ m K}$	323.71	
x	0.0015	
$K_{ m d}$	0.057	

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

virial coefficients are the dominant contributions to the uncertainties in the derived enthalpies of vaporization.

Crystallization of 1,2,3,4-tetrahydro-9-methylcarbazole in the adiabatic calorimeter was initiated by slowly cooling (approximately 2.5 mK \cdot 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 per cent to 20 per cent liquid) for approximately 8 h. No spontaneous warming, which would indicate incomplete crystallization, was observed in this period. The sample was cooled at an effective rate of 2 mK \cdot s⁻¹ to crystallize the remaining liquid. Finally, the sample was thermally cycled from <100 K to within 2 K of the triple-point temperature, where it was held for at least 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 h 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 solidsoluble 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.

Experimental molar enthalpies 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-offusion results. This implies that phase cr(I) was formed reproducibly by means of the tempering methods described above. The sample showed four solid phases with a

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N ª	h ^b	$\frac{T_{i}}{K}$	$\frac{T_{\rm f}}{{ m K}}$	$rac{T_{ m trs}}{ m K}$	$\frac{\Delta_{\rm tot}H_{\rm m}}{R\cdot {\rm K}}^{a}$	$\frac{\Delta_{\rm trs}H_{\rm m}}{R\cdot \rm K}^{d}$
		Single	e-phase measuren	nents 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	-13^{e}
12	1	101.830	111.259	105.0	114.95	-1.2 °
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	e-phase measuren	nents 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	i	160.780	167.323	10217	196.07	81.8
20	2	161.989	166.771		164.53	81.3 °
					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
		Sing	le-phase measure	ments in cr(I)		
20	1	214.631	308.748		2392.40	0.5
5	1	282.419	319.204		1082.95	1.1
			cr(I) to liqu	uid		
4	2	318 867	326 242	323 71	2013.09	1764.4
5	õ	319,147	326.341	020111	2007.11	1763.6
22	2	315.938	327.294		2143.91	1764.0
					Average:	1764.0
		Single	e-phase measuren	nents 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

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

^a Adiabatic series number. ^b Number of heating increments. ^{cs} $\Delta_{tot}H_m$ 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 to the heat-capacity curve described in the text for single-phase measurements. ^e This value was not included in the average. See text.



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.

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 a period of ≈ 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 h, 160 h, 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 d. 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 a period of ≈ 2 d of annealing near 103 K. Prior to measurements of the transition enthalpy, the sample was



FIGURE 6. Average heat capacities in the cr(II)-to-cr(I) transition region for 1,2,3,4-tetrahydro-9-methylcarbazole. \Box , Series 3; \bullet , series 6; \bigcirc , 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. \Box , Series 3; \blacktriangle , series 8; \bigcirc , series 9; \triangle , series 13; \textcircledline , 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.

N ^b	$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{\Delta T}{K}$	$\frac{C_{\rm sat,m}}{R}^c$	N ^b	$\frac{\langle T \rangle}{K}$	$\frac{\Delta T}{\mathrm{K}}$	$\frac{C_{\rm sat,m}}{R}^{c}$
			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
			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
			cr	(I)			
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

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	$\frac{\langle T \rangle}{\mathrm{K}}$	$\frac{\Delta T}{K}$	$\frac{C_{\rm sat,m}}{R}^{c}$	N ^b	$\frac{\langle T \rangle}{K}$	$\frac{\Delta T}{K}$	$\frac{C_{\rm sat,m}}{R}^{c}$
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
			lig	uid			
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				

TABLE 10—continued

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

^b Adiabatic series number.

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

annealed between 100 K and 103 K for 45 h, 80 h, 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.

The experimental molar heat capacities under vapor saturation pressure $C_{\text{sat,m}}$ 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 $C_{\text{sat,m}}$ 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 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),



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; \bigcirc , series 12; \bigcirc , series 14; \square , series 18; \blacksquare , series 19; $\textcircled{\bullet}$, 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.

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, and 5 h at 320 K. Estimation of the heat capacities to $T \rightarrow 0$ was made by linear extrapolation of a plot of $C_{\text{sat, m}}/T$ against T^2 for results below 10 K.

The theoretical background for the determination of molar heat capacities $C_{\text{sat,m}}$ for the liquid phase at vapor-saturation pressure 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 $C_{x,m}^{\text{II}}$ at cell volume V_x can be expressed in terms of the temperature derivatives of these quantities:

$$nC_{\mathbf{x},\mathbf{m}}^{\Pi}/T = -n(\partial^2 \mu/\partial T^2)_{\mathrm{sat}} + V_{\mathbf{x}}(\partial^2 p/\partial T^2)_{\mathrm{sat}} + (\partial V_{\mathbf{x}}/\partial T)_{\mathbf{x}}(\partial p/\partial T)_{\mathrm{sat}}.$$
(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:

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

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

Values of $(\partial p/\partial T)_{sat}$ were calculated based on the vapor pressures measured in this research. Therefore, with a minimum of two different filling levels of the cell, $(\partial^2 p/\partial T^2)_{sat}$ and $(\partial^2 \mu/\partial T^2)_{sat}$ can be determined. In this research three fillings were

m/g V(cell)/cm ^{3 a}	0.010714 0.05387	0.018054 0.05570	0.029730 0.05409	0.009255 0.05288	0.028222 0.05288	0.021491 0.05288
T/K	$C_{\rm x,m}^{\rm II}/R$					
	1,2,3,4-Tetr	ahydro-9-meth	ylcarbazole	9-	Methylcarbazo	ole
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

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

^a Volume measured at 298.15 K.

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.* $(n/V_x) \rightarrow \{1/V_m(l)\}$ where $V_m(l)$ is the molar volume of the liquid:

$$\lim_{(n/V_x)\to\{1/V_m(l)\}} (nC_{V,m}^{II}/T) = V_m(l)(\partial^2 p/\partial T^2)_{sat} - n(\partial^2 \mu/\partial T^2)_{sat}.$$
 (10)

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

$$\lim_{(n/V_x)\to\{1/V_m(l)\}} (nC_{V,m}^{II}) = n[C_{\text{sat},m} - \{T(\partial p/\partial T)_{\text{sat}}(dV_m(l)/dT)\}].$$
(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 K \cdot s⁻¹ and a 120 s equilibration period between heatings. Sample decomposition precluded heat-capacity measurements above 760 K for 9-methylcarbazole and above 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 heating at a rate of 0.333 K \cdot 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. $C_{sat,m}$ 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 $(\partial p/\partial T)_{sat}$.

$$C_{V,m}^{\mathrm{II}} = C_{\mathrm{x},m}^{\mathrm{II}} - (T/n) \{ (\partial V_{\mathrm{x}}/\partial T)_{\mathrm{x}} (\partial p/\partial T)_{\mathrm{sat}} \}.$$
(12)

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

$$\ln(p/p_{\rm c}) = (1 - 1/T_{\rm r})\exp(A + BT_{\rm r} + CT_{\rm r}^2), \tag{13}$$

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:

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

For compounds where sufficient information was available to evaluate reliably $(\partial^2 \mu / \partial T^2)_{sat}$ (e.g. benzene),⁽⁴⁷⁾ four terms (*i.e.* expansion to j = 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 was minimized:

$$\Delta = C_{V,m}^{II}/R - \{V_m(I)T/nR\}(\partial^2 p/\partial T^2)_{sat} + (T/R)(\partial^2 \mu/\partial T^2)_{sat}.$$
(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 $C_{V,m}^{II}(\rho = \rho_{\text{sat}})$ with densities obtained using equation (7). The results for $C_{V,m}^{II}(\rho = \rho_{\text{sat}})/R$ and $C_{\text{sat,m}}/R$ are reported in table 13°. The estimated uncertainty in these values is 1 per cent. Differences between $C_{V,m}^{II}(\rho = \rho_{\text{sat}})/R$ 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⁾

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-methyl carbazole 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.)

		9-Methy	lcarbazole	
A	2.58407		b_0	-0.45003
В	-1.30663		b_1	-1.31438
С	0.81455		b_2	2.64332
			b_3	-2.65174
	$T_{\rm c} = 890 {\rm ~K}$	$p_{\rm c} = 3376 \text{ kPa}$	$ ho_{\rm c} = 317 \; {\rm kg} \cdot {\rm m}^{-3}$	$\omega = 0.473$
		1,2,3,4-Tetrahydro	o-9-methylcarbazole	
A	2.62392		b_0	-0.54101
В	-1.28111		b_1	-1.27334
С	0.76201		b_2	2.23873
			b_3	-1.98844
	$T_{\rm c} = 854 {\rm ~K}$	$p_{\rm c} = 2709 \text{ kPa}$	$ ho_{\rm c} = 309 \ {\rm kg} \cdot {\rm m}^{-3}$	$\omega = 0.521$

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

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

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 leastsquares 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

T/K	$C_{V,m}^{\mathrm{ll}}(ho= ho_{\mathrm{sat}})/R$	$C_{\rm sat,m}/R$	T/K	$C_{V,\mathrm{m}}^{\mathrm{II}}(ho= ho_{\mathrm{sat}})/R$	$C_{\rm sat,m}/R$
		9-Methylo	carbazole		
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-methylcarbaz	ole	
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 13. Values of $C_{V,m}^{II}(\rho = \rho_{sat})/R$ and $C_{sat,m}/R$ $(R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$

$\frac{T}{K}$	$\frac{C_{\rm sat,m}}{R}$	$\frac{\Delta_0^T S_{\mathbf{m}}^{\circ}}{R}$	$\frac{\Delta_0^T H_{\rm m}^{\circ}}{RT}$	$\frac{T}{K}$	$rac{C_{\mathrm{sat,m}}}{R}$	$\frac{\Delta_0^T S_{\mathbf{m}}^{\circ}}{R}$	$\frac{\Delta_0^T H_{\rm m}^{\circ}}{RT}$
			cr(IV)			
5.00	0.047	0.016	0.012	60.00	7.563	5.547	3.414
10.00	0.384	0.127	0.096	65.00	8.171	6.177	3.757
15.00	1.052	0.402	0.297	70.00	8.745	6.803	4.093
20.00	1.843	0.812	0.584	75.00	9.280	7.425	4.421
25.00	2.643	1.309	0.916	80.00	9.790	8.040	4.741
30.00	3.413	1.859	1.268	85.00	10.277	8.649	5.052
35.00	4.165	2.442	1.628	90.00	10.743	9.249	5.355
40.00	4.889	3.046	1.991	95.00	11.188	9.842	5.651
45.00	5.589	3.662	2.352	100.00	11.612	10.427	5.938
50.00	6.277	4.287	2.710	102.00 ^b	11.787	10.659	6.051
55.00	6.938	4.916	3.065	103.80 ^b	11.951	10.866	6.152
			cr(III)			
103.80 ^b	12.119	10.866	6.152	150.00	16.213	16.024	8.610
105.00	12.223	11.006	6.221	153.00	16.514	16.348	8.762
110.00	12.658	11.585	6.504	156.00	16.848	16.672	8.914
120.00	13.523	12.723	7.052	158.00	17.114	16.888	9.016
130.00	14.384	13.840	7.583	160.00^{b}	17.436	17.105	9.120
140.00	15.278	14.938	8.101	162.00 ^b	17.814	17.324	9.225
145.00	15.739	15.482	8.356	162.40 ^b	17.896	17.368	9.246
			cr	(II)			
162.40 ^b	17.253	17.871	9.749	195.00	20.080	21.254	11.218
164.00 ^b	17.340	18.041	9.823	200.00	20.668	21.770	11.447
166.00 ^b	17.444	18.252	9.914	202.00	20.920	21.977	11.539
168.00	17.558	18.461	10.004	204.00	21.175	22.184	11.632
170.00	17.697	18.670	10.094	206.00	21.433	22.392	11.726
175.00	18.145	19.189	10.317	208.00	21.698	22.600	11.821
180.00	18.615	19.707	10.541	210.00^{b}	21.983	22.809	11.916
185.00	19.095	20.223	10.766	210.40^{b}	22.043	22.851	11.936
190.00	19.585	20.739	10.991				
			cr	(I)			
210.40^{b}	21.036	22.851	11.936	280.00	27.090	29.618	14.891
215.00	21.305	23.309	12.133	290.00	28.124	30.586	15.329
220.00	21.633	23.802	12.345	298.15	29.027	31.378	15.691
230.00	22.391	24.780	12.765	300.00	29.244	31.558	15.774
240.00	23.251	25.751	13.184	310.00	30.486	32.537	16.228
250.00	24.162	26.719	13.605	320.00 ^b	31.872	33.526	16.695
260.00	25.111	27.685	14.029	323.71 ^b	32.429	33.897	16.872
270.00	26.092	28.651	14.457				
			liq	uid			
298.15 ^b	34.953	36.396	21.159	480.00	48.301	55.987	28.931
300.00 ^b	35.085	36.613	21.245	500.00	49.700	57.987	29.734
320.00^{b}	36.535	38.923	22.155	520.00	51.141	59.965	30.530
323.71 ^b	36.808	39.346	22.321	540.0	52.48	61.92	31.32
340.00	38.016	41.183	23.044	560.0	53.80	63.85	32.10
360.00	39.516	43.398	23.918	580.0	55.09	65.76	32.87
380.00	41.022	45.575	24.778	600.0	56.33	67.65	33.63
400.00	42 521	47 717	25 628	620.0	57 50	60.52	24 28

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

$\frac{T}{K}$	$rac{C_{\mathrm{sat,m}}}{R}$	$\frac{\Delta_0^T S_{\rm m}^{\circ}}{R}$	$\frac{\Delta_0^T H_{\rm m}^{\circ}}{RT}$	$\frac{T}{K}$	$rac{C_{\mathrm{sat,m}}}{R}$	$\frac{\Delta_0^T S_{\rm m}^{\circ}}{R}$	$\frac{\Delta_0^T H_{\rm m}^{\circ}}{RT}$
420.00 440.00 460.00	44.006 45.467 46.898	49.828 51.909 53.962	26.468 27.298 28.120	640.0 660.0	58.61 59.66	71.36 73.18	35.12 35.85

TABLE 14—continued

^a Values listed in this table are reported with one digit more than is justified by the experimental uncertainty to avoid round-off errors in the calculation of values listed in table 15.

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

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.

Standard molar enthalpies and entropies at selected temperatures for the gaseous state were calculated using values in tables 7 and 14 and are listed in columns 2 and 4 of table 15. Molar entropies and enthalpies of compression to 101.325 kPa were calculated based on the virial equation truncated as follows:

$$pV_{\rm m} = RT + Bp + C'p^2. \tag{16}$$

Formulations used to calculate the molar entropy and enthalpy of compression are: $^{(48)}$

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

$$\Delta H_{\rm comp,\,m} = \{B - T(dB/dT)\}p + \{C' - T(dC'/dT)\}(p^2/2).$$
(18)

Equatios (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 molar 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 molar entropy of compression. Equation (18) gives the "gas-imperfection correction" to the molar enthalpy of compression directly. ($\Delta H_{\rm comp,\,m} = 0$ for the ideal gas.) The gas-imperfection corrections are listed in table 15. Uncertainties in these values are difficult to assess because temperature derivatives of estimated values are involved. Uncertainties of 10 per cent of the calculated corrections were assumed.

^s The derived standard molar enthalpies and entropies for gaseous 1,2,3,4tetrahydro-9-methylcarbazole were combined with the condensed-phase enthalpy of formation given in table 3 to calculate the standard molar 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

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

$\frac{T}{K}$	$\frac{\Delta_0^T H_{\rm m}^{\circ}}{RT}$	$\frac{\Delta_{\rm imp}H_{\rm m}^{\circ}}{RT}^{a}$	$\frac{\Delta_0^T S_{\rm m}^{\circ}}{R}$	$\frac{\Delta_{\rm imp}S_{\rm m}^{\circ}}{R}^{b}$	$\frac{\Delta_{\rm f} H_{\rm m}^{\circ}}{RT}$	$\frac{\Delta_{\rm f} S_{\rm m}^{\circ}}{R}$	$rac{\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\mathrm{o}}}{RT}$				
	9-Methylcarbazole										
298.15 ^{c,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 ^{c,d}	51.83 <u>+</u> 0.04	0.00	50.44 ± 0.05	0.00	79.76 ± 0.20	-56.64 ± 0.05	136.39 ± 0.20				
320.00 ^{c,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 ^{c,d}	48.73 ± 0.03	0.00	53.63 <u>+</u> 0.04	0.00	69.22 ± 0.18	-57.87 ± 0.04	127.09 ± 0.18				
360.00 ^{c,d}	47.54 ± 0.02	0.00	55.19 <u>±</u> 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 <u>+</u> 0.04	0.00	60.92 <u>+</u> 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 <u>+</u> 0.16				
420.00	45.01 <u>+</u> 0.03	0.00	59.77 <u>+</u> 0.05	0.00	54.25 <u>+</u> 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 <u>+</u> 0.07	0.01	48.80 <u>+</u> 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 <u>+</u> 0.10	0.02	44.27 <u>+</u> 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 <u>+</u> 0.14	0.04	40.47 ± 0.16	-61.81 <u>+</u> 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 <u>+</u> 0.17	0.08	37.25 <u>+</u> 0.18	-62.25 ± 0.17	99.51 ± 0.24				
600.00	42.64 ± 0.16	0.14	72.90 <u>±</u> 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 <u>+</u> 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 <u>+</u> 0.29	0.33	30.04 ± 0.25	-63.15 ± 0.29	93.19 <u>+</u> 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 <u>+</u> 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				
		1	,2,3,4-Tetrahyo	lro-9-methy	lcarbazole						
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 <u>+</u> 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 <u>+</u> 0.06	0.00	33.91 ± 0.13	-85.26 ± 0.06	119.17 ± 0.12				
340.00 °	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 <u>+</u> 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 <u>+</u> 0.08	-90.16 ± 0.05	109.69 ± 0.10				
480.00	45.66 ± 0.03	0.02	69.34 <u>+</u> 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 <u>+</u> 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 <u>±</u> 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 ± 0.1 h	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 included in the standard molar enthalpy of the gas.
 ^b Gas-imperfection correction included in the standard molar entropy of the gas.
 ^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.

by Good⁽¹⁰⁾ and Jiménez *et al.*⁽⁴⁹⁾ The value reported by Good: $\Delta_c U_m^{\circ} = -(6787.6 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$ was revised slightly in this research to $\Delta_c U_m^{\circ} = -(6786.6 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$. 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 $\Delta_f H_m^{\circ} = (104.1 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$ employed here for the calculations of standard quantities for the gas is derived from the average of the energy-of-combustion values.

Standard molar enthalpies and entropies for $N_2(g)$ and equilibrium $H_2(g)$ were determined from JANAF tables.⁽⁵¹⁾ Values for C(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. This convention is used because uncertainties due to the elements cancel in equilibria calculations.

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 standard molar thermodynamic functions of the gas (table 15) and of 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:

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

in the temperature region 298.15 K to 362.5 K with $p_0 = 1$ Pa.

4. Discussion

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

All crystal-to-crystal transformations encountered in the adiabatic calorimetric measurements of the heat capacity of 1,2,3,4-tetrahydro-9-methylcarbazole were termed "phase transitions". The nature of the structural changes associated with these events is unknown. Crystal structures determined by X-ray crystallography above and below $T_{\rm trs}$ might or might not show a clear difference. The structural changes might be associated with a subtle event, such as the onset of a molecular rotation or vibration which is restricted in the low-temperature form.

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.



FIGURE 9. 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. \bullet , Jiménez *et al.*⁽⁴⁹⁾

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