

## **Comparison of heat capacities measured by adiabatic calorimetry and by scanning calorimetry: thermodynamic properties of 9-methylcarbazole at temperatures between 4 K and 345 K <sup>a</sup>**

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We have measured the heat capacity of 9-methylcarbazole at  $4 \leq T/\text{K} \leq 345$  by adiabatic calorimetry and compared it with that measured by differential scanning calorimetry (d.s.c.) at  $120 \leq T/\text{K} \leq 355$ . The d.s.c. measurements were made by both a scanning method and by an enthalpic, or intermittent heating, method. The molar heat capacities  $C_{p,m}$  determined by d.s.c. agreed with the values obtained by adiabatic calorimetry within the usual error associated with d.s.c., about  $0.01 \cdot C_{p,m}$ . No anomalies or transitions were observed up to 350 K. Thermodynamic functions obtained from these values are tabulated at selected temperatures.

### **1. Introduction**

Facilities for the determination of heat capacities by classical precision calorimetry, commonly considered an “absolute” measurement, have become scarce in the Western Hemisphere. This decrease has been paralleled by a meteoric rise in the number of commercially available comparative instruments that can be used to determine heat capacity.<sup>(1)</sup> These heat capacities lead in turn to the determination of thermodynamic properties. A serious need exists for basic thermodynamic values for

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a variety of materials over wide temperature ranges, particularly at  $400 \leq T/K \leq 1000$ . This temperature region is rarely accessible to adiabatic calorimetry and can be difficult for drop calorimetry, two of the classical techniques used for heat-capacity determinations.

The study described in this paper had three aims. First, we wished to evaluate the capability of differential scanning calorimetry (d.s.c.), a widely used comparative tool, for the determination of thermodynamic properties of materials. The d.s.c. has significant advantages. The accessible temperature range ( $120 \leq T/K \leq 1500$ ) is large. Small samples (mg) are sufficient. The instrument is readily available commercially at relatively low cost. Its operation is simple by comparison with most adiabatic or drop calorimeters. Major disadvantages include the comparative nature of the measurements, the requirement for suitable reference materials, extreme sensitivity to manipulative techniques, and the need for time-consuming replicate measurements.

Second, we wished to determine whether it was feasible to use a d.s.c. to develop reference materials for use in the calibration and correction of heat-capacity measurements made with a d.s.c., an admittedly unorthodox procedure. The Boulder Laboratory of NIST has had considerable success in the development of reference materials for temperature and enthalpy of transition, by d.s.c., for use with d.s.c. Normally a reference material is developed by an absolute technique, by two independent techniques, or by one comparative technique accompanied by round-robin results. Because of differences in behavior of various materials in a d.s.c., particularly differences related to thermal conductivity, there is a need for reference substances suitable for use with different types of materials. Efforts to accomplish these certifications by precision calorimetry had proved largely impractical. At the request of various standards groups, studies were undertaken in the Boulder Laboratory to determine the feasibility of the use of d.s.c. for these purposes. The results of these studies<sup>(2, 3)</sup> and of subsequent work demonstrate the utility of these methods for temperature and enthalpy of transition. Recent results obtained by both precision calorimetry and d.s.c. are given in table 1.

Our third aim was to study a pure compound, for which heat-capacity results had not been published, by both adiabatic calorimetry and by d.s.c. Because very pure 9-methylcarbazole was available and no published results were found in the literature, we proceeded with the measurements. After their completion, measurements of the heat capacity of 9-methylcarbazole made in 1958 were brought

TABLE 1. Comparison of measurements of transition temperatures and specific enthalpies of transition

	$T/K$	$\Delta_{\text{trs}} h / (\text{J} \cdot \text{g}^{-1})$
	Tin (same lot)	
Drop calorimetry d.s.c.	$505.10 \pm 0.01$	$60.22 \pm 0.19^{(4)}$
	$505.11 \pm 0.14$	$60.15 \pm 0.15^{(5)}$
	Biphenyl (different lots)	
Adiabatic calorimetry d.s.c.	342.098	$120.45 \pm 0.02^{(6)}$
	$342.42 \pm 0.27$	$120.41 \pm 0.57^{(7)}$

to our attention. These results have since been published and will be compared with the present measurements.<sup>(8)</sup>

Several factors affect the accuracy and precision of d.s.c. measurements. Equipment design is a prime consideration. Whether a particular instrument design is suitable for heat-capacity determinations must be evaluated by comparison of results obtained with that instrument for a reference material with the accepted values. It is essential that the values be adjusted, or calibrated, through concurrent measurements of a suitable reference material.<sup>(9)</sup> If a reference material similar to the material to be studied (liquid, metal, inorganic, organic) is available, it should be used.<sup>(10,11)</sup> Internal instrument-calibration routines are not a substitute for adjustment of values with results for a reference material. These chemical calibrations, so called because chemical substances are used, are particularly necessary for heat capacities because the specific energies measured ( $\approx 0.3 \text{ J} \cdot \text{g}^{-1}$ ) are small by comparison with transition energies ( $\approx 11 \text{ J} \cdot \text{g}^{-1}$  to  $\approx 160 \text{ J} \cdot \text{g}^{-1}$ ). Replicate specimens are required; at least one specimen should be rerun to evaluate potential irreversibility.<sup>(12)</sup>

Samples should be either very pure or homogeneous or, for an inhomogeneous substance, representative. The specimens should be relatively large, of mass at least 8 mg to 15 mg, and prepared so that they are in good thermal contact with the specimen pan. The heating rate should ensure either that temperatures are uniform throughout the specimen or that the temperature gradient is negligible by comparison with other potential errors. The placement of the specimen cell in the calorimeter should be stable throughout the measurement and readily reproducible. Inconsistent placement of specimens, and of lids if they are used, will cause significant variability and non-reproducibility in the results.

Two methods are in general use for heat-capacity measurements: scanning and enthalpic. In the scanning method, measurements are made by heating continuously over relatively wide temperature ranges. Heat capacities are determined from the displacement of the curves for the empty pan, the standard, and the sample from the isothermal baseline. The enthalpic method, which is so named because heat capacities are determined from  $C_{p,m} = \Delta H_m / \Delta T$ , utilizes an intermittent heating procedure that allows for return to the isothermal baseline and equilibration every few kelvins, as is done in adiabatic calorimetry.<sup>(13-17)</sup>

## 2. Experimental

The 9-methylcarbazole (*N*-methylcarbazole, CAS Registry # 1484-12-4) used in this study was an American Petroleum Institute Standard Reference Material.<sup>(18)</sup> It is certified as  $(99.995 \pm 0.005)$  moles per cent pure and was used as received.

For the adiabatic calorimetry, a mass of 7.481003 g ( $\cong 0.04127745$  mol, based on the IUPAC 1985 scale) was placed in a gold-plated copper calorimeter (laboratory designation W-99) with four internal vanes and a central entrant well for (thermometer + heater).<sup>(19)</sup> For buoyancy corrections, a calculated crystallographic density of  $1.21 \text{ g} \cdot \text{cm}^{-3}$ , as determined from the structural studies of Popova and Chetkina,<sup>(20)</sup> was used.

After loading, the calorimeter was evacuated and helium gas was added to the vessel to a pressure of 2.4 kPa to facilitate thermal equilibration. The vessel was then sealed with an annealed gold gasket that was pressed tightly on to a stainless-steel knife edge of the calorimeter top by means of a screw closure about 5 mm in diameter.

The molar heat capacity  $C_{p,m}$  was measured at  $7 < T/K < 344$  in the Mark XIII adiabatic cryostat, which is an updated version of the Mark II cryostat described previously.<sup>(19)</sup> A guard shield was incorporated to surround the adiabatic shield. A Leeds and Northrup capsule-type platinum resistance thermometer (laboratory designation A-5) was used for temperature measurements. The thermometer was calibrated at the U.S. National Bureau of Standards (N.B.S., now NIST) against the IPTS-1948 (as revised in 1960)<sup>(21)</sup> for temperatures above 90 K, against the N.B.S. (NIST) provisional scale at  $10 \leq T/K \leq 90$ , and by the technique of McCrackin and Chang<sup>(22)</sup> below 10 K. These calibrations are judged to reproduce thermodynamic temperatures to within 0.03 K at  $10 \leq T/K \leq 90$  and within 0.04 K above 90 K.<sup>(23)</sup>

For the acquisition of heat capacities, the controlling computer<sup>(24, 25)</sup> was programmed for a series of determinations. During the drift periods, the computer recorded both the calorimeter temperature and the first and second derivatives of temperature with time. This allowed the equilibrium temperature of the calorimeter to be established before and after the energy input. While the calorimeter was heating, the magnitude of the heater current and potential and the duration of the heating interval were obtained. Also recorded were the apparent heat capacities of the system, which included the calorimeter, heater, thermometer, and sample.

Specimens for the d.s.c. measurements were prepared both from material used for the adiabatic measurements and from material which had not been previously heated. Specimens ranged in mass from 1.835 mg to 12.515 mg; they were pelletized with hand pressure in a commercial pellet press. The hermetic aluminum cells were sealed in a nitrogen atmosphere.

The procedures normally used in the Boulder laboratory for the preparation of the d.s.c. were followed.<sup>(9)</sup> For calibration of the temperature scale of the instrument, fusion temperatures of 2,2-dimethylbutane (125.81 K),<sup>(26)</sup> mercury (234.30 K),<sup>(27, 28)</sup> and naphthalene (353.39 K),<sup>(29)</sup> were used. Calorimetry Conference sapphire<sup>(30)</sup> was used as the reference material for the calibration of the d.s.c. heat-capacity results. Sapphire was selected as the reference material for its stability and because it is the only reference material certified for heat capacity over the range of measurements to be made.

Heat capacities reported here were determined from measurements made in the heating mode at  $0.083 \text{ K} \cdot \text{s}^{-1}$  over various ranges at  $125 \leq T/K \leq 350$ . Additional measurements were made at a scan rate of  $0.021 \text{ K} \cdot \text{s}^{-1}$ . In the lower-temperature regions, cooling was provided by a liquid-nitrogen reservoir; for higher-temperature series of measurements, a mechanical refrigeration system was used. For measurements made with liquid nitrogen as coolant, a mixture of helium and neon was used as purge gas rather than the argon used as purge gas at higher temperatures.

The d.s.c. measurements were made both by the commonly used scanning method

and by an enthalpic method, the software for which was developed in our laboratory. For the enthalpic studies, 10 K temperature intervals were used. For one series of measurements the intervals were chosen to provide heat-capacity values at 120 K, 130 K,  $\dots$ ; in an alternate series, the intervals provided values at 125 K, 135 K,  $\dots$ . In this way, heat-capacity values over the entire temperature range were obtained at 5 K intervals. The ranges over which these measurement series extended were  $120 \leq T/K \leq 220$ ,  $170 \leq T/K \leq 280$ ,  $200 \leq T/K \leq 250$ ,  $220 \leq T/K \leq 320$ ,  $220 \leq T/K \leq 355$ ,  $225 \leq T/K \leq 355$ , and  $300 \leq T/K \leq 350$ . Scanning measurements covered the temperature intervals:  $120 \leq T/K \leq 235$ ;  $120 \leq T/K \leq 280$ ;  $235 \leq T/K \leq 355$ ;  $300 \leq T/K \leq 350$ .

The heat-capacity values were corrected for differences in pan mass by use of the procedures suggested by Luebke and Tria,<sup>(31)</sup> the required equation for the heat capacity of aluminum was derived from the work of Giauque and Meads<sup>(32)</sup> and McDonald.<sup>(33)</sup> The corrected values were transmitted to the computer for further correction and fitting.<sup>(9, 12)</sup> The accuracy of the heat-capacity measurements, at the calibration settings for temperature range and for type of measurement, was assessed through comparison of values obtained for sapphire, treated as a sample, with the literature values.<sup>(9)</sup> Precision for each set of measurements was determined from the deviations from the fitted curve.<sup>(9, 12)</sup>

### 3. Results and discussion

The experimental molar heat capacities for 9-methylcarbazole, as determined by adiabatic calorimetry, are presented in table 2. As there was no evidence that the  $C_{p,m}$  values depended on the thermal history of the sample, they are given in the order of increasing temperature. The estimated errors in these heat capacities decrease from  $\approx 0.01 \cdot C_{p,m}$  at 10 K to  $< 0.005 \cdot C_{p,m}$  at temperatures above 30 K. The

TABLE 2. Experimental molar heat capacity of 9-methylcarbazole ( $M = 181.23704 \text{ g} \cdot \text{mol}^{-1}$ ;  $R = 8.31452 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) determined by low-temperature adiabatic calorimetry

$T/K$	$C_{p,m}/R$	$T/K$	$C_{p,m}/R$	$T/K$	$C_{p,m}/R$	$T/K$	$C_{p,m}/R$	$T/K$	$C_{p,m}/R$
9.41	0.4915	31.16	3.883	100.62	10.57	189.70	16.85	282.17	24.81
10.18	0.5982	33.66	4.337	106.09	10.67	197.60	17.48	287.81	25.35
11.04	0.7164	36.49	4.655	111.62	11.04	203.23	17.91	293.46	25.85
11.91	0.8453	39.49	4.970	117.13	11.50	208.85	18.41	299.11	26.37
12.79	0.9845	42.75	5.298	122.66	11.78	214.47	18.90	307.74	26.90
13.69	1.121	46.24	5.670	128.20	12.21	220.11	19.37	310.37	27.33
14.60	1.283	49.97	6.064	133.74	12.61	225.73	19.90	316.02	27.90
15.51	1.436	54.17	6.486	139.32	12.95	231.37	20.31	321.67	28.45
16.65	1.631	58.86	6.909	144.88	13.44	237.01	20.84	327.31	29.01
18.00	1.858	63.62	7.369	150.47	13.77	242.65	21.33	332.96	29.54
19.36	2.083	68.66	7.830	156.06	14.22	248.28	21.80	338.61	30.05
20.94	2.354	73.95	8.184	161.64	14.67	253.92	22.35	344.26	30.61
22.74	2.645	79.26	8.624	167.24	15.18	259.58	22.74		
24.55	2.930	84.44	9.162	172.85	15.49	265.22	23.26		
26.60	3.238	89.68	9.580	178.46	15.97	270.87	23.80		
28.87	3.563	95.14	9.811	184.07	16.41	276.52	24.29		

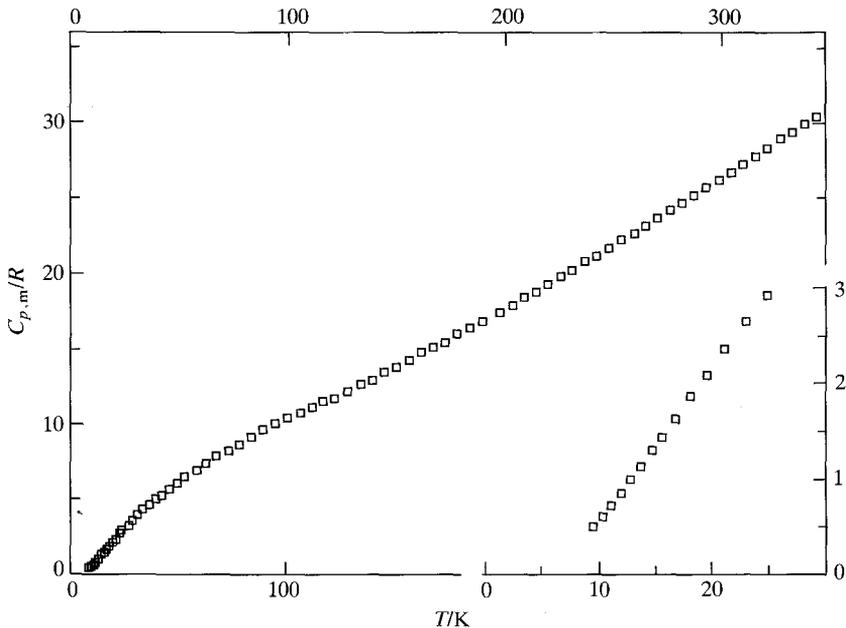


FIGURE 1. Experimental molar heat capacities  $C_{p,m}$  at constant pressure plotted against temperature.

sample heat capacity represented from 0.42 to 0.78 of the total measured heat capacity.

A plot of  $C_{p,m}$  against  $T$  at  $4 \leq T/K \leq 345$  is shown in figure 1. No transitions or anomalies were observed up to 350 K. Smoothed values were obtained from a large plot of the experimental heat capacities. Integration of these smoothed values yielded the thermodynamic functions. Values of  $C_{p,m}/R$  and the derived functions are presented at selected temperatures in table 3. The heat capacity of 9-methylcarbazole below 9 K was determined by fitting our experimental values below 20 K to the limiting form of the Debye equation with a plot of  $C_v$  against  $T^2$  and extrapolating to  $T \rightarrow 0$ .

The recently published values of the heat capacity of 9-methylcarbazole<sup>(4)</sup> are lower than those obtained in this work for most temperatures greater than 30 K. These differences, which varied from  $+0.010 \cdot C_{p,m}$  to  $-0.013 \cdot C_{p,m}$ , are shown in figure 2. The material used in all our determinations of heat capacity was not taken through the fusion transition at any time during the measurements. Thus, its thermal history differed from that of the material used by Messerly *et al.*,<sup>(4)</sup> this difference might have a bearing on the differences observed.

The accuracy of the heat-capacity values measured by d.s.c., as evaluated from the heat capacities of sapphire measured with the same instrumental settings, was  $\pm 0.006 \cdot C_{p,m}$  or better except for  $250 \leq T/K \leq 285$ , where it was  $\pm 0.01 \cdot C_{p,m}$ . Occasionally, two points out of 25 would show a larger deviation. Some measurements were made with a d.s.c. head of slightly lower sensitivity than that

TABLE 3. Standard molar thermodynamic functions for 9-methylcarbazole

 $(M = 181.23704 \text{ g} \cdot \text{mol}^{-1}; R = 8.31452 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}; \Phi_m^{\circ} = \Delta_0^T S_m^{\circ} - \Delta_0^T H_m^{\circ} / T)$ 

$\frac{T}{\text{K}}$	$\frac{C_{p,m}}{R}$	$\frac{\Delta_0^T S_m^{\circ}}{R}$	$\frac{\Delta_0^T H_m^{\circ}}{R \cdot \text{K}}$	$\frac{\Phi_m^{\circ}}{R}$
(0)	(0)	0	0	0
(5.00)	(0.1600)	(0.0800)	(0.4000)	(0.0000)
10.00	0.5580	0.2995	2.195	0.0800
15.00	1.365	0.6665	7.002	0.1997
20.00	2.182	1.167	15.87	0.3732
25.00	2.984	1.738	28.78	0.5865
30.00	3.752	2.349	45.62	0.8281
35.00	4.452	2.980	66.14	1.090
40.00	5.030	3.612	89.84	1.366
45.00	5.560	4.235	116.3	1.650
50.00	6.060	4.847	145.4	1.940
55.00	6.540	5.447	176.9	2.232
60.00	7.020	6.037	210.8	2.524
65.00	7.492	6.618	247.0	2.817
70.00	7.935	7.189	285.6	3.109
75.00	8.367	7.752	326.4	3.400
80.00	8.802	8.306	369.3	3.690
85.00	9.188	8.851	414.3	3.977
90.00	9.565	9.387	461.1	4.263
95.00	9.923	9.914	509.9	4.547
100.00	10.29	10.43	560.4	4.828
110.00	10.96	11.44	666.6	5.384
120.00	11.65	12.43	779.6	5.931
130.00	12.36	13.39	899.6	6.468
140.00	13.07	14.33	1026.7	6.996
150.00	13.78	15.26	1161.0	7.516
160.00	14.55	16.17	1302.6	8.029
170.00	15.34	17.08	1452.1	8.534
180.00	16.11	17.97	1609.3	9.034
190.00	16.88	18.87	1774.3	9.528
200.00	17.68	19.75	1947.1	10.02
210.00	18.50	20.63	2128.0	10.50
220.00	19.37	21.52	2317.3	10.98
230.00	20.24	22.40	2515.3	11.46
240.00	21.10	23.28	2722.1	11.93
250.00	21.97	24.15	2937.3	12.41
260.00	22.83	25.03	3161.3	12.87
270.00	23.73	25.91	3394.1	13.34
280.00	24.62	26.79	3635.9	13.81
290.00	25.53	27.67	3886.6	14.27
300.00	26.44	28.55	4146.5	14.73
310.00	27.38	29.43	4415.5	15.19
320.00	28.31	30.32	4694.0	15.65
330.00	29.26	31.20	4981.8	16.11
340.00	30.19	32.09	5279.1	16.56
350.00	30.69	32.97	5583.4	17.02
298.15	26.27 ± 0.03	28.39 ± 0.03	4097.7 ± 5.6	14.64 ± 0.02

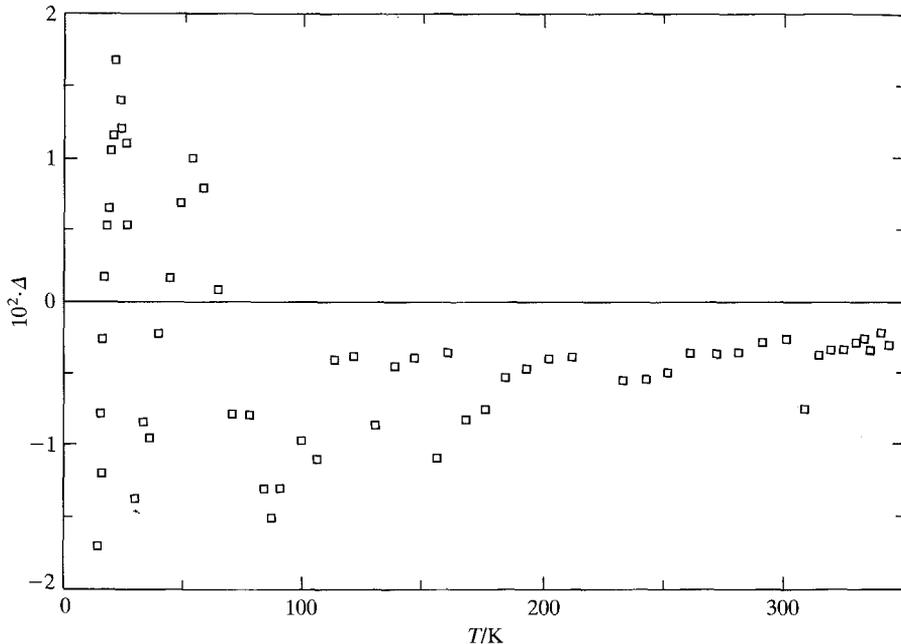


FIGURE 2. Comparison of experimental heat capacities from reference 8 with the present adiabatic measurements:  $\Delta = \{(C_{p,m})_{lit} - (C_{p,m})_{present}\} / (C_{p,m})_{present}$ .

normally used in our laboratory; the accuracy of those measurements was  $\pm 0.01 \cdot C_{p,m}$  over the entire temperature range.

The precision of the measurements depended on several factors: specimen size; measurement mode; the refrigeration system in use; and the temperature range of the measurements. Heat-capacity measurements made with specimens having a mass less than 9 mg were not considered satisfactory and no results are reported for them. The precisions of measurements with liquid nitrogen as coolant were: scanning,  $\pm 0.006 \cdot C_{p,m}$ ; enthalpic,  $\pm 0.01 \cdot C_{p,m}$ . For measurements made with mechanical refrigeration, the precision was  $\pm 0.01 \cdot C_{p,m}$ . The precision in studies made with liquid nitrogen as coolant deteriorated as the temperature increased. This is attributed to the fact that, during a series of measurements, the depth of immersion of a cold finger in the liquid varied through evaporation of the coolant. The effect on precision was observed particularly with enthalpic measurements because the intermittent equilibration steps significantly increased the time required for a series of measurements.

Heat capacities obtained by d.s.c., corrected for pan-mass differences and instantaneous instrument behavior,<sup>(9,12)</sup> were fitted and are compared with the adiabatic values in table 4. The deviation plot for both enthalpic and scanning measurements, compared with our smoothed adiabatic values, is given in figure 3. We note, however, that the deviations of the experimental adiabatic heat capacities from the smoothed curve over this same temperature range varied by up to  $\pm 0.005 \cdot C_{p,m}$ .

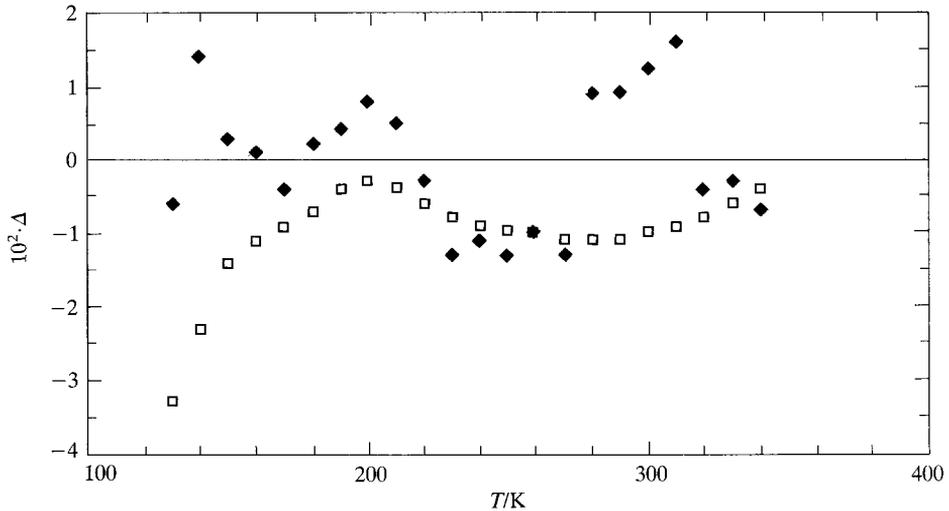


FIGURE 3. Deviations,  $\Delta = \{(C_{p,m})_{d.s.c.} - (C_{p,m})_{ad}\} / (C_{p,m})_{ad}$ , of heat capacities determined by  $\blacklozenge$ , scanning d.s.c., and  $\square$ , enthalpic d.s.c., from the values obtained in this work by adiabatic calorimetry.

The enthalpic heat capacities show negative deviations over the entire temperature range. We find this both surprising and puzzling. In theory, the enthalpic procedure compensates for any thermal lag present in the system. The entire area under the curve is taken to determine heat-capacity values rather than a point-by-point consideration of displacement from the isothermal baseline. In the enthalpic procedures used in this work, an equilibration period of 5 min was allowed between successive steps. One possible explanation for the observed negative deviations is that the repeated return to the baseline and rise to full-scale displacement in some way does not account fully for the thermal lag. The total area  $\Delta H$  under the curve registered in each step is smaller than it should be, so the heat capacity calculated from it is smaller.

TABLE 4. Comparison of heat capacities obtained by adiabatic calorimetry, enthalpic d.s.c., and scanning d.s.c.

T/K	$C_{p,m}/R$			T/K	$C_{p,m}/R$		
	Adiabatic	Enthalpic	Scanning		Adiabatic	Enthalpic	Scanning
130	12.36	11.95	12.43	240	21.10	20.90	20.86
140	13.07	12.77	13.26	250	21.97	21.75	21.68
150	13.78	13.58	13.82	260	22.83	22.60	22.60
160	14.55	14.39	14.57	270	23.73	23.48	23.43
170	15.34	15.20	15.28	280	24.62	24.35	24.85
180	16.11	16.00	16.14	290	25.53	25.26	25.74
190	16.88	16.81	16.94	300	26.44	26.18	26.77
200	17.68	17.62	17.82	310	27.38	27.12	27.81
210	18.50	18.43	18.60	320	28.31	28.08	28.21
220	19.37	19.25	19.31	330	29.26	29.08	29.25
230	20.24	20.07	19.98	340	30.19	30.08	29.99

Values obtained from measurements made at a slow scan rate or on very light specimens showed poorer precision and were considered unsatisfactory. The poorer precision is thought to be the result of the considerably smaller power to be detected under those experimental conditions. No dependence of heat capacity on scan rate was observed in this work; indeed, if the scan rate selected is suitable, given the nature, size, and configuration of the specimen, no scan-rate dependence is to be expected. No significant difference was observed between specimens prepared from previously unheated material and those prepared from material used for the adiabatic measurements. In fact, most of the specimens were reused up to 10 times; no differences that could be attributed to their thermal history were observed.

In summary, satisfactory heat-capacity measurements and the subsequent thermodynamic functions can be determined from d.s.c. measurements though the error limits are larger than those expected from classical precision calorimetry. If highly precise values are required, it is more satisfactory to carry out the measurements by classical methods. The great care required by d.s.c. measurements, the need for careful adjustment and interpretation of results, and the time consumed by replicate measurements to ensure satisfactory precision, make the d.s.c. measurements a poorer option.

For many purposes, however, the accuracy and precision of d.s.c. measurements are satisfactory. In those instances, d.s.c. is a convenient and practical tool; for scarce materials or in difficult temperature regions, it is indeed a desirable one.

Because of the difficulties mentioned here, we would not recommend that d.s.c. be used in general for the preparation of heat-capacity reference materials. Only in instances of a pressing need for a particular type of material that is considered unsuitable for precision calorimetry or in a temperature range that cannot be satisfied by classical methods should the arduous d.s.c. measurement procedures required to certify a reference material be undertaken.

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