

## Glassy Carbon Low-temperature thermodynamic properties†

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*(Received 16 June 1970)*

The heat capacity of Glassy Carbon was measured by adiabatic calorimetry from 5 to 350 K and has no transitions or thermal anomalies. It parallels that of pyrolytic graphite annealed at 2600 °C in showing an approximate  $T^2$  dependence up to 30 K suggesting that the structure of this material may involve microdomains of lamellar graphite. At 298.15 K, the measured heat capacity at constant pressure ( $C_p$ ), the entropy ( $S^\circ - S_0^\circ$ ), and the enthalpy function  $\{(H^\circ - H_0^\circ)/T\}$  are 2.055, 1.406, and 0.857 cal K<sup>-1</sup> mol<sup>-1</sup>.

### 1. Introduction

“Glassy Carbon”,<sup>(1,2)</sup> an essentially amorphous form of carbon developed by the Tokai Electrode Mfg. Co., is expected to be an excellent high-temperature material useful as a refractory in metallurgy of high purity metals as well as in nuclear applications because of its extremely low gas permeability,<sup>(1)</sup> its ultimate strength at high temperature,<sup>(3)</sup> and its relative immunity to radiation damage.<sup>(4)</sup> Its physical properties have been investigated rather extensively,<sup>(1,5,6)</sup> and many interesting differences between its properties and those of ordinary graphites have been revealed. As its name “Glassy Carbon” suggests, this material shows many properties of the vitreous state. Although several structural models of Glassy Carbon have been proposed<sup>(7-10)</sup> to elucidate these properties, they are still not definitive.

Several determinations, however, have been made on the heat capacity of graphite.<sup>(11-14)</sup> The results of DeSorbo and Tyler<sup>(11)</sup> are said to yield a  $T^2$  dependence of the heat capacity for the temperature range between 13 and 54 K, which has been interpreted in terms of the predominantly lamellar-type structure of graphite, confirmed by the measurements of DeSorbo and Nichols<sup>(12)</sup> and those of Keesom and Pearlman,<sup>(13)</sup> but has been disputed by others.<sup>(15)</sup>

The low-temperature heat capacity of Glassy Carbon is here investigated by adiabatic calorimetry to provide reliable thermal data on Glassy Carbon relative to that of graphite and to elucidate the structural nature of this material. Significant differences in the bonding characteristics of Glassy Carbon from those in the fundamental lamellar structure of graphite would be reflected in the temperature dependence of the heat capacity.

† This research was supported in part by the United States Atomic Energy Commission.

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## 2. Experimental

### CHARACTERIZATION OF SAMPLE

The Glassy Carbon sample in the form of rods approximately 3 mm in diameter and 100 mm in length was prepared by the Tokai Electrode Mfg. Co. at Nagoya, Japan, designated by them as GC-30S, and reported to have been heat-treated at 3000 °C as well as chemically treated to minimize metallic impurities. Determination of metallic impurities by spectrochemical analysis showed the following (in p.p.m. by mass): Cr, 2.2; Cu, 13.6; Fe, 12.3; Mg, 0.1; Si, 1.4. Direct analytical results were unavailable on probable impurities such as oxygen and nitrogen. Noda *et al.*<sup>(10)</sup> have, however, reported that the oxygen content of the sample heat-treated at 1300 °C was determined as 0.3 per cent by chemical analysis and this value coincides with the reported results by Furukawa<sup>(8)</sup> (0.1 to 0.2 per cent of oxygen) in preliminary activation analysis experiments on <sup>16</sup>O. The calorimetric sample was found to contain  $(0.2 \pm 0.1)$  per cent of oxygen by vacuum fusion methods. The mass of this sample was 117.561 g. Buoyancy corrections were made using a density<sup>(1)</sup> of  $1.46 \text{ g cm}^{-3}$  for Glassy Carbon.

### CALORIMETRIC APPARATUS

Measurements were made in the Mark II adiabatic vacuum cryostat previously described.<sup>(15)</sup> The gold-plated copper calorimeter (laboratory designation W-31) used has a capacity of 102 cm<sup>3</sup>. The heat capacity of the empty calorimeter was determined in a separate series of measurements in which the same amounts of indium + tin solder for sealing the calorimeter and Apiezon-T grease for thermal contact with the heater-thermometer assembly were used. The heat capacity of the sample represented over 50 per cent of the total heat capacity. A pressure of 142 Torr of helium at 300 K was used to facilitate thermal equilibrium in the sample space. Temperatures were determined with a capsule-type, strain-free, platinum-resistance thermometer (laboratory designation A-5) contained within an entrant well of the calorimeter and are considered to accord with the thermodynamic temperature scale to within 0.03 K from 20 to 350 K. Temperature increments may be determined with more precision and are probably correct to a few tenths of a millikelvin after correction for quasi-adiabatic drift. All measurements of mass, resistance, potential, temperature, and time are referred to calibrations or standardizations of the National Bureau of Standards.

## 3. Results and discussion

### HEAT CAPACITIES AND THERMAL PROPERTIES

The experimental heat capacities are presented in table 1 in chronological order at the mean temperatures of the determinations. These data have been corrected for curvature, i.e. for the difference between  $\Delta H/\Delta T$  and the corresponding derivative. The approximate values of  $\Delta T$  used in the heat capacity determinations can usually be estimated from the increments between adjacent mean temperatures given in table 1. These heat capacity values are considered to have a probable error decreasing

TABLE 1. Experimental heat capacity of Glassy Carbon. (cal = 4.184 J,  $M_r(\text{Glassy Carbon}) = 12.01115$ ,  $T_{\text{ice}} = 273.15$  K.)

$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal K}^{-1} \text{mol}^{-1}}$	$\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal K}^{-1} \text{mol}^{-1}}$
Series I		243.43	1.588	7.11	0.0027	14.12	0.0114
		253.78	1.678	8.15	0.0036	15.95	0.0145
87.01	0.334	264.05	1.765	9.33	0.0051	17.91	0.0185
96.68	0.393	274.24	1.853	10.69	0.0066	19.85	0.0229
105.57	0.450	284.39	1.938	12.25	0.0084	21.82	0.0279
114.69	0.513	294.34	2.024	13.89	0.0109	24.02	0.0341
124.12	0.582	304.19	2.105			26.65	0.0421
133.72	0.655	314.39	2.188			29.76	0.0524
143.63	0.733	324.92	2.275			33.49	0.0660
153.82	0.816	335.46	2.358	Series III		37.95	0.0837
163.93	0.900	345.79	2.439			43.03	0.1050
173.66	0.982			6.13	0.0020	47.93	0.1267
183.36	1.065			6.81	0.0024	52.49	0.1478
193.03	1.150			7.57	0.0031	58.00	0.1742
202.75	1.233	Series II		8.52	0.0042	64.56	0.208
212.71	1.319			9.64	0.0055	71.87	0.246
222.92	1.410	5.56	0.0017	10.95	0.0068	79.74	0.289
233.15	1.499	6.34	0.0022	12.46	0.0087	88.09	0.341

from about 5 per cent at 5 K to 0.5 per cent at 20 K and to less than 0.1 per cent above 30 K.

The heat capacities, entropy increments ( $S^\circ - S_0^\circ$ ), and enthalpy functions  $\{(H^\circ - H_0^\circ)/T\}$  presented in table 2 at selected temperatures were obtained from the heat capacities by integration of a least-squares-fitted curve (carefully compared with a large-scale plot). Both fitting and quadrature were performed by high-speed digital computers using programs previously described.<sup>(16)</sup> The thermodynamic functions are considered to have a precision corresponding to a probable error of less than 0.1 per cent about 100 K. Additional digits beyond those significant are given in table 2 for internal consistency and to permit interpolation and differentiation. The entropies have not been adjusted for nuclear spin and isotopic mixing contributions and hence are practical values for use in chemical thermodynamic calculations. It should be noted, however, that the usual  $T^3$  Debye limiting law has been used for the (small) extrapolation below 6 K and that the third law cannot be used to deduce  $S_0^\circ$  for a vitreous substance.

The present values of  $C_p$  and ( $S^\circ - S_0^\circ$ ) at 298.15 K may be compared with those of graphite from Kelley and King<sup>(17)</sup> based on the measurements by DeSorbo and Tyler<sup>(11)</sup> and those by Jacobs and Parks<sup>(18)</sup>:  $C_p = 2.05 \text{ cal K}^{-1} \text{ mol}^{-1}$ , and  $S^\circ = (1.36 \pm 0.02) \text{ cal K}^{-1} \text{ mol}^{-1}$ .

#### TEMPERATURE DEPENDENCE OF THE HEAT CAPACITY

It is of theoretical interest to determine the significance of the temperature dependence of the heat capacity in order to test predictions based on models. Temperature dependence has been determined conventionally by plotting  $\log C_p$  against  $\log T$ .

TABLE 2. Thermodynamic functions of Glassy Carbon. (cal = 4.184 J,  $M_r(\text{Glassy Carbon}) = 12.01115$ ,  $T_{\text{ice}} = 273.15$  K.)

$T$ K	$C_p$ cal K <sup>-1</sup> mol <sup>-1</sup>	$S^\circ - S_0^\circ$ cal K <sup>-1</sup> mol <sup>-1</sup>	$(H^\circ - H_0^\circ)/T$ cal K <sup>-1</sup> mol <sup>-1</sup>
5	0.0015	0.0005	0.0004
10	0.0055	0.0025	0.0018
15	0.0128	0.0060	0.0041
20	0.0233	0.0111	0.0076
25	0.0369	0.0177	0.0120
30	0.0533	0.0258	0.0175
35	0.0719	0.0354	0.0239
40	0.0922	0.0463	0.0312
45	0.1136	0.0584	0.0391
50	0.1369	0.0715	0.0477
60	0.1845	0.1006	0.0664
70	0.2362	0.1328	0.0869
80	0.2917	0.1679	0.1090
90	0.3509	0.2057	0.1326
100	0.4141	0.2459	0.1575
110	0.4811	0.2885	0.1839
120	0.5518	0.3333	0.2115
130	0.6262	0.3804	0.2406
140	0.7037	0.4296	0.2709
150	0.7840	0.4809	0.3024
160	0.8665	0.5341	0.3350
170	0.9508	0.5892	0.3688
180	1.0364	0.6460	0.4035
190	1.123	0.7043	0.4391
200	1.210	0.7641	0.4754
210	1.297	0.8252	0.5125
220	1.384	0.8876	0.5501
230	1.471	0.9510	0.5883
240	1.558	1.0155	0.6269
250	1.645	1.0808	0.6658
260	1.731	1.147	0.7051
270	1.817	1.214	0.7447
280	1.902	1.282	0.7845
290	1.987	1.350	0.8245
300	2.070	1.419	0.8647
310	2.153	1.488	0.9049
350	2.473	1.786	1.066
298.15	2.055	1.406	0.857

The slope of this log-log plot has been regarded as the exponent in a function of the form:  $C_p = AT^n$ , representing the heat capacity. This interpretation is true if and only if the log-log plot is linear. For any other case, to interpret the slope as the exponent for a single term is a gross oversimplification. To demonstrate this, let the heat capacity for a substance be represented by a polynomial of the form:

$$C_p = \sum_{n=0}^m A_n T^n.$$

The degree of the polynomial is given by the highest exponent of  $T$  therein. However,

this degree does not necessarily represent the temperature dependence very well, since the coefficient for this term may be quite small, making the contribution of this term insignificant except at the highest temperatures. In cases where the heat capacity may be adequately represented by a polynomial having only positive coefficients an interpretation of the slope:

$$d \log C_p / d \log T,$$

may be devised. If  $\eta(T)$  is defined as:

$$\eta(T) = \sum_{n=0}^m n A_n T^n / C_p.$$

It is a weighted average of all exponents with respect to the contribution of each term to the total heat capacity at a given temperature. Simple rearrangement shows that

$$\eta(T) = d \log C_p / d \log T.$$

Thus the slope of a log-log plot may be considered as a weighted average of exponents under the condition of positive coefficients. The fundamental property of this weighted average is that it will increase as a function of temperature between the limits of the lowest and highest exponents in the polynomial. Hence in such a plot, the slope at a particular temperature may be interpreted as a weighted average of exponents *only* if this slope is increasing. In a situation for which a monotonic increasing slope ceases to persist, interpretation of the decreasing slope as the weighted average is not valid—since the decrease in slope implies that negative coefficients must be used in the polynomial fit to  $C_p$ . In the region in which  $\eta(T)$  is a valid weighted average there is still an intrinsic ambiguity as to which terms are present or absent in a polynomial fit. However, if  $\eta(T)$  rises above a certain integral value  $n$ , the polynomial requires at least one term of degree greater than  $n$ .

A  $T^2$  dependence of the heat capacity of graphite was first observed for the data of DeSorbo and Tyler<sup>(11)</sup> between 13 and 50 K and was explained by a treatment of the layer structure of graphite as a two-dimensional array.<sup>(19-21)</sup> Later measurement down to 1.4 K by DeSorbo and Nichols<sup>(12)</sup> revealed that the  $T^2$  dependence did not hold at these very low temperatures and shifted to  $T^3$  dependence. This observation was also interpreted satisfactorily by several investigators,<sup>(22, 23)</sup> upon introduction of a weak interaction between neighboring layers.

The theory claims that at very low temperatures the long wavelength phonons caused by the weak interactions of the neighboring layers contribute to the heat capacity and give the  $T^3$  dependence, while at intermediate temperatures an "apparent"  $T^2$  dependence still holds. It should be pointed out that, as stated before, the  $T^2$  dependence of graphite at these temperatures is a result of a weighted average of terms and should be regarded as an apparent one.

The present results on the low-temperature heat capacity of Glassy Carbon in the region 5 to 30 K shows an apparent temperature dependence of  $T^{2.04}$ . This result does not establish that Glassy Carbon has a definite graphite-like, two-dimensional layer structure, but suggests that it may have predominant two-dimensional bonding characteristics, rather than an isotropic three-dimensional array.

## STRUCTURE OF GLASSY CARBON

The heat capacity values for Glassy Carbon are plotted in figure 1, together with those of other investigations<sup>(11-13,24)</sup> on various graphites. In order to avoid confusion, the data of DeSorbo and Nichols<sup>(12)</sup> are represented by dots and dashes. The data on Glassy Carbon are virtually indistinguishable above 50 K from those of pyrolytic graphite heat-treated at 2600 °C.<sup>(24)</sup> Although all other measurements showed considerable scatter, the heat capacity of Glassy Carbon is slightly higher than that of the other graphites over the entire temperature range of the measurements and especially so below 30 K. This trend is consistent with the view that Glassy Carbon is an extremely amorphous form of graphite since the heat capacity of graphite increases with decrease of graphitization.<sup>(12,25,26)</sup> The amorphous state

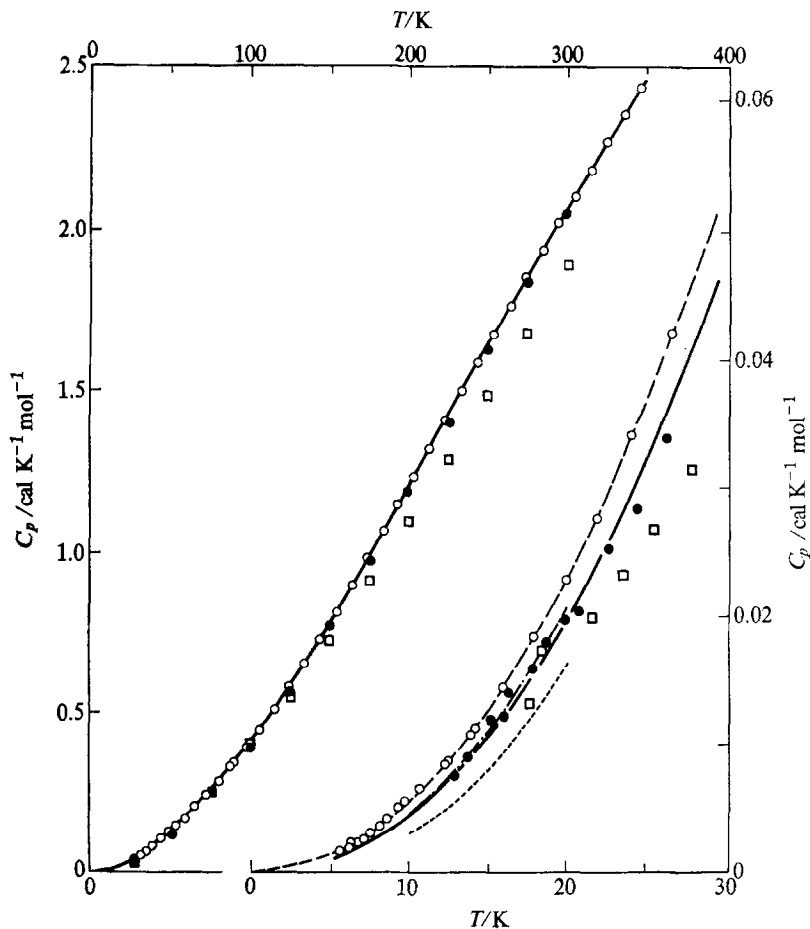


FIGURE 1. The heat capacity of Glassy Carbon GC-30S (--- ○ ---), of Acheson graphite<sup>(11)</sup> (●), of Ceylon natural graphite<sup>(13)</sup> (□), of Canadian natural graphite<sup>(12)</sup> (.....), of lamp black<sup>(12)</sup> (-·-·-·-) and of pyrolytic graphite heat-treated at 2600 °C<sup>(24)</sup> (—). Experimental values are plotted throughout except for the higher temperature region of Ceylon and Acheson graphites for which only smoothed points at rounded temperatures are shown to avert confusion.

has, on the average, looser bondings than the ordered graphite. This view is also supported by the fact that the density of Glassy Carbon,  $1.46 \text{ g cm}^{-3}$ ,<sup>(1)</sup> is considerably less than that of graphite.

The excess heat capacity, defined as

$$\Delta C_p = \{C_p(\text{Glassy Carbon}) - C_p(\text{Canadian natural graphite})\},$$

is calculated over the (available) temperature range between 10 and 20 K, and found to be almost linear in temperature. Recently, Delhaes and Hishiyama<sup>(26)</sup> studied heat capacities of soft carbons heat-treated to temperatures between 1600 and 3100 °C and found that the linear (electronic) component of the heat capacity increased with decrease of heat-treatment temperature. The contributions were too large to be explained solely by conduction carriers. Thus, the excess heat capacity of Glassy Carbon may have some lattice contributions to the linear term in temperature although its origin is still unexplained. Shortage of reliable data on near-ideal graphite over wider ranges of temperature hinders further interpretation.

The apparent approximately  $T^2$  dependence of the heat capacity of Glassy Carbon, nevertheless, provides strong support for the view that the elemental atomic configuration is a micro-domain of graphite-like lamellar structure, rather than an isotropic three-dimensional random network configuration of carbon atoms such as proposed by Furukawa.<sup>(8)</sup> A structural model for Glassy Carbon was proposed by Noda *et al.*<sup>(7,10)</sup> from the analysis of the radial distribution curve obtained from X-ray diffraction. This model which assumes the presence of a significant proportion of tetrahedral carbon atoms forming random cross-linkages between graphite-like laminae would seem more appropriate. Kakinoki's<sup>(9)</sup> model, which assumed the cross-linkage of the laminae by impurity oxygen atoms, would be tenable only for higher oxygen contents than those of the present samples. Hence, although a definitive conclusion regarding the structure of Glassy Carbon is still precluded at present, a graphitic-type seems favored.

The authors appreciate the partial financial support of the United States Atomic Energy Commission and the cooperation of Dr Wen-Kuei Wong with the measurements.

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