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The thermal properties of four allotropes of carbon [1]

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Abstract

The heat capacities of diamond, graphite, and the fullerenes C_{60} and C_{70} are compared and linked to their approximate vibrational spectra. Because all the allotropes have the chemical composition C, their ultimate heat capacity is the Dunlog–Petit value $3R = 24.9\,J\,K^{-1}\,mol^{-1}$. At low temperatures (0–50 K), the fullerenes have a much higher heat capacity than the other two allotropes. As the temperature is increased, graphite and the fullerenes approach approximately equal heat capacities. Up to 1000 K, diamond has a lower heat capacity, but then, because of its weaker C–C bonds compared to the conjugated double bonds in graphite and the fullerenes, it exceeds the heat capacities of the latter. Fullerenes have crystal to plastic-crystal transitions in the region 250–350 K with entropies in agreement with the orientational entropy increase derivable from Walden's rule. Their sublimation pressures reach atmospheric pressure at about 1500 K, and the entropies of transition, when corrected for the entropy of fusion (Richards' rule), obey Trouton's rule. Carbon is thus a textbook example for the differences in thermal behavior possible as a function of chemical bonding and structure.

INTRODUCTION AND EXPERIMENTAL DETAILS

In addition to diamond and graphite, the two well-known crystalline allotropes of carbon, a totally new form of crystalline carbon was discovered a few years ago [1]. It consists of ball-shaped C_{60} molecules (buckminsterfullerene or just fullerene) and has become well known because of its special structure, displayed in Fig. 1 [2]. Before 1990, most research on C_{60} was limited to theoretical studies [3–12] because of insufficient material to undertake large-scale experimental studies. In 1990, Krätschmer and coworkers first reported a method of synthesizing C_{60} in macroscopic quantities [13, 14]. Since then, the study of this new class of compounds and their derivatives has received more attention and other fullerenes, such as C_{70} have also become available for research [15].

Initial information about a phase transition in C_{60} below room

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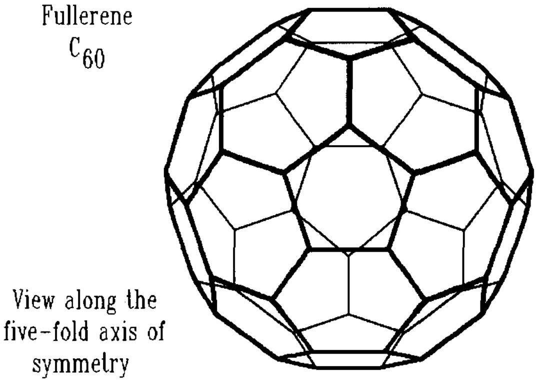

Fig. 1.

temperature was derived through DSC measurements, as shown in Fig. 2 [16–18]. Orientational ordering was suggested to occur on cooling. The vapor pressure was estimated from Knudsen measurements of a mixture of C_{60} and C_{70}, and permitted an estimation of the heats of sublimation [19]. Recently, extensive measurements of heat capacities and computations of heat capacities, based on approximate vibrational spectra, were carried out on C_{60} and C_{70} in our ATHAS laboratory [20a,b]. These new data permit quantitative interpretation of the transitions of the fullerenes, the generation of complete thermodynamic functions (enthalpy H, entropy S, and Gibbs function G) and a comparison of the different allotropes of carbon. The latter is the main focus of this paper.

The heat capacities of C_{60} and C_{70} were measured in our laboratory from 120 to 560 K using a single-run DSC technqiue [21] which needs only 20–30 mg of sample to produce quality data (see Fig. 2). The heat capacity contribution from vibrations was calculated, based on existing normal mode and lattice vibration frequencies [9–12, 22, 23], and compared to the

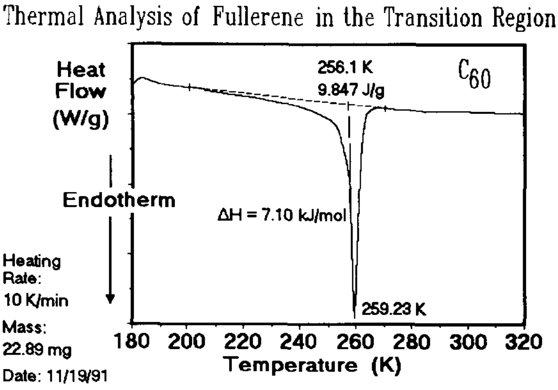

Fig. 2.

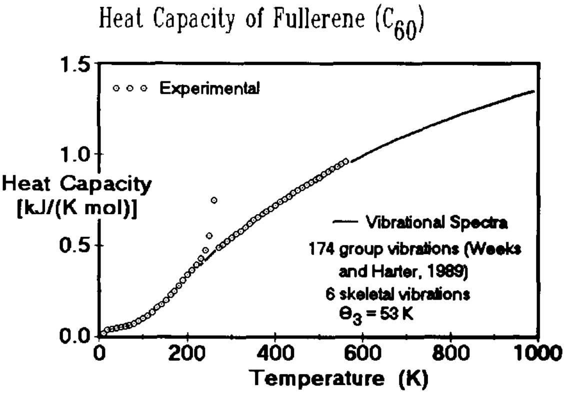

Fig. 3.

experimental data. The agreement between experiment and computation is shown in Fig. 3 for C_{60}, for which most data are available [20b].

The phase transition that occurs at 256 K is a crystal to plastic-crystal transition with an entropy of 27.3 J K^{-1} mol^{-1}, typical for such transitions involving orientational disordering. Similarly, C_{70} shows three disordering transitiosn with a total entropy change of 22.7 J K^{-1} mol^{-1} at 275, 321 and 338 K. The broad beginning of the disordering transitions of the fullerenes can be linked to a gradual change in motion from jump-like rotations, initiated at much lower temperatures, to isotropic rotation. This interpretation is based on the known solid state NMR spectrum [24–26], and confirmed by the heat capacity investigation [20a,b]. A small jump in the heat capacity of C_{60} at 90 K, observed by adiabatic calorimetry at low temperature, was interpreted as a glass-like transition of a part of the molecules in the crystal that are disordered between two possible arrangements [27]. This jump in heat capacity is too small to be seen in Fig. 3 [20b].

The fullerenes discussed in this paper were extracted from fullerene-rich soot (Texas Fullerenes, Inc.) using a Soxhlet extractor with toluene, benzene, or hexane solvents. The extracted C_{60} was separated from C_{70} and the higher fullerenes in a chromatographic column. The C_{60} powder was then washed in ether and dried in a vacuum at about 475 K. The purity of the sample was better than 99.5%, checked by mass and Raman spectroscopy. The C_{70} (98% purity) contianed one mole of toluene in a complex that could be decomposed to pure C_{70} above 450 K.

All heat capacities were measured at 10 K min^{-1} heating rate with N_2 gas flow of 10 ml min^{-1} above 300 K, and the error is estimated to be <1% above 300 K, and <3% below 200 K and <2% between 200 and 300 K. No weight loss was observed over the temperature range of heat capacity analysis.

A check for melting temperatures was carried out at 50 K min^{-1} heating

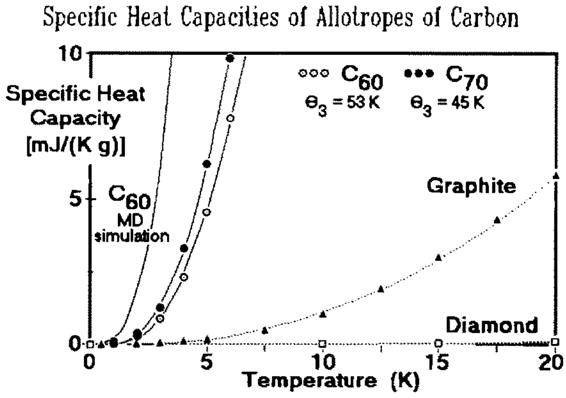

Fig. 4.

rate in a qualitative mode. For this experiment, the samples were enclosed in non-hermetically-sealed copper pans. No melting temperature could be detected for C_{60} or C_{70} up to 950 K, the temperature limit of our calorimeter. The weight losses after these experiments, presumably through sublimation, were less than 2%.

The calculation of the heat capacity of solids from vibrational spectra is well documented in several publications from our laboratory [28–31]. The heat capacity at constant volume C_V is calculated based on a separation of the vibrational spectrum into group and lattice vibrations. The molecules of C_{60} and C_{70} have a total of $N = 3 \times (60 \text{ or } 70)$ vibrational modes which consist of 6 lattice vibrations and 174 or 204 group vibrations, respectively. The heat capacity contributions of the lattice vibrations were fitted to the low-temperature heat capacities and resulted in the characteristic Debye temperatures Θ_D of 53 and 45 K for C_{60} and C_{70}, respectively [20b]. For C_{60} it was also possible to convert a lattice vibration spectrum, computed from molecular dynamics simulation [22], to heat capacity [20a]. All these results are compared in Fig. 4. The conversion of heat capacity at constant volume to that at constant pressure C_p is done by a modified Nernst–Lindemann equation [32]. Once the heat capacity is established, the enthalpy H, entropy S and Gibbs function G can be easily calculated.

DISCUSSION OF THE VARIOUS ALLOTROPES

The allotropes of solid carbon, diamond, graphite, and C_{60}, have been reviewed recently by Huffman [33]. The carbon in diamond is tetrahedrally coordinated with neighbouring carbon atoms with sp^3 hybridization in which each atom is connected to its four nearest neighbors by equivalent, directed bonds. Graphite, however, is a highly anisotropic crystal in which three of the carbon valence electorns form directed sp^2 bonds that link the atoms to a hexagonal, planar arrangement. Adjacent planes are connected by much weaker van der Waals bonds. Solid C_{60} and C_{70} are similar to

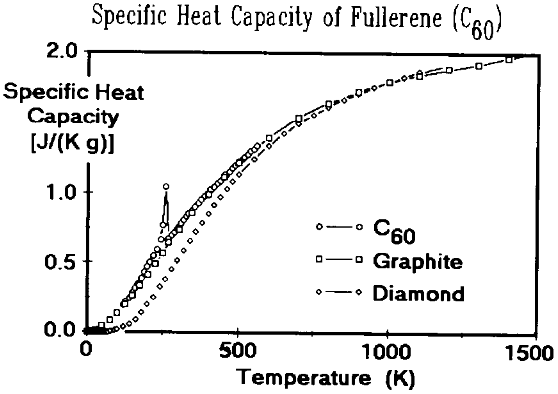

Fig. 5.

graphite in their molecular structure. They achieve the curvature of the strongly-bonded, hexagonal "chicken-wire" planes of graphite by incorporating "pentagons" into the molecule. For C_{60}, there are 12 pentagons and 20 hexagons (see Fig. 1), and for C_{70}, 12 pentagons and 25 hexagons. Within the molecules of the fullerenes, the bonding remains largely the sp^2 bonding of the graphite. The intermolecular bonding is analogous to the weak interplanar bonding between graphite layers, but is weakened by the unfavorable geometry of packing when compared to the layer structure of graphite. A comparison of the densities (1.7 Mg m^{-3} for C_{60} [32] versus 2.30–2.72 Mg m^{-3} for graphite) reveals this fact.

When one compares the specific heat capacities of diamond and graphite [34] with that of C_{60}, as is done in Fig. 5, the heat capacity of C_{60} (and also C_{70}) is similar to that of graphite and much different from that of diamond, as one would expect from the similairty in bonding. The higher heat capacities below about 1000 K for graphite and the fullerenes is caused by the lower transverse out-of-plane vibrational frequencies with respect to the curved or planar molecular surfaces. The stronger in-plane sp^2 bonds in graphite relative to the three-dimensional sp^3 bonds in diamond cause the cross-over in C_p at about 1000 K. Ultimately all carbon allotropes are expected to reach the Dulong–Petit limit of $C_V = 3R = 24.9\ \mathrm{J\ K^{-1}}$ per mol of carbon.

At very low temperatures, the order of the specific heat capacities is $C_{70} > C_{60} >$ graphite > diamond, reflecting the low intermolecular vibration frequencies of the fullerenes and graphite, and also revealed by the higher density of diamond (3.01–3.52 Mg m^{-3}). Figure 4 shows the heat capacities from 0 to 20 K. For isotropic solids, the Debye T^3-law is known to give a good account of the low temperature heat capacity. Diamond and graphite have heat capacities that follow such a T^3-law, with Θ_D temperatures of 2050 and 760 K fitted at a temperature of $\Theta_D/2$ [33]. For C_{60} and C_{70}, in turn, the data of Fig. 4 can be fitted with Θ_D temperatures of about 53 K and

45 K for the six lattice vibrations, illustrating the weak intermolecular van der Waals bonding. Note, that the somewhat higher specific heat capacity c_V of C_{70} compared to C_{60} does not reflect the different values of Θ_D, but is caused by the larger molecular mass of C_{70} [$c_V = C_V/$(molecular mass)).

The T^3-law is caused by a quadratic vibrational frequency distribution, so that one can also estimate the range of fit of the Debye equation by the upper limit of the initial, approximately quadratic, part of the frequency spectrum. It occurs at about 2×10^{13} Hz or 960 K for diamond and 5×10^{12} Hz or 240 K for graphite [35]. For the fullerenes, constant Θ_D temperatures could not be reached at the lowest temperatures of measurement, but above 10 K the experimental data are represented by the given values of Θ_D in Fig. 4, to within ±5% [20b]. The molecular dynamics calculation gives, according to Fig. 4, vibrational frequencies that are too low (heat capacities too high).

Knowing the heat capacities, the thermodynamic functions can be calculated. Tabular values are available through the ATHAS data bank. The discontinuity in enthalpy on isotropization (melting) should, according to Richards' rule $\Delta S_f = 7\text{–}14\ \mathrm{J\,K^{-1}\,mol^{-1}}$, have an approximate value of 10–20 kJ $\mathrm{mol^{-1}}$($\approx$1000–1500 K × 7 − 14 J $\mathrm{K^{-1}\,mol^{-1}}$), about the same order of magnitude as the disordering transitions. The sublimation pressure reaches atmospheric pressure at about 1500 K [19], and the entropy of transition, when corrected for the estimated entropy of fusion (Richards' rule), obeys Trouton's rule ($\Delta S_V = 113\ \mathrm{J\,K^{-1}\,mol^{-1}}$). Diamond and graphite sublime, in turn, by breaking strong bonds (at about 4000 K). Carbon is thus a textbook example for the differences in thermal behavior possible as a function of chemical bonding and structure.

Since the presentation of this discussion at the 21st NATAS conference, a series of experimental, low-temperature heat capacity measurements have been published and announced [27, 36]. These confirm the special shape of the C_{60} and C_{70} heat capacities at the lowest temperatures (Fig. 4) originally based only on molecular mechanics simulation, and have been included in Fig. 3, and also in Fig. 4 along with the data on C_{70}. A full discussion of some deivation among these new data is given in ref. 20b, also added after the conference data. Because new data are continually being published, we suggest that the interested reader requests the latest "recommended experimental heat capacities" from the ATHAS data bank at the address of the authors.

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