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Thermodynamics of allotropic modifications of carbon: Synthetic diamond, graphite, fullerene C_{60} and carbyne

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Abstract

In an adiabatic vacuum calorimeter, a temperature dependence of heat capacity of four allotropic modifications of carbon, viz. synthetic diamond, graphite, carbyne and fullerene C_{60}, has been studied in the (5–340) K range. The diamond sample studied is a commercial crystalline product containing impurities, according to a certificate, in an amount less than 1%; graphite is a spectrally pure crystalline substance with 99.9999 mass% of carbon; the carbyne sample with the content of carbon 99.5% is almost amorphous; crystalline fullerene C_{60} has the content of a main substance ca. 99.98%. From the experimental data obtained for all objects under study, the thermodynamic functions C_p^0, $H^0(T) - H^0(0)$, $S^0(T)$ and $G^0(T) - H^0(0)$ have been calculated over the (0–340) K range. The calculation results and literature data on enthalpies of combustion have been used to calculate standard thermochemical parameters of formation $\Delta_f H^0$, $\Delta_f S^0$, $\Delta_f G^0$ of synthetic diamond, fullerene C_{60} and carbyne from graphite at $T = 298.15$ K and $p = 101.325$ kPa. A comparison of thermodynamic properties of the allotropic carbon modifications has been made and the order of their thermodynamic stability has been found to be: carbyne (a) > graphite (cr) > diamond (cr) > fullerene C_{60}(cr).

Keywords: Diamond; Fullerenes; Graphite; Heat capacity; Thermodynamic function

1. Introduction

Diamond and graphite are modifications of carbon known to man for a long time. A crystalline diamond has a three-dimensional structure. Graphite is a highly anisotropic (two-dimensional) crystal: its planar layers from condensed benzene rings are bound with weak Van der Waals links. In the sixties, the existence of a third (one-dimensional) modification of carbon, viz. carbyne, was established. This third modification is a linear polymer with conjugated bonds [1]. Some years ago, a fourth form of carbon showing the geometry of a truncated icosahedron, i.e. fullerene C_{60}, was revealed [2].

The availability of many modifications for carbon makes it a convenient object for the illustration of a dependence of thermodynamic properties of substances on their structure and the character of chemical links.

The goal of the present work is to compare thermodynamic characteristics of synthetic diamond, graphite, carbyne and fullerene C_{60}, to establish their dependence on structure, and to determine a relative thermodynamic stability of the above-mentioned allotropic modifications of carbon.

2. Experimental

2.1. Sample

A completely crystalline sample of graphite of grade 'for spectral measurements', containing 99.9999 mass% of carbon, was obtained from one

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of the Japanese firms and given to the Faculty of Electronics of the Moscow State University. The commercial synthetic sample of diamond, according to All-Union State Standard, contained not more than 1 mass% of impurities. The sample of fullerene C_{60} with not less than 99.98 mass% of the main substance was prepared at the Institute of Organometallic Compounds (Nizhny Novgorod) using a procedure [3] similar to that of Krätschmer–Huffman [4]. As a starting carbon material, graphite rods (electrodes) manufactured from graphite of OSCH-7-3 grade were used. An analysis of impurities present in the sample of C_{60} was conducted with the help of the HPLC method at the Moscow State University by A.M. Davydov. It turned out that the impurity content did not exceed 0.02%. As results of X-ray structure analysis (a Dron-3 device) show, the fullerene C_{60} sample is crystalline at room temperature. The molecules of fullerene form a faced-centered cubic lattice with $a_0 = 14.2$ A. The carbyne sample under study was prepared at the Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow) by the procedure described elsewhere [5]. According to X-ray analysis data, the sample is substantially amorphous and consists of a mixture of macromolecules of polyyne and cumulene structure.

2.2. Apparatus

To study the temperature dependence of heat capacity, temperatures and enthalpies of physical transitions, a thermophysical automatic device TAU-1 – an adiabatic vacuum calorimeter designed and manufactured at the All-Union Institute of Physicotechnical and Radiotechnical Measurements, Moscow – was employed. The design of the calorimeter and the procedure have been described elsewhere [6]. All measurements were controlled with a computer-measurement system consisting of a computer, an analog-to-digital and a digital-to-analog converters and a voltage switch. A calorimetric ampule is a thin-walled steel vessel of 1.5 cm^3 capacity and 2.06 g mass. Temperature was measured with an iron–rhodium resistance thermometer ($R_0 \approx 100\,\Omega$). The difference in temperature between the ampule and the adiabatic shields was controlled by a four-junction copper–iron–chromel thermocouple. The sensitivity of a thermometric circuit was 1 mK, of the analog-to-digital converter 0.1 μV. The speed of the computer-measurement system was 10 measurements per second. The calorimeter was calibrated by us with an electric current. The heat capacity of an unloaded calorimetric ampule C_{cal} changes from 0.0038 J K^{-1} at 5 K to 1.275 J K^{-1} at 340 K. The root-mean-square scatter of the experimental points of C_p^0 from the smoothed curve $C_{\mathrm{cal}} = f(T)$ does not always exceed 0.16%. The reliability of the calorimeter operation was tested by measuring the heat capacity of especially pure copper (OSCH 11-4), standard synthetic sapphire and K-2 benzoic acid in the (5–340) K range. An analysis of the data obtained by us shows that the uncertainty of heat capacity measurements of substances at helium temperatures is within 2%. With temperature rising up to 40 K, it decreases to 0.5 and 0.2% between 40 and 340 K.

3. Results and discussion

3.1. Heat capacity

The heat capacities of synthetic diamond, graphite, fullerene C_{60} and carbyne were measured in the interval from 9.2, 5, 4.97 and 6.25 to 340 K, respectively. The masses of the samples loaded into the calorimetric ampule were 1.8242, 1.5907, 0.7009 and 0.5332 g, respectively. The ampule with carbyne was heated for a period of 2 h at 390 K under vacuum, then it was filled with a heat-exchange gas – helium – up to a pressure of 1.3×10^3 Pa at room temperature. Helium was also introduced while studying the heat capacity of diamond and graphite. For the carbon modification, by 130–150 experimental values of C_p^0 were obtained in 12–18 series of measurements. The heat capacity of graphite, carbyne and fullerene C_{60} was 17, 13 and 30%, respectively, at 20 K and 20% or more at 100 K and above this temperature of the summary heat capacity of the calorimetric ampule and the substance. With the diamond sample, the heat capacity was 1.4% at 20 K and more than 20% above 200 K of the above summary heat capacity. The root-mean-square scatter of the C_p^0 experimental points of graphite, carbyne and fullerene C_{60}, from the averaged curve $C_p^0 = f(T)$, changes from 0.6 to 0.4% between 5 and 100 K and from 0.4% to 0.2% in the (100–340) K range. For diamond, characterized by small values of

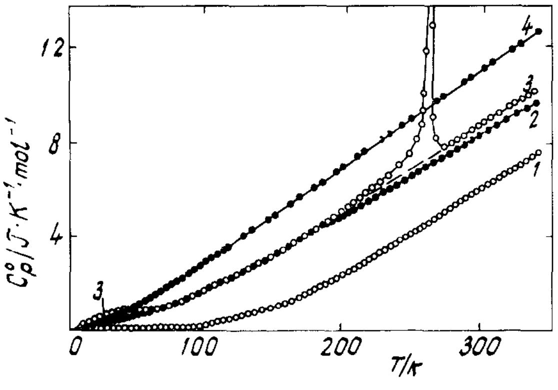

Fig. 1. Heat capacity of (1) – diamond, (2) – graphite, (3) – fullerene C_{60} and (4) – carbyne.

the heat capacity, the root-mean-square deviation varies in the (5–100) K range from 0.9 to 0.5% and between (100–340) K range, it is 0.4%.

The measurement results are shown in Fig. 1. The heat capacities of diamond, graphite and carbyne gradually increase with rising temperature and, on the curve $C_p^0 = f(T)$, there are some anomalies for fullerene C_{60}. It was found that in the temperature interval studied, fullerene C_{60} exists in three physical states: in a glasslike crystalline state crII′, crystalline crII and as plastic crystal crI [7]. On the curve of heat capacity, the mutual transformations of crystals crII′$\rightleftarrows$crII and crII$\rightleftarrows$crI are distinctly observed (Figs. 2 and 3). At present, the nature of these transitions is quite clear [7,8]. The transformation of crystals crII′ → crII takes place between 81 and 88.5 K; section BF on the curve of the relationship $C_p^0 = f(T)$ corresponds to it (Fig. 3). The transition temperature is $T_G^0 = 86$ K, the increase in the heat capacity at the transition temperature is $\Delta C_p^0(T_G^0) = 4.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (section CD, Fig. 3). The temperature at which the increase of the heat capacity in the course of crII′ → crII transition is half of the numerical magnitude of $\Delta C_p^0(T_G^0)$ is regarded to be T_G^0, as it is usually done on estimating glass transition temperatures. The numerical values of T_G^0 and $\Delta C_p^0(T_G^0)$ are close to those in Ref. [7].

The transformation crII → crI occurs in the (185–275) K range. T (crII → crI) = 260.7 K was taken as the transition temperature. It is the temperature at which an apparent heat capacity in the transition range has a maximum value $C_{p,\max}^0 = 34747\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

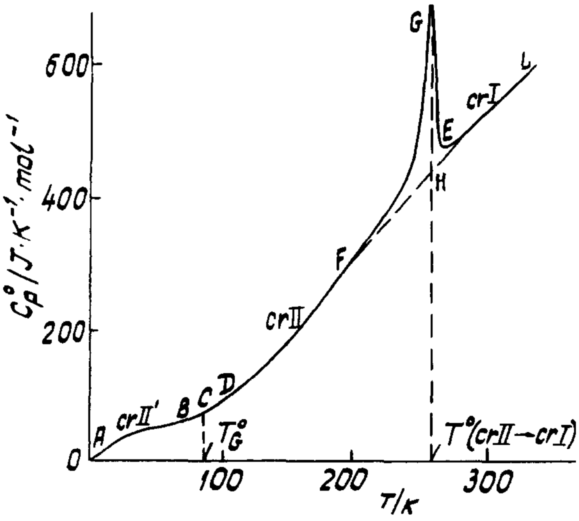

Fig. 2. Temperature dependence of heat capacity of fullerene C_{60}: ABC – in the state of a glasslike crystal crII′; CDFH – of crystals crII; HEL – of crystals crI; FGE – the apparent heat capacity in the transition range crII → crI; BD – the heat capacity in the range of glasslike transition crII′ → crI; T_G^0 is the temperature of glasslike transition; and T^0 (crII → crI) the temperature of crystal transiton crII → crI.

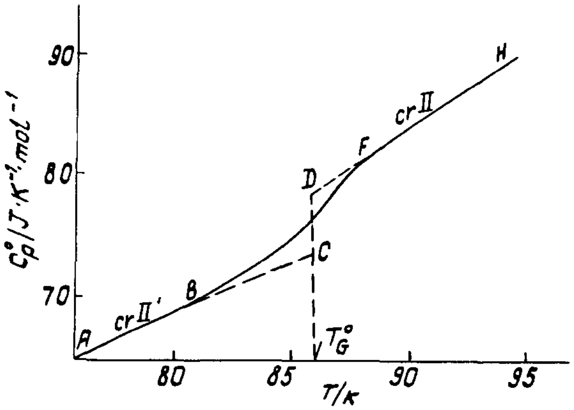

Fig. 3. Temperature dependence of heat capacity of fullerene C_{60} in the range of glasslike transition: ABC – the heat capacity of crystals crII′; DFH – the heat capacity of crystals crII; CD – the increase of the heat capacity on the transition crII′ → crII at T_G^0; and BF – the heat capacity in the range of crII′ → crII transition.

The enthalpy of transition $\Delta H^0(\text{crII} \rightarrow \text{crI}) = 7.46 \pm 0.15\,\mathrm{kJ\,mol^{-1}}$ was measured calorimetrically by the known method of a continuous energy input described earlier [9]. The entropy of transition $\Delta S^0(\text{crII} \rightarrow \text{crI}) = 2.86 \pm 0.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$ was calculated from the enthalpy and temperature of transition by means of the following equation:

$$\Delta S^0(\text{crII} \rightarrow \text{crI}) = \Delta H^0(\text{crII} \rightarrow \text{crI})/T^0(\text{crII} \rightarrow \text{crI}). \quad (1)$$

Relatively identical thermodynamic characteristics of this transition were reported elsewhere [7,10,11].

It is obvious that the heat capacity of the fullerene calculated per 1/60 of a C_{60} molecule coincides with the heat capacity of the graphite between 80 and 160 K with an error of 3%. The heat capacity of the carbyne and graphite (fullerene C_{60}) is 16 and 9.2 times that of the diamond at 80 K and 1.7 and 1.3 times at 340 K, respectively. This can be explained by the fact that the rigidity of an oscillating atomic skeleton of the above-mentioned substances decreases in the same sequence. While in the case of the graphite and fullerene C_{60}, its decrease relative to the diamond is associated with a change-over from a three-dimensional structure to a two-dimensional one, the further reduction of the rigidity of the carbyne skeleton, as compared to graphite, corresponds to a transfer from a layered to a chain structure. As the analysis of the curves $C_p^0 = f(T)$ showed, the heat capacity of diamond in the (25–90) K range is described by T^3-law of Debye, the heat capacity of graphite in the (25–60) K range by the T^2-dependence, characteristic of layer structures. and that of the carbyne in the (40–240) K range by the T^1-dependence typical of chain structures with a weak interaction between chains.

3.2. Thermodynamic functions

From the experimental data, the thermodynamic functions of the diamond, graphite, fullerene C_{60} and carbyne were estimated for the (0–340) K range. The heat capacity was extrapolated from (5–9) K to 0 K by using the Debye function for the heat capacity

$$C_p^0 = nD(\Theta_D/T) \quad (2)$$

where D represents the Debye function and n and Θ_D are adjustable parameters. The enthalpy of heating and entropy were calculated by numerical integration, on a computer, of the relations $C_p^0 = f(T)$ and $C_p^0 = f(\ln T)$, respectively. The Gibbs function was evaluated from the expression

$$G^0(T) - H^0(0) = [H^0(T) - H^0(0)] - TS^0(T) \quad (3)$$

In calculating $S^0(T)$ of the fullerene, its zero entropy – a residual entropy at $T = 0$ K, $S^0(0)$ – is equal to 4.9 J K^{-1} mol^{-1}, as determined in Ref. [8], was taken into consideration. The estimation of the zero entropy of an amorphous carbyne was not successful; therefore, in the given work it was not taken into account while calculating the functions. Table 1 lists the thermodynamic characteristics obtained by us for the modifications of carbon.

3.3. Thermochemical parameters of formation

Table 2 presents the literature data of combustion enthalpy $\Delta_{comb}H^0$ of graphite (cr) [12], carbyne (a) [1], fullerene C_{60} (cr) [13] and enthalpy of formation $\Delta_f H^0$ of the above substances and diamond (cr) [12] at $T = 298.15$ K and standard pressure as well as, calculated by us, entropies $\Delta_f S^0$, Gibbs functions $\Delta_f G^0$ of reactions of formation of diamond, fullerene C_{60} and carbyne from graphite under the same physical conditions. The calculation procedure of magnitudes of these quantities is similar to that demonstrated earlier [14]. From the value and the sign of the

Table 1
Thermodynamic functions of allotropic modifications of carbon; $T = 298.15$ K, $p = 101.325$ kPa

Substance [a]	$C_p^0/(\text{J K}^{-1}\text{ mol}^{-1})$	$H^0(T) - H^0(0)/(\text{kJ mol}^{-1})$	$S^0(T)/(\text{J K}^{-1}\text{ mol}^{-1})$	$-[G^0(T) - H^0(0)]/(\text{kJ mol}^{-1})$
Diamond (cr)	5.933	0.5125	3.321	0.1794
Graphite (cr)	8.239	1.023	5.568	0.6371
Fullerene C_{60} (crI)	8.747 [b]	1.207 [b]	7.108 [b]	0.9120 [b]
Carbyne (a)	11.46	1.624	10.16	1.404

[a] cr (crI) – crystalline state, a – amorphous state.
[b] The values are given per 1/60 of a C_{60} molecule.

Table 2
Thermochemical parameters of formation of diamond, fullerene C_{60} and carbyne from graphite; $T = 298.15$ K, $p = 101.325$ kPa

Substance	$\Delta_{comb}H^0/(\text{kJ mol}^{-1})$	$\Delta_fH^0/(\text{kJ mol}^{-1})$	$\Delta_fS^0/(\text{J K}^{-1}\ \text{mol}^{-1})$	$\Delta_fG^0/(\text{kJ mol}^{-1})$
Diamond (cr)		1.828±0.084 [12]	−3.25±0.02	2.796
Graphite (cr)	−393.51 [12]	0	0	0
Fullerene C_{60} (crI)	−432.75±0.20 [a] [13]	39.25±0.25 [a]	1.54±0.02 [a]	38.79±0.25 [a]
Carbyne (a)	−356.48 [1]	−37.03	4.59±0.02	−38.40

[a] The values are given per 1/60 of a C_{60} molecule.

standard Gibbs function Δ_fG^0, it is possible to arrange the thermodynamic stability of the allotropic carbon modifications: carbyne (a) > graphite (cr) > diamond (cr) > fullerene C_{60} (cr). It is seen that carbyne is thermodynamically the most stable allotropic modification of carbon, whereas fullerene C_{60} is the least stable.

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