THERMODYNAMIC PROPERTIES OF HYDROFULLERENE $C_{60}H_{36}$ FROM 5 TO 340 K

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Abstract

The temperature dependence of the molar heat capacity (C_p^o) of hydrofullerene $C_{60}H_{36}$ between 5 and 340 K was determined by adiabatic vacuum calorimetry with an error of about 0.2%. The experimental data were used for the calculation of the thermodynamic functions of the compound in the range 0 to 340 K. It was found that at T=298.15 K and p=101.325 kPa $C_p^o(298.15)$=690.0 J K^{-1} mol^{-1}, $H^o(298.15)–H^o(0)$= 84.94 kJ mol^{-1}, $S^o(298.15)$=506.8 J K^{-1} mol^{-1}, $G^o(298.15)–H^o(0)$= –66.17 kJ mol^{-1}. The standard entropy of formation of hydrofullerene $C_{60}H_{36}$ and the entropy of reaction of its formation by hydrogenation of fullerene C_{60} with hydrogen were estimated and at T=298.15 K they were $\Delta_f S^o$= –2188.4 J K^{-1} mol^{-1} and $\Delta_r S^o$= –2270.5 J K^{-1} mol^{-1}, respectively.

Keywords: adiabatic vacuum calorimeter, heat capacity, hydrofullerene $C_{60}H_{36}$, thermodynamic functions

Introduction

Hydrides of fullerenes are a new and, in many respects, promising class of fullerene derivatives. In particular, hydrofullerenes are of interest as a material used in the development of hydrogen storage cells [1–3]. In this connection, the investigation of hydrofullerene properties, especially because of an extremely high content of hydrogen in them, is an important task. As theoretical and experimental studies showed [4–7], the main product of fullerene C_{60} reduction with hydrogen is hydrofullerene $C_{60}H_{36}$. Its thermodynamic properties have not been studied yet. The goal of the present work was to determine the temperature dependence of the heat capacity and possible physical transitions of the compound in the range 5 to 340 K, to calculate the thermodynamic functions between 0 and 340 K, the standard entropy of formation of $C_{60}H_{36}$ and the entropy of hydrogenation reaction of fullerene C_{60} by hydrogen at p=101.325 kPa and to compare the thermodynamic properties of hydrofullerene $C_{60}H_{36}$ with those of fullerene C_{60} and fluorofullerene $C_{60}F_{36}$.

Experimental

Hydrofullerene $C_{60}H_{36}$ was prepared through the reaction of hydrogen transfer from 9,10-dihydroanthracene on to fullerene C_{60} by the procedure described earlier [2]. Initial fullerene C_{60} (99.5%) was produced by the method of Kratschmer–Huffman [8]. 9,10-Dihydroanthracene was supplied with Lancaster Synthesis Ltd and additionally purified by twice sublimation. The synthesis of hydrofullerene was conducted in glass ampoules under dry argon during 30 min. The product was purified from unreacted 9,10-dihydroanthracene and other reaction products by vacuum sublimation at 393 K for 8–10 h. The yield of $C_{60}H_{36}$ was 98 mol% of theoretical. By appearance, hydrofullerene $C_{60}H_{36}$ was a light-yellow powder. Elemental analysis indicated (mass%): C, 95.0; H, 5.1; theoretical: C, 95.2; H, 4.8. The structure of hydrofullerene $C_{60}H_{36}$ was confirmed by mass spectrometry (a Varian MAT-731 device) and IR spectroscopy (a Perkin Elmer-1600 spectrophotometer). ^{13}C NMR spectra (a Bruker MSL-300 instrument) and ^1H NMR spectra of $C_{60}H_{36}$ in a solid state were also recorded. Lobach *et al.* [2] described in detail the procedures of spectral measurements. It is to be noted that according to Goldshleger [1], in the synthesis of $C_{60}H_{36}$ 63 isomers of this compound are formed. Austin and colleagues [9] showed that the most stable isomer is T-symmetric $C_{60}H_{36}$. The isomeric composition of hydrofullerene sample investigated by us was not analyzed. The sample is suggested to be an isomer mixture with the predominant amount of $C_{60}H_{36}$ isomer of T-symmetry.

To study the temperature dependence of the heat capacity of hydrofullerene $C_{60}H_{36}$ in the range 5 to 340 K, an automatic thermophysical device TAU-1 – an adiabatic vacuum calorimeter designed and manufactured at the Research Institute of Physicotechnical and Radiotechnical Measurements of the State Standard Committee of Russian Federation – was employed. In [10, 11], the calorimeter design and the operational procedure were described. Here it should be noted only that all measurements were monitored by a computer-measuring system consisting of a computer, an analog-to-digital and a digital-to-analog converter and a switch. The calorimetric ampoule is a thin-walled cylindrical vessel from stainless steel of $1.5 \cdot 10^{-6}$ m^3. Its mass is $2.04 \cdot 10^{-3}$ kg. The temperature was measured with an iron-rhodium resistance thermometer ($R \cong 100$ Ω) calibrated according to ITS-90. The difference in temperatures between the ampoule and an adiabatic shield was controlled by a four-junction copper-iron-chromel thermocouple. The sensitivity of the thermometric circuit was $1 \cdot 10^{-3}$ K, of the analog-to-digital converter 0.1 μV. The speed of the computer-measuring system was 10 measurements per second. The calorimeter was calibrated electrically. The heat capacity of the unloaded calorimetric ampoule C_{cal} changed from 0.0047 J K^{-1} at 5 K to 1.460 J K^{-1} at 340 K. The root-mean-square deviation of the experimental points of C_{cal} from the smoothed curve $C_{cal}=f(T)$ did not exceed 0.06%. The reliability of the calorimeter operation was tested by measuring the heat capacity of special purity copper (OSCH 11-4), standard synthetic sapphire and K-2 benzoic acid prepared at metrology institutions of the State Standard of Russian Federation in the range 5 to 340 K. The analysis of the results showed that the measurement error of the heat capacity for the substances at helium temperature was about 2%; with in-

creasing temperature up to 40 K it decreased to 0.5% and at $T>40$ K it was approximately 0.2%. Liquid helium and nitrogen were used as cooling agents, and special purity helium was taken as a heat-exchange gas.

Results and discussion

Heat capacity

The heat capacity of hydrofullerene was measured between 4.8 and 340 K. The mass of the substance placed in the calorimetric ampoule was 0.3749 g. 226 experimental values of C_p^o were obtained in 4 series of measurements. In the range 5 to 100 K, the heat capacity of the sample was from 30 to 7% of the total heat capacity of the calorimetric ampoule and the substance, between 100 and 200 K from 7 to 15% and over the range 200 to 340 K from 15 to 25%. The experimental values of the heat capacity were averaged on a computer by means of degree and semilogarithmic polynomials so that the root-mean-square scatter of the experimental points from the smoothed curve $C_p^o=f(T)$ did not exceed the uncertainty of the heat capacity measurements (about 0.2%).

The experimental C_p^o values and the averaged curve $C_p^o=f(T)$ for hydrofullerene $C_{60}H_{36}$ are illustrated in Fig. 1 (curve 1). The root-mean-square deviation of the C_p^o points from the corresponding curve $C_p^o=f(T)$ was 0.11% in the range 5 to 90 K and 0.03% between 90 and 340 K. As seen in Fig. 1, the temperature dependence of the heat capacity of hydrofullerene does not exhibit any peculiarities: it gradually increases with rising temperature in the whole interval studied. In the same figure, a lattice component of isochoric heat capacity $C_{v,lat}$ (curve 2) obtained with using the experimental data C_p^o of for hydrofullerene is shown. With this purpose, as it was accepted in [12], the heat capacity of molecular crystals is supposed to be only a lattice contribution at $T<30$ K since atomic vibrations are not excited yet. Provided this condition, the reverse calculations with using the experimental C_p^o data allowed to obtain $\theta_D=48.45$ K and $n=6$ in the Debye function of the heat capacity:

$$C_p^o=nD(\theta_D/T) \tag{1}$$

where D denotes the Debye function of the heat capacity, n and θ_D are special parameters. With these parameters in Eq. (1), the lattice contribution of isochoric heat capacity $C_{v,lat}$ of hydrofullerene $C_{60}H_{36}$ was derived in the range 0 to 340 K (Fig. 1, curve 2). It is seen that $C_{v,lat}$ *vs.* T plot is a saturation curve. The value of $C_{v,lat}$ becomes constant at $T\cong30$ K. It corresponds to the contribution of vibrations of $C_{60}H_{36}$ molecules in the crystal lattice nodes of this compound to its heat capacity. As a frequency spectrum was unavailable, we did not succeed in estimating the contribution of atomic vibrations to the heat capacity. Besides, since the molar volume, the temperature coefficient of volumetric expansion and the isothermal compressibility are unknown, the calculation of the isochoric heat capacity of hydrofullerene under study was unsuccessful. However it is obvious that the principal contribution to the heat ca-

pacity of $C_{60}H_{36}$ is the contribution of atomic vibrations which could be evaluated by
the expression:

$$C_{v,at} = \sum_{i=1}^{282} E(\Theta_i) \qquad (2)$$

where E is the symbol of Einstein's function for the heat capacity, θ_i is the character-
istic temperature for each of 282 atomic vibrations of $C_{60}H_{36}$ molecule. Assuming that
at $T \cong 300$ K, C_p^o/C_v is commonly equal to 1.3–1.5 and $C_v = C_{v,lat} + C_{v,at}$, one can conclude
that at the above temperature the contribution of atomic vibrations to C_v of hydro-
fullerene $C_{60}H_{36}$ is about 10 times higher than that of the lattice one.
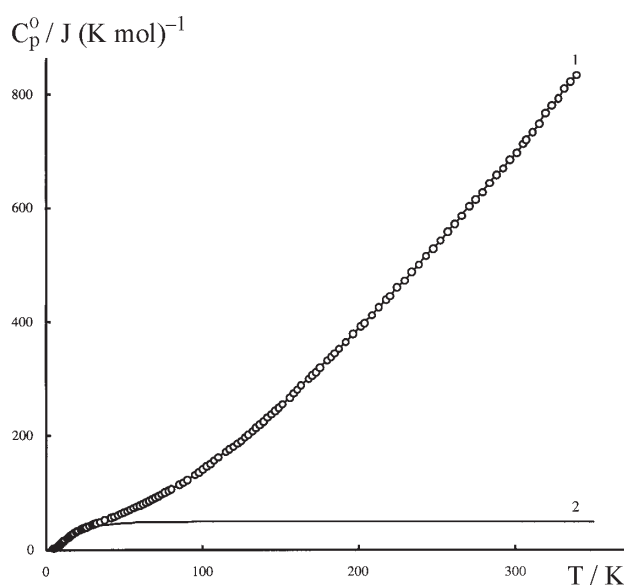
Fig. 1 Temperature dependence of heat capacity of hydrofullerene $C_{60}H_{36}$ (curve 1) and
lattice component of its isochoric heat capacity (curve 2)

In Fig. 2 temperature dependences of the heat capacity C_p^o for hydrofullerene
$C_{60}H_{36}$ (curve 1), fullerene C_{60} (curve 2) [13] and fluorofullerene $C_{60}F_{36}$ (curve 3) are
shown [14]. It is seen that, unlike fullerene C_{60}, hydrofullerene $C_{60}H_{36}$ and
fluorofullerene $C_{60}F_{36}$ have no physical transitions in the temperature interval studied.
By the shape, the plots C_p^o *vs.* T of fullerene C_{60} and $C_{60}H_{36}$ are similar, especially at
$T<250$ K, i.e. at $T<T_{tr}^o$ (T_{tr}^o is the temperature of the first-order phase transition in C_{60}).
It is certainly not accidental since for C_{60} and $C_{60}H_{36}$, the main contribution to the heat
capacity is made by the skeletal vibrations of spherical carbon surfaces of the above
molecules in this temperature range. The addition of hydrogen atoms – atoms of a
small atomic mass and an electronegativity close to that of carbon atoms {2.1 and 2.5
eV [15], respectively} – seems to slightly affect the change of the above skeletal vi-
brations and their contribution to the heat capacity of hydrofullerene in comparison

with the corresponding skeletal contribution of fullerene C_{60}. On the contrary, the addition of large fluorine atoms with the electronegativity equal to 4 eV [15] results in significant changes in skeletal vibration frequencies of fluorofullerene surface and the adequate changes in the contribution to its heat capacity. Moreover, because of a quite smaller intermolecular interaction in fluorofullerenes, as compared to hydrofullerene and fullerene C_{60} {$\Delta_v H^o(C_{60}F_{36})$=135±8 kJ mol^{-1} and $\Delta_v H^o(C_{60}H_{36})$= 175±3 kJ mol^{-1} [14]}, fluorofullerene has a somewhat larger contribution of lattice vibrations to the heat capacity than the above compounds. As to the role of the atomic vibration contributions at C–H and C–F bonds, the following may be noted. The frequencies of their vibrations are great due to a large strength of these bonds (the energies of dissociation of the bonds were found to be 300 and 403 kJ mol^{-1}, respectively [14]) and therefore, owing to high values of characteristic temperatures, their contribution to the heat capacity estimated by Einstein's function of the heat capacity [16] is likely to be small and to influence little the C_p^o values and the shape of the relation *vs. T*.
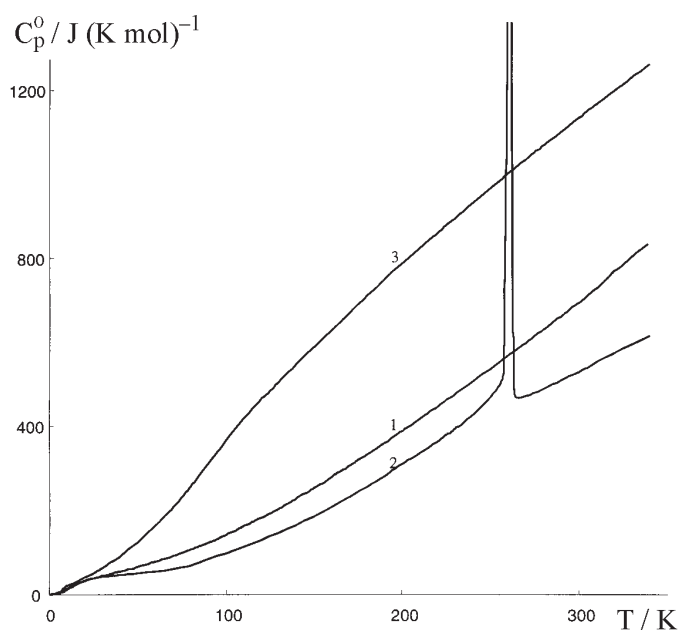
Fig. 2 Heat capacity of hydrofullerene $C_{60}H_{36}$ (curve 1), fullerene C_{60} (curve 2) and fluorofullerene $C_{60}F_{36}$ (curve 3)

Thermodynamic functions

The extrapolation of heat capacity of $C_{60}H_{36}$ from 5 to 0 K necessary to calculate the thermodynamic functions was made by Eq. (1) with specially selected parameters

n=6 and θ_D=63.25 K. With the above parameters it reproduces the heat capacity of hydrofullerene in the range 7 to 10 K within about 1%. It was suggested that at T<7 K Eq. (1) reproduces the heat capacity of hydrofullerene with the same uncertainty. The calculations of the enthalpy and entropy were made by numerical integration of relations C_p°=$f(T)$ and C_p°=$f(\ln T)$, and Gibbs function was estimated from the proper values of $H^\circ(T)$–$H^\circ(0)$ and $S^\circ(T)$. The zero entropy of C$_{60}$H$_{36}$was assumed to be zero. The calculation results are summarized in Table 1. The calculation procedure of the functions is similar to that described previously [11]. The uncertainty of the values of the thermodynamic functions was evaluated to be approximately 1.5% at T<30 K, 0.5% between 30 and 80 K and *ca* 0.2% from 80 to 340 K.

The thermodynamic functions of fullerene C$_{60}$, hydrofullerene C$_{60}$H$_{36}$ and fluorofullerene C$_{60}$F$_{36}$ at T=298.15 K and p=101.325 kPa calculated from the results of the present work and the data cited in [13, 14] are given in Table 2. A substantial difference in these values is obvious. The difference arose, certainly, for the same reasons as in the case of the heat capacities of these compounds.

Table 1 Thermodynamic functions of solid hydrofullerene C$_{60}$H$_{36}$ (M=756.9444 g mol^{-1}); p=101.325 kPa

T/K	C_p°/ J K^{-1} mol^{-1}	$H^\circ(T)$–$H^\circ(0)$/ kJ mol^{-1}	$S^\circ(T)$–$S^\circ(0)$/ J K^{-1} mol^{-1}	–[$G^\circ(T)$–$H^\circ(0)$]/ kJ mol^{-1}
5	2.45	0.0024	0.6396	0.0008
10	12.07	0.0344	4.685	0.0124
15	23.53	0.1245	11.85	0.0532
20	32.20	0.2650	19.87	0.1324
25	38.50	0.4423	27.76	0.2517
30	44.00	0.6486	35.27	0.4094
35	49.19	0.8818	42.45	0.6038
40	54.08	1.140	49.32	0.8334
45	59.28	1.423	55.99	1.097
50	65.19	1.734	62.54	1.393
60	77.65	2.448	75.52	2.083
70	91.30	3.291	88.50	2.903
80	106.3	4.277	101.6	3.854
90	122.4	5.419	115.1	4.937
100	141.2	6.732	128.9	6.156
110	161.6	8.246	143.3	7.516
120	182.4	9.926	158.2	9.024
130	204.0	11.90	173.7	10.68
140	228.0	14.06	189.7	12.50

Table 1 Continued

T/K	C_{p}°/ J K^{-1} mol^{-1}	$H^{\circ}(T)-H^{\circ}(0)$/ kJ mol^{-1}	$S^{\circ}(T)-S^{\circ}(0)$/ J K^{-1} mol^{-1}	$-[G^{\circ}(T)-H^{\circ}(0)]$/ kJ mol^{-1}
150	253.0	16.46	206.3	14.48
160	279.0	19.12	223.4	16.63
170	304.5	22.04	241.1	18.95
180	332.0	25.22	259.3	21.45
190	360.4	28.68	278.0	24.14
200	387.8	32.42	297.2	27.01
210	416.8	36.44	316.8	30.08
220	446.2	40.76	336.8	33.35
230	475.0	45.36	357.3	36.82
240	505.4	50.26	378.2	40.50
250	535.2	55.47	399.4	44.38
260	566.8	60.98	421.0	48.48
270	599.6	66.81	443.0	52.80
280	630.6	72.96	465.4	57.35
290	662.8	79.42	488.1	62.11
298.15	690.0	84.94	506.8	66.17
300	696.2	86.22	511.1	67.11
310	730.0	93.35	534.5	72.34
320	766.0	100.8	558.2	77.80
330	803.6	108.7	582.4	83.50
340	842.5	116.9	606.9	89.45

Table 2 Thermodynamic functions of fullerene C$_{60}$, hydrofullerene C$_{60}$H$_{36}$ and fluorofullerene C$_{60}$F$_{36}$; T=298.15 K, p=101.325 kPa

Substance	$C_{\mathrm{p}}^{\circ}(T)$/ J K^{-1} mol^{-1}	$H^{\circ}(T)-H^{\circ}(0)$/ kJ mol^{-1}	$S^{\circ}(T)$/ J K^{-1} mol^{-1}	$-[G^{\circ}(T)-H^{\circ}(0)]$/ kJ mol^{-1}
C$_{60}$	524.8	72.44	426.5	54.72
C$_{60}$H$_{36}$	690.0	84.94	506.8	66.17
C$_{60}$F$_{36}$	1134.0	167.5	1015.7	135.3

The standard molar entropy of formation of solid hydrofullerene C$_{60}$H$_{36}$ at T=298.15 K, $\Delta_{\mathrm{f}}S^{\circ}$= –(2188.4±2.8) J K^{-1} mol^{-1}, corresponds to the process:

$$60\ \mathrm{C_{(gr)}}+18\ \mathrm{H_{2(g)}}\rightarrow\mathrm{C_{60}H_{36(cr)}}.$$
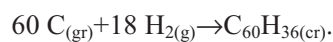
The values of absolute entropies of carbon in the form of graphite (*gr*) and gaseous hydrogen (*g*) were taken from [17] and the entropy of hydrofullerene is given in Table 1 of the present work.

In Table 3 the entropies of formation reaction of $C_{60}H_{36}$ by hydrogenation of fullerene C_{60} with molecular hydrogen are listed:

$$C_{60(cr)} + 18\ H_{2(g)} \rightarrow C_{60}H_{36(cr)}$$
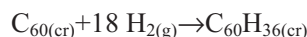
The appropriate values of the entropy of C_{60} and H_2 were taken from [13, 17], and for $C_{60}H_{36}$ from Table 1.

Table 3 Entropy of hydrogenation reaction of fullerene C_{60} with molecular hydrogen; p=101.325 kPa

T/K	Physical state of reagents[*]	$-\Delta_r S^o$/J K^{-1} mol^{-1}
100	crII, g; cr	1792.6
200	crII, g; cr	2084.4
298.15	crI, g; cr	2270.5
340	crI, g; cr	2313.6

[*]cr – crystalline, g – gaseous

In the calculation of $\Delta_f S^o$ and $\Delta_r S^o$ values it was assumed that $S_o(0)=0$.

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