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Thermodynamics of C_{70} fullerene in the 0—390 K temperature range

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The temperature dependence of heat capacity of C_{70} fullerene was studied by calorimetry in the range between 6 and 390 K. Phase transitions were established and their thermodynamic characteristics were determined. From the experimental data obtained, the thermodynamic functions $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$, $G^\circ(T) - H^\circ(0)$ for temperatures between 0 and 390 K were calculated. The results were used to calculate the standard values of $\Delta_f S^\circ$, $\Delta_f G^\circ$, and $\log K_f^\circ$ for the formation of C_{70} from graphite.

Key words: C_{70} fullerene, heat capacity; temperatures, enthalpies, and entropies of transitions, free energy of formation.

The thermodynamic properties of C_{70} fullerene, unlike those of C_{60}, have not yet been adequately studied. The majority of the calorimetric measurements, mostly accomplished using differential scanning calorimeters (DSC), have been devoted to the analysis of physical transformations in solid fullerene.[1—4] The temperature dependence of the heat capacity of C_{70} has been studied.[2,3,5] Experimental C_p° values were reported[2] only for the 120—560 K range. The C_p° values were also found[6] by QCFF/PI calculations. These values are in satisfactory agreement for the temperature ranges in which no phase transitions occur. Thermodynamic functions (enthalpy, entropy, and Gibbs energy) for C_{70} for the 0—560 K range were calculated;[2] however, the results of these calculations were presented only as plots without precise numerical values. The heats of combustion of C_{70} were measured by calorimetry, and the results obtained were used to calculate the standard enthalpies of its combustion and formation.[7—9] The standard entropy and Gibbs energy of formation have not been found, because the absolute entropy of C_{70} fullerene at T = 298.15 K and at standard pressure is unknown.

In view of the vigorous development[10,11] of the chemistry of C_{70} fullerene, in this work we studied it by calorimetry in the 6—390 K range. The temperature dependence of heat capacity C_p° and the temperatures and enthalpies of its phase transformations were investigated; the obtained experimental data were used to determine thermodynamic characteristics of phase transitions of C_{70} and standard thermochemical parameters of formation of C_{70} from graphite.

Experimental

A sample of C_{70} fullerene ("Materials and Electrochemical Research", USA) containing 99.7.% (w/w) of the major substance was used.

The temperature dependence of the heat capacity and the temperatures and enthaplies of phase transitions in the 6—340 K range were studied using a TAU-1 thermal automatic setup, which is an adiabatic vacuum calorimeter designed and produced at the NIIFTRI (Moscow). The design of the calorimeter and the procedure for its operation have been described previously.[12] Using samples of copper of the "extra pure" grade, standard synthetic sapphire, and standard benzoic acid studied in the 5—340 K temperature range, it was shown that the error of the measurement of heat capacity at helium temperatures does not exceed 2%; at 40 K, the error decreases to 0.5%, and in the 40—340 K range, it is as low as 0.2%. The C_p° values at 220—400 K were measured using an ADKTTM thermoanalytical complex, which is a dynamic calorimeter operating as a triple thermal bridge.[13] The design of the ADKTTM and the procedure of measurements have been published previously.[14] According to the certificate, the error of measurement of C_p° in this calorimeter ranged from 1 to 4%. However, since the heat capacities determined in the adiabatic vacuum calorimeter and in the dynamic calorimeter in the 220—340 K temperature range coincided with an accuracy of 0.5%, we assumed that the error of the measurements of C_p° in ADKTTM at $T > 340$ K amounts to 0.5—1.5%.

The heat capacity of C_{70} fullerene was measured in the adiabatic vacuum calorimeter in the 6—340 K range and in the dynamic calorimeter between 250 and 390 K. The weights of the samples were $0.4644 \cdot 10^{-3}$ and $0.4667 \cdot 10^{-3}$ kg, respectively. The heat capacity of the samples of C_{70} studied in both calorimeters amounted to 20—50% of the total heat capacity of the calorimetric ampule with the substance. In seven series of measurements in the adiabatic vacuum calorimeter, 139 experimental C_p° values were obtained. The values of C_p° were averaged on a computer. The root-mean square deviation of the experimental C_p° points from the averaged $C_p^\circ = f(T)$ curves in the 6—100 K range was ±0.13%, and that in the 100—340 K range was ±0.02%. The measurements of C_p° in the dynamic calorimeter were carried out under conditions of continuous heating at three heating rates. The C_p° values were recorded every 22 s. The experimental C_p° points and the averaged $C_p^\circ = f(T)$ curves are shown in Fig. 1. For the 340—390 K range, Fig. 1 shows the dependence $C_p^\circ = f(T)$ for C_{70},

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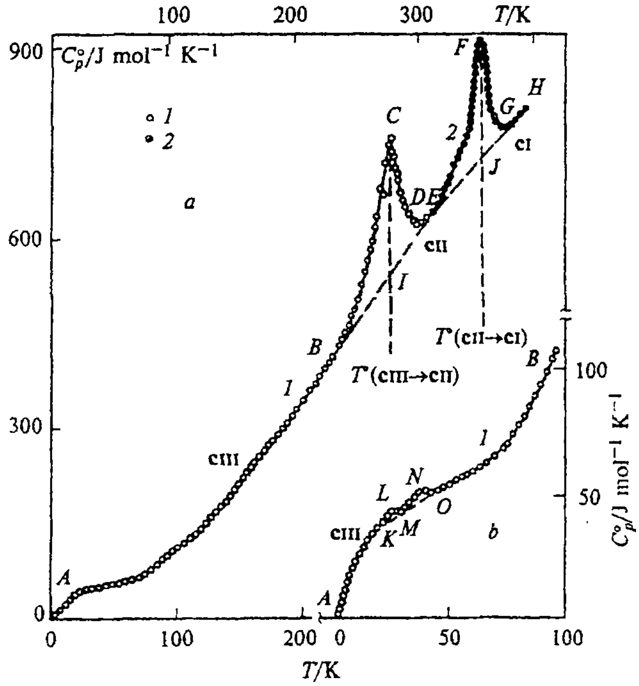

Fig. 1. *a*. Temperature dependence of heat capacity of C_{70} fullerene: cIII (*AB*), cII (*DE*), and cI (*GH*) crystals; *BCD* and *EFG* are apparent heat capacities in the ranges of the cIII → cII and cII → cI transitions, respectively; *BID* and *EJG* show the "normal" pattern of heat capacity curves in the ranges of these transitions (dashed lines). *b*. Anomalous temperature dependence of heat capacity (*KLMNO*); *KMO* is the normal heat capacity pattern in the same temperature range. Experimental C_p° values were obtained in the adiabatic vacuum calorimeter (*1*) or in the dynamic calorimeter (*2*).

obtained when the rate of heating of the calorimeter with the substance was $1.7 \cdot 10^{-2}$ K s^{-1}; this was the lowest heating rate used in this study in the experiments with ADKTTM; the C_p° points correspond to each third value of heat capacity of those measured over 1 s.

Table 1 presents the results of the determination of the temperatures and enthalpies of transformations in C_{70} fullerene obtained using the ADKTTM calorimeter.

Table 1. Experimental data on phase transitions of C_{70} fullerene obtained in the dynamic calorimeter

$v \cdot 10^2$ /K s^{-1}	T_s° K	T_{end}° K	$C^\circ_{p,max}$ /J mol^{-1} K^{-1}	T°_{max} /K	ΔH° /kJ mol^{-1}
			cIII → cII		
1.7	250	300	758.6	280.8	3.39
2.5	260	300	745.9	281.4	3.26
3.3	260	305	767.0	282.9	3.12
			cII → cI		
1.7	320	370	923.9	349.7	3.07
2.5	320	370	889.4	351.7	2.64
3.3	330	375	915.8	354.0	2.52

Note: v is the rate of heating of the calorimeter with the substance, T_s° and T_{end}° are the temperatures of the onset and the end of the transformations, $C^\circ_{p,max}$ is the maximum apparent heat capacity in the transformation range, T°_{max} is the temperature corresponding to $C^\circ_{p,max}$; ΔH° is the enthalpy of transformations.

Results and Discussion

Our experiments showed that in the temperature range studied, C_{70} fullerene exists in three phase states, cI, cII, and cIII. These states are matched by sections *AB*, *DE*, and *GH* in the temperature dependence of heat capacity (see Fig. 1). The cIII → cII and cII → cI transformations are clearly manifested in the temperature dependence of heat capacity (see Fig. 1). They are well reproducible during both heating and cooling of the fullerene. According to published data,[15,16] C_{70} fullerene tends to form polymorphic phases, and at present, five crystalline modifications of this material are known. The crystals of cI are built of a hexagonal lattice ($a = b =$ 10.56 Å, $c/a = 1.63$), and fullerene molecules rotate virtually freely in the lattice points, *i.e.*, this material is characterized by molecular orientational disorder, which is usually typical of plastic crystals.[17] When crystals of cI are cooled to $T < T^\circ$ (cII → cI), the lattice rearranges but remains hexagonal, and its parameters change: $a =$ $b = 10$ Å and $c/a = 1.82$. This is accompanied by substantial orientational ordering of C_{70} molecules in the crystal lattice: the free rotation of molecules around a fivefold axis is "frozen" but rotation around the *c* axis is retained.[16] On subsequent cooling to $T < T^\circ$ (cIII → cII), the hexagonal lattice rearranges into a monoclinic one, and the free rotation of C_{70} molecules around the *c* axis becomes "frozen", *i.e.*, the molecules of C_{70} in the crystals of cIII are completely orientationally ordered. Cooling of the cIII crystals in the 19—45 K range leads to anomalous change in the heat capacity; two anomalous sections, *KM* and *MO*, can be clearly distinguished in the (Figs. 1 and 2). We denoted the first anomaly by **A**, and the second, by **B**. According to our results obtained by calorimetry, they are characterized by the following thermodynamic parameters: anomaly **A** occurs in the 19—31 K range, and the maximum deviation of heat capacity from the normal plot for C_p° *vs* T is observed at $T = 29$ K and is equal to 1.96 J mol^{-1} K^{-1}; the enthalpy change found from the difference between the integrated C_p° *vs* T curves, *KLM* and *KM*, is equal to 139 J mol^{-1}; the entropy change found in a similar way using the curves of C_p° *vs* $\ln T$ amounts to 0.54 J mol^{-1} K^{-1}. Anomaly **B** is registered in the 31—45 K range, $\Delta C_p^\circ = 2.9$ J mol^{-1} K^{-1} at $T = 38$ K, $\Delta H^\circ =$ 176 J mol^{-1}, and $\Delta S^\circ = 0.47$ J mol^{-1} K^{-1}. The nature of these anomalies is unknown. They are also well reproduced during cooling and heating of the fullerene sample studied. Unlike C_{60} fullerene, C_{70} fullerene exhibits no G-type glass-like transition; it is not manifested in the $C_p^\circ = f(T)$ dependence. In previous studies,[3,5] this transition has not been observed either. According to published data,[2,16] at elevated temperatures ($T > 400$ K), the crystals of cI can rearrange into an orthorhombic lattice, which, in turn, is partly converted into a facecentered cubic lattice, and these two structures occur in thermodynamic equilibrium. On cooling, the orthorhombic lattice is not transformed[16] into a hexagonal system. However, study of $C_p°$ of C_{70} fullerene in the 340—560 K range did not reveal[2] any transformations. The thermodynamic characteristics of the transformations of C_{70} fullerene, found from the results of calorimetric measurements carried out here and in previous studies,[1—5] are listed in Table 2. We studied the cIII → cII transition in the vacuum adiabatic and dynamic calorimeters. It can be seen that the results obtained by these two procedures are in good agreement with each other. In both cases, the $T°$ (cIII → cII) temperature was found as the point corresponding to the maximum apparent heat capacity over the transition range (point *C* in Fig. 1). The transition temperatures, determined from the results of measurements in the dynamic calorimeter at different heating rates, were extrapolated (*cf.* Ref. 18) to the zero heating rate (see Table 1). The $T°$ (cIII → cII) values obtained by both methods coincided with an accuracy of ±1 K. The parameters of the cIII → cII transition determined in this study coincide with the published data to within the determination errors.[1,4] Some distinctions from the results obtained in other works can be explained by different qualities of the samples studied (contents of impurities, history) and, perhaps, by methodical reasons.

Two transformations in the 303—347 K range were found.[2] Their overall characteristics are close to the corresponding values for the cII → cI transition. $\Delta H° = 2.48$ kJ mol^{-1}, $\Delta S° = 8.1$ J mol^{-1} K^{-1}. In addition to the cII → cI and cIII → cII transitions, an endothermal transformation at $T = 307$ K was also observed.[3] The overall enthalpy for both transformations at $T = 307$ K and $T°$ (cII → cI) amounts to 1.7 kJ mol^{-1}. It was suggested[2] that the additional transition is associated with the presence of other polymorphic forms of C_{70} in the samples under study.

Table 2. Thermodynamic characteristics of the phase transitions in C_{70} fullerene*

$T°$/K	$\Delta H°$ /kJ mol^{-1}	$\Delta S°$ /J mol^{-1} K^{-1}	Determination method**	Reference
		cIII → cII		
277.4	3.22	11.6	AVC	This work
276.4	3.3±0.2	11.8±0.6	DC	This work
276	2.9±0.4	10.5±1.5	DSC	1
280	4.7	17	AVC	5
261—275	4.44	14.3	DSC	2
280	2.7	9.6	DSC	3
274	3.2	11.5	DSC	4
		cII → cI		
340	2.7±0.4	8±1	DSC	This work
337	2.3±0.8	6.8±0.9	DSC	1
337	1.84	5.5	DSC	3

* In the text, the thermodynamic parameters of the transformations are denoted by $T°$ (cIII → cII), $\Delta H°$ (cIII → cII), $\Delta S°$ (cIII → cII); $T°$ (cII → cI), $\Delta H°$ (cII → cI), $\Delta S°$ (cII → cI).

** AVC is adiabatic vacuum calorimetry, DC is dynamic calorimetry, DSC is differential scanning calorimetry.

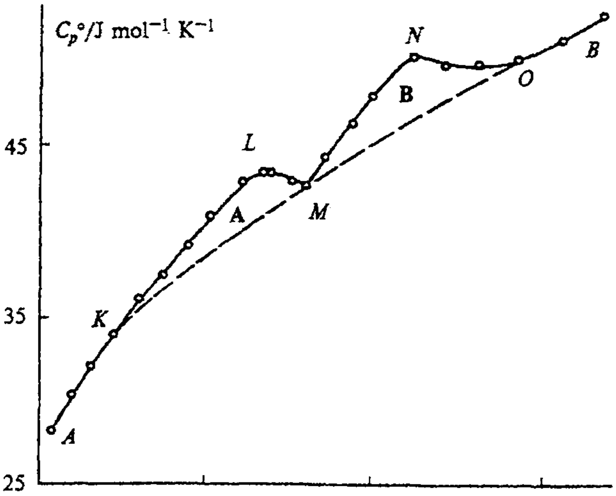

Fig. 2. Heat capacity of C_{70} fullerene in the *KO* section of the anomalous dependence of $C_p°$ on *T*: *KLM* is the first anomaly (**A**), *MNO* is the second one (**B**); *KMO* is the normal heat capacity pattern.

It is difficult to interpret unambiguously the cIII → cII and cII → cI transitions considered here. They are not exothermal; the plots for the dependence of the apparent heat capacities $C_p°$ on *T* exhibit no breaks in the regions of these transitions. Both transitions are accompanied by changes in the crystal structure of C_{70}, which is a significant criterion indicating first-order transitions. However, both of them are accompanied by the change

Table 3. Thermodynamic functions of C_{70} fullerene

T /K	$H°(T) - H°(0)$ /kJ mol^{-1}	$S°(T)$ /J mol^{-1} K^{-1}	$-[G°(T) - H°(0)]$ /kJ mol^{-1}
		cIII crystals	
6	0.00937	2.07	0.00306
10	0.05347	7.46	0.02116
20	0.3176	25.06	0.1836
30	0.7141	41.00	0.5159
40	1.183	54.43	0.9942
50	1.691	65.76	1.597
60	2.244	75.83	2.305
70	2.857	85.25	3.111
80	3.555	94.56	4.010
90	4.368	104.1	5.004
100	5.348	114.4	6.095
150	13.03	175.3	13.26
200	26.57	252.3	23.90
250	47.04	343.0	38.70
		cII crystals	
298.15	77.17	452.7	57.80
		cI crystals	
370	130.8	613.0	95.95
390	146.7	654.6	108.6

in the orientation of molecules from complete order in the crystals of cII to complete disorder in the crystals of cI, *i.e.*, we observe transitions of the "order—disorder" type, which are normally classified as second-order transitions.

We used the experimental results to calculate the thermodynamic functions of C_{70} for the 0—390 K range (Table 3). The heat capacity in the range between 0 and 6 K was calculated from the Debye heat capacity function

$$C_p{}^\circ = nD(\Theta_D/T), \qquad (1)$$

where D is the symbol of the Debye heat capacity function, and n and Θ_D are specially selected parameters. Equation (1) for $n = 5$ and $\Theta_D = 47.91$ K corresponds to the experimental $C_p{}^\circ$ values found for the 6—12 K range to within 1%. We assumed that it describes the heat capacity of C_{70} in the 0—6 K range with approximately the same error.

The enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T)$, and the Gibbs function $G^\circ(T) - H^\circ(0)$ were calculated from the equations

$$H^\circ(T) - H^\circ(0) = \int_0^T C_p{}^\circ(T)\mathrm{d}T, \qquad (2)$$

$$S^\circ(T) = \int_0^T C_p{}^\circ(T)\mathrm{d}\ln T, \qquad (3)$$

$$G^\circ(T) - H^\circ(0) = [H^\circ(T) - H^\circ(0)] - T \cdot S^\circ(T), \qquad (4)$$

where $C_p{}^\circ(T)$ is the temperature dependence of heat capacity (curve *ABCDEFGH* in Fig. 1). The procedure for the calculation of these functions was described in detail previously.[19]

The standard enthalpies (kJ mol^{-1}) of combustion $\Delta H_c{}^\circ$ and formation $\Delta H_f{}^\circ$ of C_{70} fullerene (see Ref. 8) as well as the $\Delta S_f{}^\circ$/kJ mol^{-1} K^{-1}, $\Delta G_f{}^\circ$/kJ mol^{-1}, and $\log K_f{}^\circ$ values for the formation of crystalline C_{70} fullerene (cII) from graphite at $T = 228.15$ K and $p = 101.325$ kPa, calculated in this work, are given below.

$\Delta H_c{}^\circ$	$\Delta H_f{}^\circ$	$\Delta S_f{}^\circ$	$\Delta G_f{}^\circ$	$\log K_f{}^\circ$
−30101±10 [8]	2555±12 [8]	62.94±1.41	2536±12	−445

These values were calculated using a procedure similar to that reported previously.[20] It can be seen that the standard Gibbs function $\Delta_f G^\circ$ is a large positive value; this means that the spontaneous process 70 C(gr.) → C_{70} (cII), where C(gr.) is carbon in the form of graphite, is completely forbidden from the thermodynamic viewpoint. Only a non-spontaneous process is possible, which is in full agreement with the experimental results;[21] this reaction proceeds only in an arc discharge.

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