Thermodynamics of C_{60} fullerene in the 0—340 K range

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The temperature dependence of the heat capacity of C_{60} fullerene in the range of 5 to 340 K has been studied by calorimetry. The temperatures and enthalpies of physical transformations were measured. From the experimental results, the thermodynamic functions $C_p°$, $H°(T) - H°(0)$, $S°(T)$, and $G°(T) - H°(0)$ were calculated for the 0—340 K range. The zero entropy $S°(0)$ and the contribution of configurational entropy $S_c°$ to it, which is due to the transformation of fullerene to a glassy modification at 86 K, were estimated. The thermochemical parameters of formation of C_{60}, *viz.*, $\Delta_f H°$, $\Delta_f S°$, $\Delta_f G°$ and $\log K_f°$, at 298.15 K and at the standard pressure were calculated.

Key words: C_{60} fullerene, heat capacity, thermophysical transformations; enthalpy, entropy, free Gibbs energy; adiabatic vacuum calorimeter.

At present, C_{60} fullerene[1—3] is the object of various investigations, in particular, of calorimetric studies. Recently, studies on thermodynamic properties of fullerenes have been surveyed in a review.[4] Although a large number of calorimetric studies dealing with the temperature dependence of heat capacity and with the temperatures and enthalpies of physical transformations of C_{60} fullerene between 1 and 560 K have been reported,[5—10] neither the numerical values for its heat capacity nor data on the thermodynamic functions or standard thermochemical parameters of its formation can be found in the literature.

The purpose of the present work is to study by calorimetry the temperature dependence of the heat capacity of C_{60} fullerene in the 5—340 K range, to measure the temperatures of its physical transformations and the enthalpy of its phase transition in the range from 180 to 260 K, and to use the experimental results for calculating the thermodynamic characteristics of physical transformations and the thermodynamic functions $C_p°$, $H°(T) - H°(0)$, $S°(T)$, $G°(T) - H°(0)$ for the 0—340 K range as well as the standard thermochemical parameters of the formation of C_{60}, *viz.*, the enthalpy ($\Delta_f H°$), the entropy ($\Delta_f S°$), the Gibbs free energy ($\Delta_f G°$), and the logarithm of the equilibrium constant ($\log K_f°$) at 298.15 K.

Experimental

A sample of C_{60} fullerene containing no less than 99.98% w/w major substance was prepared at the Institute of Organometallic Chemistry of the RAS (Nizhnii Novgorod)[11] by a procedure similar to the Krätschmer—Huffman method.[3] Rods of graphite of the "extra pure 7-3" grade were used as the initial carbon. Combustion of the graphite rods in an arc discharge (the Krätschmer—Huffman process) was carried out in a specially designed setup, which has been described previously.[12] The combustion proceeded in a quasi-steady-state regime. The resulting mixture of fullerenes was extracted with toluene in a steel Sohxlet apparatus. The C_{60} fullerene was isolated from the extract by preparative liquid flash-chromatography using a ~1 m long glass column 4.5 cm in diameter. A mixture of activated carbon (Norit A) and silica gel (Merck 60 Å, grade-60, 230—400 mesh) in 1 : 1 ratio (v/v) was used as the stationary phase, and toluene was used as the mobile phase. The sample was dried *in vacuo* at ~400 K. The proportion of impurities was no more than 0.02%.* According to the data of X-ray diffraction analysis (a Dron-3 diffractometer), the C_{60} sample obtained was a crystalline material at room temperature. The molecules of fullerene form a face-centered cubic lattice with a_0 = 14.2 Å, which is in good agreement with literature data.[13]

The temperature dependence of the heat capacity and the temperatures and enthalpies of physical transformations were studied using a TAU-1 thermal automatic setup, which is an adiabatic vacuum calorimeter designed and produced at the VNIIFTRI (Moscow). The design of the calorimeter and the procedure for its operation have been described previously.[14] All the measurements were monitored by a measuring and computing set-up, which included a computer, analog-to-digital and digital-to-analog converters, and a voltage switch.

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* Impurities in the C_{60} sample obtained were analyzed using HPLC by A. M. Davydov (M. V. Lomonosov Moscow State University).

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A thin-wall stainless-steel vessel with a volume of $1.5 \cdot 10^{-6}$ m^3 and weighing $2.06 \cdot 10^{-3}$ kg was used as the calorimetric ampule. The temperature was measured with an iron-rhodium resistance thermometer ($R_0 \approx 100$ Ω). The temperature difference between the ampule and the adiabatic shell was monitored by a copper to iron-chromel four-component thermocouple. The sensitivity of the thermometric scheme was $1 \cdot 10^{-3}$ K, that of the analog-to-digital converter was 0.1 μV; the speed of response of the measuring and computing system amounted to 10 s^{-1}. The calorimeter was calibrated with electric current. The heat capacity of the empty calorimetric ampule (C_a) varied from 0.0038 J K^{-1} (5 K) to 1.275 J K^{-1} (340 K). The root-mean square deviation of experimental $C_p°$ points from the averaging $C_a = f(T)$ curve did not exceed ±0.16%. The reliability of the operation of the calorimeter was verified by measuring the heat capacities of copper of the "extra pure 11-4" grade, standard synthetic sapphire, and standard K-2 benzoic acid in the 5—340 K temperature range. Analysis of the data obtained indicates that the error of the measurements of the heat capacities of substances at temperatures close to that of liquid helium does not exceed ±2%. When the temperature increases to 40 K, the error decreases to 0.5%, and in the 40—340 K range, it is as low as 0.2%.

The heat capacity of C_{60} fullerene was measured in the 4.97—339.08 K temperature range. The weight of the sample under study placed into the calorimetric ampule was 0.7009 g. The ampule containing the substance was filled with a heat-exchange gas (He) up to a pressure of $1.3 \cdot 10^3$ Pa at room temperature. In 13 series of measurements, we obtained 150 experimental values of $C_p°$. The heat capacities of the fullerene sample studied (with respect to the overall heat capacity of the calorimetric ampule with the substance) at 5, 15, 30, 100, 200, and 340 K amounted to 33, 40, 27, 19, 19, and 17%, respectively. The root-mean square deviation of the experimental $C_p°$ points from the average $C_p° = f(T)$ curve (Fig. 1) in the range between 5 and 100 K varied from ±0.5 to ±0.4%, and that in the 100—340 K range was no more than ±0.2%.

Results and Discussion

Our experiments showed that in the temperature range studied, C_{60} fullerene exists in three physical states: in a glassy crystalline state C-II′, in the crystalline state C-II, and as plastic crystals C-I. The C-III′ $\rightleftharpoons$ C-II and C-II $\rightleftharpoons$ C-I interconversions are clearly manifested on the heat capacity curve (Figs. 1 and 2). The C-I crystals have a face-centered cubic lattice (FCC), in the nodes of which spherical C_{60} molecules execute virtually free rotation,[15] *i.e.*, there exists orientational molecular disorder typical of plastic crystals.[16] When the C-I crystals are cooled to $T < T°$ (C-II → C-I), the FCC-packing rearranges to a simple cubic lattice (SC) and, simultaneously, orientational ordering of the C_{60} molecules in the nodes of the SC lattice occurs.[10,17] According to published data,[17,18] in the C-II crystals, the C_{60} molecules may occur in two energetically nonequivalent orientational states, which are separated by a relatively low energy barrier of 1.12±0.01 kJ mol^{-1}. The populations of these states depend on the temperature. It has been shown[18,19] that in the temperature range between 5 and 90 K, the proportion of molecules with the more energetically favorable orientation is 0.833; as the temperature increases from 90 to 260 K it decreases to 0.630, and after the C-II → C-I transformation, this proportion amounts to 0.500. The fact that the populations of the orientational states are constant at $T < 90$ K is due to the fact that these states are frozen during the transformation to the glassy modification, *i.e.*, during the G-type transition[20] (see Fig. 2). The C-II′ → C-II transformation of crystals occurs in the 81.0—88.5 K temperature range; this is matched by the section *BD* in the $C_p° = f(T)$ plot. The temperature of the $T_G°$ transformation is 86 K (the

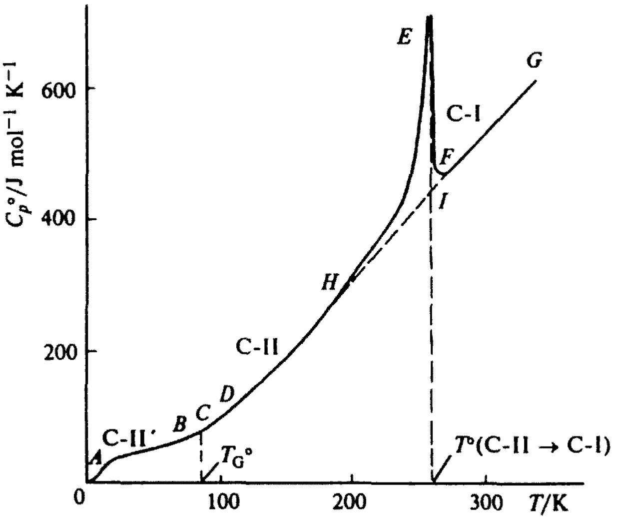

Fig. 1. Temperature dependence of the heat capacity of C_{60} fullerene in various states: *ABC*, for the C-II′ glassy crystal; *CDHI*, for the C-II crystals; *IFG*, for the C-I crystals, *HEF*, the apparent heat capacity in the range of the C-II → C-I transition; *BD*, that in the range of the C-II′ → C-II transition to the glassy state; $T_G°$ is the temperature of the transformation to the glassy state; $T°$(C-II → C-I) is the temperature of the C-II → C-I transition of crystals.

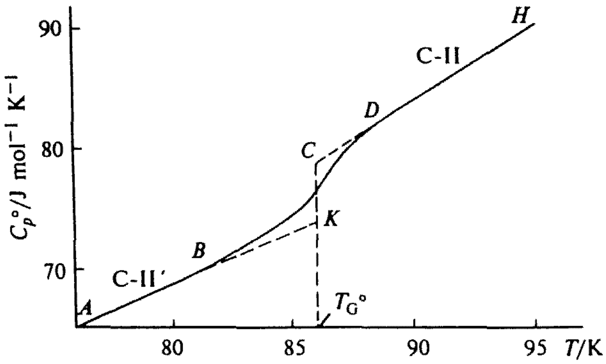

Fig. 2. Temperature dependence of the heat capacity of C_{60} fullerene over the range of the transformation to the glassy state: *ABK*, for the C-II′ crystals, *CDH*, for the C-II crystals; *KC*, $\Delta C_p°$ for the range of the C-II′ → C-II transition at $T = T_G°$; *BD*, for the range of the C-II′ → C-II transition.

temperature at which the increase in the heat capacity during the C-II′ → C-II transition is half the numerical value of $\Delta C_p°(T_G°)$ is taken as $T_G°$, as in the definition of glass transition temperatures[21]); the increase in the heat capacity at the transition temperature $\Delta C_p°(T_G°)$ = 4.5 J mol^{-1} K^{-1} (see Fig. 2, section *KC*). The $T_G°$ and $\Delta C_p°(T_G°)$ values obtained are close to published data.[8] The nature of the C-II′ → C-II transition has been confirmed by previously reported[8] results of calorimetric studies of relaxation characteristics of C-II′ crystals.

The relatively rapid increase in the heat capacity in section *HE* of the curve (see Fig. 1) is apparently due to the contribution to the $C_p°$ value of the energy of the transition of molecules from the lower-energy orientational state to the higher-energy state. It has been shown[8,9] that the variation of the fraction of molecules that have passed from one orientational state to the other as a function of the temperature is adequately described by the van't Hoff equation. The corresponding contribution to the heat capacity (the difference between the heat capacities represented by the curves *HE* and *HI* at the corresponding temperatures, see Fig. 1) also varies adequately.

The C-II → C-I transformation occurs in the 185—275 K temperature range. The temperature $T°$(C-II → C-I) = 260.7 K, at which the apparent heat capacity is the greatest ($C°_{p(\max)}$ = 34747 J mol^{-1} K^{-1}) over the range of transition, was taken as the temperature of transition. The enthalpy of transition $\Delta H°$(C-II → C-I) = 7.46±0.15 kJ mol^{-1} was measured by calorimetry using the known technique of the continuous introduction of energy.[21] The average result over four experiments is presented together with the arithmetic mean deviation. The entropy of transition $\Delta S°$(C-II → C-I) = 28.6±0.6 J mol^{-1} K^{-1} was calculated from the enthalpy and the temperature of the transition.

$$\Delta S°(\text{C-II} \rightarrow \text{C-I}) = \Delta H°(\text{C-II} \rightarrow \text{C-I})/T°(\text{C-II} \rightarrow \text{C-I}) \quad (1)$$

Thermodynamic characteristics of this transition, relatively close to our results, have been reported in a series of papers.[5,8—10] The nature of the phase transition has been interpreted fairly comprehensively previously.[8,13,17] Note only that this transition can be in principle regarded as a combination of two transformations: a second-order transition of the "order—disorder" type and a first-order phase transition. The former corresponds to disordering of the molecules in the crystal lattice, and the latter corresponds to SC to FCC rearrangement during the C-II → C-I transformation.

From the experimental data obtained, we calculated the thermodynamic functions of C_{60} (Table 1). The extrapolation of the heat capacity to 0 K was accomplished using the Debye heat capacity function

$$C_p° = nD(\theta_D/T), \quad (2)$$

where *D* is the Debye heat capacity function, and *n* and θ_D are specially selected parameters. When n = 10 and θ_D = 58.82 K, Eq. (2) describes the experimental values of $C_p°$ in the 8—12 K temperature range with an error of ±0.7%. The functions were calculated with the assumption that in the 0—8 K temperature range, the error of the determination of heat capacity from this equation is approximately the same. It was also assumed that in the temperature range of the C-II → C-I phase transition, the normal values of heat capacity are represented by the dashed line *HIF* (see Fig. 1). This $C_p° = f(T)$ dependence was chosen in a way similar to that described for adamantane,[22] which exhibits a very similar $C_p° = f(T)$ dependence in the same temperature range. The $C_p°(T)$ values presented in Table 1 correspond to the data of the $C_p° = f(T)$ dependence shown in Fig. 1 (the *ABCDHIFG* curve). The enthalpy $H°(T) - H°(0)$, the entropy $S°(T)$, and the Gibbs function $G°(T) - H°(0)$ were calculated from Eqs. (3)—(5)

$$H°(T) - H°(0) = \int_0^T C_p°(T)\mathrm{d}T + \Delta H°(\text{C-II} \rightarrow \text{C-I}), \quad (3)$$

$$S°(T) = S°(0) + \int_0^T C_p°(T)\mathrm{d}\ln T + \Delta S°(\text{C-II} \rightarrow \text{C-I}), \quad (4)$$

$$G°(T) - H°(0) = [H°(T) - H°(0)] - TS°(T), \quad (5)$$

where $C_p°(T)$ corresponds to the *ABCDHIFG* curve in Fig. 1. The procedure for the calculation of the functions was described in detail in our previous study.[23]

The $S°(T)$ value was calculated taking into account the zero entropy $S°(0)$ of fullerene, *i.e.*, the residual entropy at 0 K. This is the sum of two terms: $\Delta S_c°$, which is the configurational entropy associated with freezing of the fullerene structure during the G-transition, and $S°_{\text{mix}}$, which is the entropy of mixing of the various orientational positions of the molecules, their ratio being constant at $T < T_G°$.

$$S°(0) = \Delta S_c° + \Delta S°_{\text{mix}} \quad (6)$$

The $\Delta S_c°$ term was calculated from the equation[24]

$$\Delta S_c° = \Delta C_p°(T_G°) \cdot \ln 1.29, \quad (7)$$

and $\Delta S°_{\text{mix}}$ was found from the Schottki—Wagner formula[25]

$$\Delta S°_{\text{mix}} = -R(N_1 \ln N_1 + N_2 \ln N_2), \quad (8)$$

where N_1 and N_2 are the mole fractions of molecular orientations in positions 1 and 2 frozen at $T < T_G°$. By substituting the corresponding values $\Delta C_p°(T_G)$ = 4.5 J mol^{-1} K^{-1}, N_1 = 0.835, and N_2 = 0.165 into Eqs. (7) and (8),[8,19] we obtained $\Delta S_c°$ = 1.15 J mol^{-1} K^{-1}, $\Delta S°_{\text{mix}}$ = 3.72 J mol^{-1} K^{-1}, and $S°(0)$ = 4.9±0.5 J mol^{-1} K^{-1}. The $S°(0)$ value found by us is in good agreement with published data:[26] $S°(0)$ = 4.7±0.5 J mol^{-1} K^{-1}.

The enthalpies of combustion ($\Delta_c H°$/kJ mol^{-1}) and of formation ($\Delta_f H°$) of C_{60} fullerene at 298.15 K and at

Table 1. Thermodynamic functions of C_{60} fullerene for the 0—340 K range

T/K	C_p°* /kJ mol^{-1} K^{-1}	$H^{\circ}(T) - H^{\circ}(0)$ /kJ mol^{-1}	$S^{\circ}(T)$ /J mol^{-1} K^{-1}	$-[G^{\circ}(T) - H^{\circ}(0)]$ /kJ mol^{-1}
C-II′ crystals				
0	0	0	4.9	0
5	2.368	0.00296	5.7	0.02554
10	13.78	0.04061	10.4я	0.06339
15	24.99	0.1394	18.3	0.1351
20	33.18	0.2867	26.7	0.2473
25	39.00	0.4677	34.7	0.3998
30	41.82	0.6717	42.2	0.5943
35	43.62	0.8850	48.7	0.8189
40	45.66	1.108	54.7	1.080
50	49.71	1.585	65.3	1.680
60	53.76	2.102	74.7	2.380
70	59.88	2.668	83.4	3.170
80	68.70	3.309	92.0	4.051
86.0	76.62	3.743	97.2	4.616
C-II crystals				
86.0	76.62	3.743	97.2	4.616
90	84.30	4.066	100.9	5.015
100	96.60	4.970	110.4	6.070
110	111.9	6.008	120.2	7.214
120	128.7	7.205	130.6	8.467
130	145.6	8.574	141.6	9.834
140	164.4	10.12	153.1	11.31
150	185.5	11.87	165.1	12.90
160	206.7	13.82	177.7	14.61
170	231.0	16.01	191.0	16.46
180	255.3	18.44	204.8	18.42
190	(279.3)	21.11	219.3	20.56
200	(303.3)	24.03	234.2	22.79
210	(327.2)	27.18	249.6	25.24
220	(351.2)	30.57	265.4	27.82
230	(375.1)	34.20	281.5	30.55
240	(399.0)	38.07	298.0	33.45
250	(422.9)	42.18	314.8	36.52
260	(445.9)	46.53	331.8	39.74
260.7	(449.4)	46.89	333.2	39.96
C-I crystals				
260.7	(449.4)	54.35	361.8	39.96
270	(467.4)	58.47	377.3	43.40
280	487.8	63.25	394.7	47.27
290	508.5	68.23	412.1	51.28
298.15	524.8	72.44	426.5	54.72
300	528.8	73.42	429.7	55.49
310	551.5	78.82	447.4	59.87
320	574.0	84.45	465.3	64.45
330	595.5	90.29	483.3	69.20
340	615.9	96.35	501.7	74.23

* The C_p° values obtained by interpolating the temperature dependence of C_p° in the 185—275 K range (see Fig. 1, the *HIF* curve) are given in parentheses.

standard pressure (see Ref. 27), as well as the entropy ($\Delta_f S^{\circ}$/J mol^{-1} K^{-1}), the Gibbs energy ($\Delta_f G^{\circ}$/kJ mol^{-1}), and the logarithm of the equilibrium constant ($\log K_f^{\circ}$) for the formation of C_{60} fullerene from graphite under the same conditions are given below.

$\Delta_c H^{\circ}$	$\Delta_f H^{\circ}$	$\Delta_f S^{\circ}$	$\Delta_f G^{\circ}$	$\log K_f^{\circ}$
-25937 ± 16^{27}	2327 ± 17^{27}	420.8 ± 1.2	2202 ± 17	-0.386

The procedure for the calculation of these values is similar to that reported previously.[23] It can be seen that $\Delta_f G^{\circ}$ is a large positive value, which means that the spontaneous process 60 C(gr) → C_{60}(cryst) (where C(gr) and C(cryst) are carbon as graphite and as crystals, respectively) is completely forbidden from the thermodynamic standpoint. Only a non-spontaneous process is possible, which is in full agreement with experimental data.[3] Note that spontaneous reactions are impossible when $\Delta_f G^\circ$ is larger than 40 kJ mol^{-1} (see Ref. 24).

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References

1. D. A. Bochvar and E. G. Gal'pern, *Dokl. Akad. Nauk SSSR*, 1973, **209**, 610 [*Dokl. Chem.*, 1973, **209** (Engl. Transl.)].
2. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, 1985, **318**, 162.
3. W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature*, 1990, **347**, 354.
4. M. V. Korobov and L. N. Sidorov, *J. Chem. Thermodyn.*, 1994, **26**, 61.
5. T. Atake, T. Tanaka, H. Kawaji, K. Kikuchi, K. Saito, S. Suzuki, I. Ikemoto, and Y. Achiba, *Physica C*, 1991, **185**, 427.
6. W. P. Beyrmann, M. F. Hundley, J. D. Thompson, F. N. Diederich, and G. Gruner, *Phys. Rev. Lett.*, 1992, **68**, 2046.
7. T. Atake, T. Tanaka, H. Kawaji, K. Kikuchi, K. Saito, S. Suzuki, Y. Achiba, and I. Ikemoto, *Chem. Phys. Lett.*, 1992, **196**, 321.
8. T. Matsuo, H. Suga, W. I. F. David, R. M. Ibberson, P. Bernier, A. Zahab, C. Fabre, A. Rassat, and A. Dworkin, *Sol. State Commun.*, 1992, **83**, 711.
9. Y. Jin, J. Cheng, M. Varma-Nair, G. Liang, J. Fu, B. Wunderlich, X. Xiang, R. Mostovoy, and A. Zettl, *J. Phys. Chem.*, 1992, **96**, 5151.
10. B. Wunderlich and Y. Jin, *Thermochim. Acta.*, 1993, **226**, 169.
11. M. A. Lopatin, V. L. Karnatsevich, V. Ya. Davydov, and G. N. Filatova, *Abstrs. of Invited Lectures and Contributed Papers, Int. Workshop "Fullerenes and Atomic Clusters"*, St. Petersburg, 1995.
12. B. S. Kaverin, V. L. Karnatsevich, and A. L. Kirilov, *Int. Workshop "Fullerenes and Atomic Clusters"*, St. Petersburg, 1993.
13. P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, A. B. Smith, and D. E. Cox, *Phys. Rev. Lett.*, 1991, **66**, 2911.
14. V. I. Kosov, V. M. Malyshev, G. A. Mil'ner, E. L. Sorkin, and V. F. Shibakin, *Izmeritel'naya Tekhnika* [*Measuring Instruments*], 1985, **11**, 56 (in Russian).
15. L. N. Yakub, *Fiz. Nizkikh Temp.* [*Low-Temperature Physics*], 1993, **19**, 726 (in Russian).
16. J. Aston, in *Physics and Chemistry of the Organic Solid State*, Eds. D. Fox, M. M. Labes, and A. Weissberger, Interscience, New York—London, 1965.
17. V. M. Egorov, V. V. Shpeizman, and I. N. Kremenskaya, *Pis'ma v ZhETF*, 1993, **19**, 49 [*JETP Lett.*, 1993, **19** (Engl. Transl.)].
18. W. I. F. David, R. M. Ibberson, T. J. S. Dennis, J. P. Hare, and K. Prassides, *Europhys Lett.*, 1992, **18**, 219, 735.
19. R. C. Yu, N. Tea, M. B. Salamon, D. Lorents, and R. Malhotra, *Phys. Rev. Lett.*, 1991, **68**, 2050.
20. *Physics and Chemistry of the Organic Solid State*, Eds. D. Fox, M. M. Laber, and A. Weissberger, Intersience, New York—London, 1965.
21. B. V. Lebedev, *Termodinamika polimerov* [*Thermodynamics of Polymers*], Izd. Gor'kovskogo Univ., Gor'kii, 1989, 43 pp. (in Russian).
22. S. S. Chang and E. F. Westrum, Jr., *J. Phys. Chem.*, 1960, **64**, 1551.
23. B. Lebedev and N. Smirnova, *Macromol. Chem. Phys.*, 1994, **195**, 35.
24. A. B. Bestul and S. S. Chang, *J. Chem. Phys.*, 1964, **40**, 3731.
25. D. K. Stull, E. F. Westrum, and G. R. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.
26. G. P. Johary, *J. Chem. Phys.*, 1994, **100**, 2220.
27. H. D. Beckhaus, S. Verevkin, C. Rüchardt, F. Diederich, C. Thilgen, H. U. Meer, H. Mohn, and W. Müller, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 996.

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