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Thermodynamic properties of 1D and 2D polymerized fullerite C_{60} between 0 and 340 K at standard pressure

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Abstract

The temperature dependence of heat capacity of one-dimensionally (1D) and two-dimensionally (2D) polymerized C_{60} produced by heating monomeric C_{60} up to 550 K at a pressure of 5 GPa and to 960 K at a pressure of 3.5 GPa, respectively, with the subsequent quenching of the samples to normal conditions has been studied in the 5–340 K range using the adiabatic vacuum calorimeter. The experimental objects were structurally identified as orthorhombic (1D) and tetragonal (2D, with some amount of 2D rhombohedral phase) crystalline modifications of polymerized C_{60}. We extrapolated the experimental temperature dependence of heat capacity C_p^0 down to 0 K and from this dependence we have calculated the following thermodynamic functions over the 0–340 K interval, enthalpy $H^0(T) - H^0(0)$, entropy $S^0(T) - S^0(0)$ and Gibbs function $G^0(T) - H^0(0)$. Assuming that $S^0(0) = 0$, we have estimated the standard entropies of formation $\Delta_f S^0$ for studied 1D and 2D polymers and entropies of hypothetical transitions, occurring at $T = 298.15$ K and standard pressure, from monomeric C_{60} to 1D and 2D polymers, as well as of the mutual transition between 1D and 2D phases under the same physical conditions.

Keywords: Monomeric C_{60}; 1D and 2D polymerized C_{60}; Heat capacity; Thermodynamic functions

1. Introduction

Under increasing pressure and temperature fullerite C_{60} tends to transform to more stable diamond and graphite through intermediate polymeric crystalline and amorphous carbon phases which can exist in metastable form at standard conditions [1–5]. Many of these metastable phases possess unique structures and extraordinary physicochemical characteristics and are of scientific and practical interest for the advanced science of inorganic materials [4–8]. In particular, 1D and 2D polymerized C_{60}, consisting of chains or planes from C_{60} molecules linked by covalent bonds, are formed with rising temperature at relatively low pressures (to 8 GPa) [1–4]. Up to present, one can talk about the identification of several modifications among low-dimensional polymers, i.e. two types of orthorhombic lattices (1D polymers) with the symmetry of a space group Immm and Pnnm [1–3,9], rhombohedral phase (2D polymer) [1–3] and tetragonal phase (2D polymer) [1–3,10]. On heating at $p > 10$ GPa, 3D polymerized crystalline C_{60} phases are formed and those may be regarded as ordered 3D covalent networks [11].

The thermodynamic properties of diverse C_{60} polymers and other metastable phases being produced

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from initial C_{60} were not practically investigated. Only in Refs. [12–14], temperature dependencies of the heat capacity of monomeric C_{60} subjected to heating at a temperature of 293–585 K under a pressure of 1–1.2 GPa and of 1D and 2D polymers were measured in the temperature intervals 5–650 and 5–300 K, respectively. On comparing the results with the corresponding data for initial C_{60}, considerable differences in the temperature dependencies of the heat capacities between the metastable phases and monomeric C_{60} were noted. Unfortunately, in the above works the numerical values were not given and this does not allow any real thermodynamic and thermophysical calculations, the objective necessity of which became by now fairly obvious [6].

The goals of the present work are the calorimetric study of the temperature dependence of isobaric heat capacity of two metastable phases of C_{60}, viz. 1D and 2D polymerized C_{60}, in the 5–340 K range at standard pressure, the analysis of the relations C_p^0 vs. T, the calculation of the thermodynamic functions $C_p^0(T)$, $H^0(T) - H^0(0)$, $S^0(T) - S^0(0)$, and $G^0(T) - H^0(0)$ over the interval 0–340 K, and the estimation of entropies of formation $\Delta_f S^0$ for 1D and 2D polymers, entropies of the transformation process of C_{60} to 1D and 2D polymers, and the conversion of the 1D to the 2D polymer.

2. Experimental

2.1. Sample

The samples of 1D and 2D polymers were prepared at the Institute for High Pressure Physics (Russian Academy of Sciences). They were synthesized from monomeric C_{60} powder prepared at the Russian Scientific Center "Kurchatovsky Institute" with the content of C_{60} not less than 99.9% and the size of crystalline grains of ca. 100 μm. A chamber with the standard torroid profile [15] and a diameter of the operation section of 15 mm was employed to create a high pressure. C_{60} powder was located into a platinum container placed in a cylindrical graphite heater-sleeve. Temperature was measured with a chromel–alumel thermocouple. The heating was carried out by passing current along the heater axis. The samples were in the form of pellets of about 4 mm diameter and approximately 1.5–2 mm height. To produce the substance in the amount necessary to make measurements, for each phase more than 10 samples were synthesized under similar conditions.

The synthesis parameters, i.e. $T = 550\,\mathrm{K}$ and $p = 5\,\mathrm{GPa}$ for the formation of 1D orthorhombic phase and $T = 960\,\mathrm{K}$ and $p = 3.5\,\mathrm{GPa}$ for the formation of 2D tetragonal phase, were selected on the basis of a phase diagram for low-dimensional polymerized C_{60} [2,3]. The synthesis of the samples was carried out by heating the initial substance at the chosen constant pressure and keeping the sample at the given temperature and pressure for 30 min in the case of the orthorhombic phase and for 10 min for the tetragonal one. Further, the samples were quenched by a rapid decrease in temperature and the subsequent release of pressure. With the tetragonal modification of C_{60}, it is known that the portion of this phase in the samples being synthesized virtually depends on the time of keeping at a high temperature and the path of synthesis on p–T plane [10]. In this connection, it was important to keep the sample for a prolonged enough period of time in the region of a relative stability of the tetragonal phase [10].

The structure of the samples was studied by X-ray diffraction (Cu Kα and Cr Kα). The X-ray diffraction picture of the synthesized samples was qualitatively in accordance with the literature data for high-pressure orthorhombic phase [1,2,9] and the mixture of tetragonal and rhombohedral phases [1,2,10]. According to the data reported in Ref. [10], the part of the tetragonal phase in our samples can be determined to be about 60%. As it was demonstrated in [3], the position of diffraction peaks and, consequently, the degree of polymerization of 1D and 2D polymers continuously changes with the synthesis temperature. The position of strong diffraction lines of the synthesized phases in our case permitted without ambiguity to determine predominantly 1D and 2D character of polymerization of the corresponding phases, the position of strong lines for different samples in each series coinciding to a precision of about 1%.

2.2. Apparatus and measurement procedure

To study the temperature dependence of heat capacity of substances, a thermophysical device BKT-3, an automatic adiabatic vacuum calorimeter, was employed. The design of the calorimeter and the procedure of the heat capacity measurements have been described elsewhere [16]. From the calibration results of the calorimeter, it was found that the uncertainty of the heat capacity measurements of substances at helium temperatures is within 2%. With rising temperature up to 40 K, it decreases to 0.5 and 0.2% between 40 and 340 K [17].

3. Results and discussion

3.1. Heat capacity

The masses of 1D polymerized C_{60} and 2D polymerized C_{60} loaded into the calorimetric ampoule were 0.6517 and 0.5183 g, respectively. The heat capacity of 1D polymer was studied in the range 4.5–340 K and of 2D between 5 and 340 K. For 1D polymer 158 experimental values were obtained in three series representing the sequence of the heat capacity measurements, and for 2D polymer 183 experimental points were measured in four series (Tables 1 and 2). The heat capacity of the samples was from 5 to 25% of the total heat capacity of the calorimetric ampoule and the substance on changing temperature from 5 to 340 K. The experimental points of C_p^0 were computationally averaged. The root-mean square deviation of the values from the corresponding smoothed curves $C_p^0 = f(T)$ for both the polymerized substances was 0.6% between 5 and 80 K and 0.04% from 80 to 340 K. All the experimental values of C_p^0 and the averaged curves are shown in Fig. 1. Besides, for comparison in this figure the temperature dependence of the heat capacity for monomeric C_{60} [18] is illustrated. It is seen that in the temperature interval studied the heat capacities for both polymers gradually increase as temperature rises, at $T < 70$ K the C_p^0 values of 1D polymerized C_{60} being larger than those of 2D. The differences in the heat capacities are specially great at $T < 10$ K (to 70%). At $T > 70$ K, the C_p^0 values of the polymerized substances are close: the differences do not exceed 0.7% which taking into account an unfavorable ratio between the heat capacities of the samples and the total heat capacity of the calorimetric ampoule and the sample is likely to be within experimental uncertainties of the heat capacity measurements. The heat capacity of starting C_{60} is

Table 1
Experimental values of heat capacity of orthorhombic 1D polymerized C_{60}

T (K)	C_p^0 (J K^{-1} mol^{-1})
Series 1	
4.77	0.2138
4.97	0.3158
5.83	0.8351
6.23	1.150
6.76	1.541
7.38	1.984
8.05	2.477
9.00	3.267
10.05	4.300
10.95	5.087
11.93	5.892
13.77	7.074
14.41	8.152
15.67	9.249
17.03	10.35
18.45	11.82
19.84	12.23
21.19	14.13
22.69	15.36
24.16	15.44
25.61	16.50
27.15	17.81
28.67	19.01
30.19	19.34
32.24	20.65
34.58	22.25
37.08	24.44
39.73	26.32
42.07	27.30
Series 2	
43.05	28.50
45.53	30.98
50.60	33.34
52.80	34.94
55.38	36.97
58.24	39.47
61.21	41.78
64.19	44.30
67.15	46.34
70.17	48.93
73.19	51.18
76.19	54.39
79.19	57.60
82.07	59.55
Series 3	
79.05	59.36
81.50	60.43
83.95	62.37
86.40	65.63
88.85	68.83

Table 1 (*Continued*)

T (K)	C_p^0 (J K^{-1} mol^{-1})
91.30	71.53
93.75	75.15
96.20	78.40
98.64	81.84
101.09	85.53
103.53	89.09
105.97	91.59
108.40	96.77
110.84	99.73
113.28	104.0
115.71	108.5
118.14	111.4
120.57	115.9
122.99	120.3
125.41	124.1
127.84	128.8
130.25	133.3
132.67	138.1
135.09	142.8
137.50	148.5
139.92	153.7
142.33	157.4
144.74	161.8
147.15	166.7
149.55	171.4
151.95	177.4
154.35	182.0
156.74	186.6
159.14	191.8
161.53	195.8
163.92	202.7
166.31	208.3
168.69	213.8
171.08	219.0
173.46	224.1
175.83	229.9
178.21	235.9
180.58	240.0
182.96	244.9
185.32	250.5
187.68	255.4
190.04	262.4
192.41	268.1
194.75	273.3
197.10	277.8
199.46	284.8
201.81	289.8
204.15	295.2
206.49	301.8
208.82	305.6
211.16	311.7
213.50	317.8
215.81	323.2
218.14	328.6
220.47	332.2

Table 1 (*Continued*)

T (K)	C_p^0 (J K^{-1} mol^{-1})
222.79	338.8
225.11	343.9
227.43	350.0
229.74	355.6
232.01	361.6
234.31	367.8
236.61	371.8
238.91	376.7
241.21	382.9
243.50	388.3
245.78	392.9
248.07	397.5
250.33	405.3
252.60	410.8
254.87	415.3
257.14	420.4
259.38	426.3
261.64	432.4
263.88	438.1
266.11	443.2
268.28	447.3
270.52	452.5
272.75	457.8
274.97	464.2
277.19	469.5
279.36	474.3
281.57	478.9
283.76	486.0
285.93	490.1
288.09	493.9
290.26	498.6
292.40	503.4
294.55	508.8
296.65	513.4
298.78	520.1
300.88	523.4
302.86	529.4
304.97	534.1
307.07	539.8
309.16	543.0
311.21	546.8
313.24	549.8
315.30	553.8
317.34	561.6
319.35	567.0
321.34	569.8
323.36	573.5
325.36	580.1
327.36	585.4
329.31	588.4
331.24	593.5
333.21	599.1
334.91	600.6
336.85	606.5
338.79	612.9

Table 2
Experimental values of heat capacity of tetragonal 2D polymerized C_{60}

T (K)	C_p^0 (J K^{-1} mol^{-1})
Series 1	
5.23	0.106
5.50	0.244
5.99	0.258
6.64	0.349
7.28	0.457
7.93	0.620
8.65	0.816
9.48	1.240
10.46	1.540
11.47	2.098
12.51	2.218
13.63	2.875
14.85	3.382
16.13	3.815
17.45	4.548
18.88	5.417
20.42	5.848
22.02	7.029
23.69	7.701
25.40	8.959
27.26	10.05
29.53	11.44
32.13	13.26
34.85	15.20
37.62	17.20
40.33	19.15
43.45	22.18
45.85	23.52
48.51	25.77
51.35	28.25
54.16	31.37
56.92	34.80
59.64	36.20
62.43	40.60
65.29	43.95
Series 2	
64.09	42.99
67.28	45.75
70.25	49.40
73.07	52.20
75.74	54.96
80.40	56.40
82.11	61.12
Series 3	
83.07	62.11
85.52	64.81
87.97	67.58
90.42	70.25
92.86	73.10
95.31	76.10
97.75	79.11
100.20	82.43
102.64	86.15
105.09	89.65
107.53	92.71
109.97	97.31
112.41	100.5
114.84	104.7
117.27	108.5
119.70	113.58
122.13	118.2
124.56	122.8
126.99	126.7
129.41	131.2
131.83	133.9
134.25	141.2
136.66	144.6
139.08	150.3
141.49	153.6
143.91	158.70
146.31	164.6
148.72	169.4
151.12	175.1
153.53	179.3
155.94	184.6
158.32	190.0
160.72	195.4
163.11	200.1
165.50	205.3
167.89	210.9
170.27	216.2
172.66	223.0
175.04	227.7
177.42	232.7
179.79	237.8
182.17	243.4
184.54	249.8
186.91	254.0
189.27	259.0
191.63	265.8
194.00	271.2
196.33	276.1
198.68	281.6
201.02	288.0
203.36	292.7
205.70	298.5
208.04	304.5
210.37	309.2
212.69	314.6
215.02	320.1
217.32	325.8
219.64	330.7
221.95	336.1
224.26	341.5

Table 2 (*Continued*)

T (K)	C_p^0 (J K^{-1} mol^{-1})
226.57	347.3
228.87	352.9
226.57	347.3
233.42	363.6
235.71	368.8
237.99	375.1
240.26	379.6
242.53	384.6
244.80	390.5
247.08	395.4
249.35	400.1
251.60	406.4
253.85	412.3
256.10	417.3
258.35	422.2
260.59	427.8
262.83	433.8
265.06	439.7
267.29	443.3
269.37	450.4
271.58	454.6
273.76	458.8
275.95	464.0
278.14	469.2
280.32	474.8
282.48	479.2
284.65	483.6
286.77	489.1
288.91	490.5
291.00	499.3
293.12	503.7
295.23	509.8
297.33	513.9
299.39	519.2
301.47	523.9
303.37	527.7
305.42	532.6
Series 4	
251.13	403.9
253.36	409.0
255.58	412.6
257.80	419.4
260.02	425.4
262.22	430.0
264.42	434.9
266.61	439.7
268.77	445.3
270.95	450.3
273.12	456.0
275.29	460.7
277.45	465.3
279.60	471.0
281.74	475.7
283.68	481.3
285.81	485.7
287.93	490.9
290.04	496.0
292.15	500.7
294.21	504.5
296.28	510.34
298.35	512.8
300.38	519.6
302.43	523.8
304.47	528.3
306.50	534.3
308.53	538.0
310.54	541.8
312.53	546.6
314.51	551.3
316.22	553.7
318.18	559.3
320.08	562.8
321.96	566.6
323.79	570.8
325.70	575.3
327.60	578.0
329.48	582.6
331.34	590.1
333.14	593.0
335.00	598.4
336.83	604.9
338.59	608.1

throughout greater than that of the corresponding polymerized C_{60}. At 25 K, for example, the heat capacity of C_{60} is 24 times that of 1D polymer and 45 times that of 2D polymer. Over the 100–200 K, range the difference in the C_p^0 values of C_{60} and the polymers is about 10% and between 260 and 340 K it is not larger than 1.5%. The analysis of the heat capacities of the polymerized C_{60} in a low temperature range ($T < 70$ K) is of special interest. It should be noted that the C_p^0 values of the polymerized C_{60} differ much and, besides, they show a different character of the temperature dependence of the heat capacity (Fig. 2). This results, certainly, from the heterodynamic structure of the polymers [19]. According to Tarasov's theory of heat capacity [19,20] which, as well as Debye's theory of heat capacity, is a particular case of the fractal theory of heat capacity [21,22], for solid bodies of a chain structure, the relation C_p^0 vs. T is directly proportional to T^1 in a low temperature interval and for solid bodies of a layer structure to T^2. In the

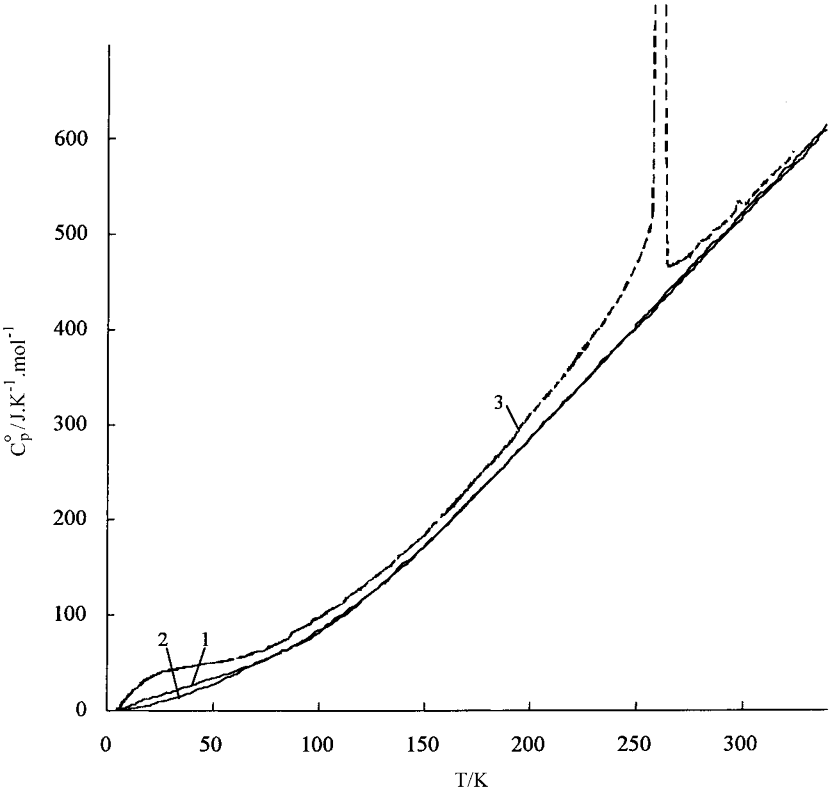


Fig. 1. Temperature dependence of heat capacity of: (1) 1D polymer; (2) 2D polymer; (3) monomeric C_{60} [12].

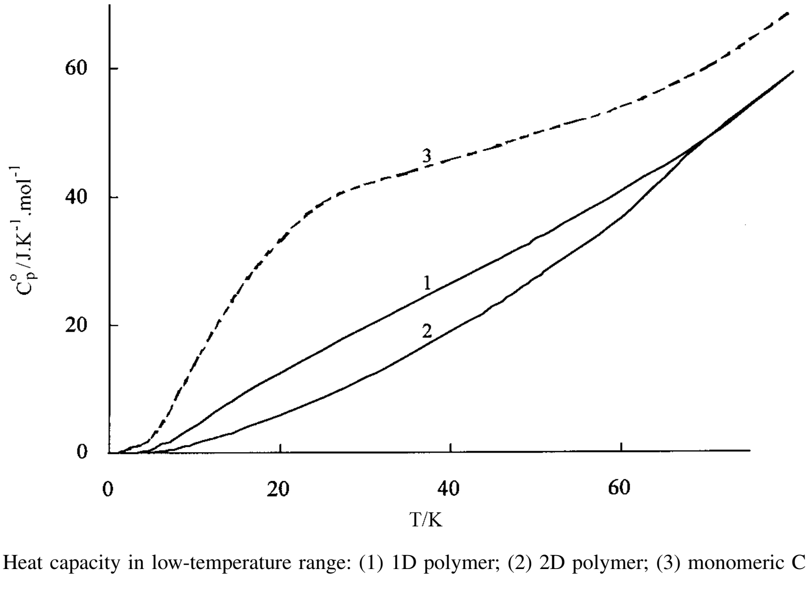


Fig. 2. Heat capacity in low-temperature range: (1) 1D polymer; (2) 2D polymer; (3) monomeric C_{60} [12].

fractal theory of heat capacity, the index of a power at T is denoted as D and called a fractal dimension [21]. As demonstrated in [21], D can be estimated from the experimental data on the temperature dependence of heat capacity with using a plot $\ln C_p^0$ vs. $\ln T$. Without a substantial uncertainty, it is possible to assume that for $T < 50{-}60\,\mathrm{K}$, $C_p^0 = C_V$ and by plotting the relation $\ln C_V$ vs. $\ln T$, to obtain the value of D. For the above temperature interval D enters into the formula [21]:

$$C_V = 3D(D+1)kN\Gamma(D+1)\xi(D+1)\left(\frac{T}{\theta_{\max}}\right)^D \qquad (1)$$

where N is the number of atoms in the repeating unit molecule, k the Boltzmann constant, $\Gamma(D+1)$ the Γ function, $\xi(D+1)$ the Riemannian ξ function, $\theta_{\max}$ the characteristic temperature and D, as it was mentioned above, is the fractal dimension which can be equal to 1–4 depending on the structure of solid bodies [22]. From the C_p^0 values of 1D and 2D polymers cited in the present paper the following values of D and $\theta_{\max}$ were calculated: $D = 1$ and $\theta_{\max} = 267\,\mathrm{K}$ for 1D polymerized C_{60} and $D = 2$, $\theta_{\max} = 270\,\mathrm{K}$ for 2D polymerized C_{60}. With these values, expression (2) derived from Eq. (1)

$$C_V = A\left(\frac{T}{\theta_{\max}}\right)^D \qquad (2)$$

where $A = 175.8$ and 860.7, respectively, describes the experimental values of the heat capacity for 1D and 2D polymers in the range 30–50 K within 0.12 and 0.44%, A being estimated by the equation, $A = 3D(D+1)kN\Gamma(D+1)\xi(D+1)$. The fractal dimensions increase with lowering temperature, because of the growth of the interchain interaction in 1D polymer and the interlayer interaction in 2D polymer. In the range 6–11 K for 1D polymer $D = 3.9\,(\theta_{\max} = 56.63\,\mathrm{K})$ and for 2D polymer it is of the same numerical magnitude ($\theta_{\max} = 69.1\,\mathrm{K}$). Eq. (2) reproduces the experimental values of the heat capacity for the polymers studied in the above temperature interval with an uncertainty of ca. 1% for 1D and 0.8% for 2D polymer. In the temperature range 6–11 K, the heat capacity of monomeric C_{60} is described by Debye's function for the heat capacity:

$$C_p^0 = nD\left(\frac{\theta_{\mathrm{D}}}{T}\right) \qquad (3)$$

where D represents the Debye function, n and θ_{D} are adjustable parameters and those are 10 and 58.52 K, respectively, i.e. for this compound the relation C_p^0 against T^3 holds [17].

3.2. Thermodynamic functions

From the data on the temperature dependencies of the heat capacity for 1D and 2D polymers, their thermodynamic functions were calculated in the range 0–340 K (Table 3). The enthalpy $H^0(T) - H^0(0)$ and entropy $S^0(T) - S^0(0)$ were evaluated by the numerical integration of the relations $C_p^0 = f(T)$ and $C_p^0 = f(\ln T)$. The Gibbs function $G^0(T) - H^0(0)$ was calculated from the values of $H^0(T) - H^0(0)$ and $S^0(T) - S^0(0)$ at corresponding temperatures as it was shown earlier [23].

3.3. Standard entropies of formation

The standard entropies of formation $\Delta_{\mathrm{f}}S^0$ of 1D and 2D polymers were estimated from the absolute magnitudes of their entropies and those of carbon in the form of graphite. The S^0 values for 1D and 2D at 298.15 K and standard pressure were taken to be equal to the corresponding values of $S^0(T) - S^0(0)$ at 298.15 K (Tables 3 and 4). The values of zero entropies for 1D and 2D polymers were neglected since in Ref. [24] it was shown that for any crystalline polymers the values of $S^0(0)$ are small and their magnitudes seem to be within uncertainties of C_p^0 measurements and $S^0(T)$ calculations. The value of $S^0(C_{\mathrm{gr}})$ was taken from reference book [25]. It was found that $\Delta_{\mathrm{f}}S^0(\mathrm{1D\,C_{60}}) = -9.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and $\Delta_{\mathrm{f}}S^0(\mathrm{2D\,C_{60}}) = -22.9\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The values obtained concern the hypothetical processes proceeding at $T = 298.15\,\mathrm{K}$ and $p = 101.325\,\mathrm{GPa}$:

$$60\mathrm{C\,(gr)} \rightarrow \mathrm{1D\,C_{60}\,(cr)}, \qquad 60\mathrm{C\,(gr)} \rightarrow \mathrm{2D\,C_{60}\,(cr)}$$

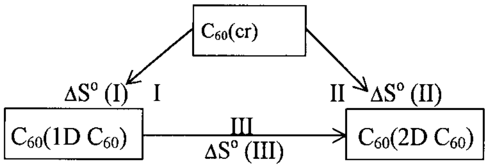
3.4. Entropies of polymerization of C_{60} to 1D and 2D polymerized C_{60} and transformation of 1D to 2D polymer

In the scheme below the changes in the entropy during a hypothetical cycle of transformations of monomeric C_{60} to 1D and 2D polymers as well as of the conversion of 1D polymer to 2D polymer at

Table 3
Thermodynamic functions of orthorhombic 1D polymerized C_{60}

T (K)	C_p^0 (J K^{-1} mol^{-1})	$H^0(T) - H^0(0)$ (kJ mol^{-1})	$S^0(T) - S^0$ (J K^{-1} mol^{-1})	$-[G^0(T) - H^0(0)]$ (kJ mol^{-1})
0	0	0.0	0	0
5	0.3240	0.0005	0.1296	0.00013
10	4.118	0.0112	1.447	0.00332
15	8.750	0.0431	3.979	0.0166
20	12.52	0.0963	7.014	0.0440
25	16.13	0.1679	10.19	0.0870
30	19.57	0.2570	13.43	0.1460
35	23.01	0.3634	16.71	0.2214
40	26.34	0.4868	20.00	0.3131
45	29.70	0.6269	23.29	0.4213
50	33.22	0.7840	26.60	0.5461
60	40.70	1.153	33.31	0.8455
70	48.62	1.599	40.17	1.213
80	58.22	2.131	47.26	1.650
90	70.39	2.773	54.81	2.159
100	83.61	3.543	62.90	2.747
110	98.31	4.451	71.55	3.419
120	114.9	5.516	80.80	4.180
130	132.8	6.754	90.69	5.037
140	152.4	8.178	101.2	5.996
150	172.5	9.802	112.4	7.064
160	193.8	11.63	124.2	8.247
170	216.2	13.68	136.7	9.551
180	238.8	15.96	149.7	10.98
190	261.2	18.46	163.2	12.55
200	285.3	21.19	177.2	14.25
210	309.2	24.16	191.7	16.09
220	333.1	27.37	206.6	18.08
230	356.9	30.82	222.0	20.22
240	380.7	34.51	237.6	22.52
250	404.3	38.44	253.7	24.98
260	427.9	42.60	270.0	27.60
270	451.4	46.99	286.6	30.38
273.15	458.8	48.43	291.9	31.29
280	474.8	51.63	303.4	33.33
290	498.2	56.49	320.5	36.45
298.15	517.2	60.63	334.6	39.12
300	521.5	61.59	337.8	39.74
310	544.7	66.92	355.2	43.20
320	567.8	72.48	372.9	46.85
330	590.8	78.28	390.7	50.66
340	613.8	84.30	408.7	54.66

$T = 298.15$ K and standard pressure calculated from the absolute entropies of reagents at the above temperature and pressure are illustrated. The value of $S^0(C_{60})$ was taken from Zhogova [17], the values of S^0(1D C_{60}) and S^0(2D C_{60}) are given in Tables 3 and 4 of the present work, the $S^0(0)$ values of 1D and 2D polymers being assumed to be equal to zero.



The values of ΔS^0(I), ΔS^0(II) and ΔS^0(III) in the scheme were found to be −91.9, −105.5 and

Table 4
Thermodynamic functions of tetragonal 2D polymerized C_{60}

T (K)	C_p^0 (J K^{-1} mol^{-1})	$H^0(T) - H^0(0)$ (kJ mol^{-1})	$S^0(T)$ (J K^{-1} mol^{-1})	$-[G^0(T) - H^0(0)]$ (kJ mol^{-1})
0	0	0	0	0
5	0.105	0.0001	0.0313	0.00003
10	1.330	0.0032	0.4027	0.00086
15	3.400	0.0148	1.322	0.0050
20	5.930	0.0380	2.638	0.0147
25	8.630	0.0743	4.249	0.0319
30	11.630	0.1251	6.090	0.0576
35	15.23	0.1921	8.145	0.0930
40	18.89	0.2774	10.42	0.1393
45	22.75	0.3815	12.87	0.1975
50	27.23	0.5062	15.49	0.2683
60	36.60	0.8271	21.31	0.4517
70	48.86	1.259	27.95	0.6973
80	59.05	1.800	35.16	1.013
90	69.81	2.443	42.72	1.402
100	82.11	3.202	50.70	1.868
110	97.31	4.097	59.21	2.417
120	113.90	5.152	68.38	3.054
130	132.70	6.383	78.22	3.786
140	152.40	7.807	88.77	4.621
150	172.40	9.431	99.97	5.564
160	193.70	11.26	111.8	6.622
170	215.70	13.31	124.2	7.801
180	238.70	15.58	137.1	9.108
190	261.40	18.08	150.7	10.55
200	285.4	20.81	164.7	12.12
210	308.5	23.78	179.2	13.84
220	332.3	26.98	194.1	15.71
230	355.9	30.43	209.3	17.72
240	379.5	34.10	225.0	19.90
250	403.0	38.01	241.0	22.22
260	426.3	42.16	257.2	24.72
270	449.6	46.54	273.7	27.37
273.15	456.9	47.97	279.0	28.24
280	472.7	51.15	290.5	30.19
290	495.8	56.00	307.5	33.18
298.15	514.5	60.11	321.5	35.74
300	518.7	61.07	324.7	36.34
310	541.6	66.37	342.1	39.68
320	564.3	71.90	359.6	43.18
330	586.9	77.66	377.3	46.87
340	609.4	83.64	395.2	50.73

−13.1 J K^{-1} mol^{-1}, respectively. As it was expected, in the 1D polymerization of monomeric C_{60} (cr) the entropy decreases to a lesser extent than during the 2D polymerization. Process (III) can be regarded as the polymerization of 1D chains with the formation of layers — the planar structure of 2D polymer. It is obvious that this process has to be accompanied by the entropy loss that is confirmed with the calculation results.

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