

Calorimetric study of crystalline dimer and polymerized phases of fullerene C₆₀

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Abstract

By high precision dynamic calorimetry the temperature dependences of heat capacity $C_p^0 = f(T)$ for dimer of C₆₀, orthorhombic and rhombohedral polymerized phases of fullerene C₆₀ were determined in the temperature range 300–650 K. Besides, endothermic transformations caused by the depolymerization of the polymerized (dimeric) phases of C₆₀ were studied and their standard thermodynamic characteristics a temperature interval, enthalpy, entropy and Gibbs function were analyzed. Based on the thermodynamic and oscillation spectroscopy data, it was established that the depolymerization proceeds completely and the products formed are a monomer fcc phase of C₆₀. From the data of the present work and the heat capacity values measured by us earlier in a low-temperature interval, the thermodynamic functions of the substances, viz. the heat capacity $C_p^0(T)$, enthalpy $H^0(T) - H^0(0)$, entropy $S^0(T) - S^0(0)$ and Gibbs function $G^0(T) - H^0(0)$, were calculated over the range from $T \rightarrow 0$ to (380–490) K at standard pressure. The results were discussed taking into account literature data. A sequence of a relative thermodynamic stability at 298.15 K and atmosphere pressure of the crystalline polymerized C₆₀ phases was arranged.

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1. Introduction

Because of extremely good prospects of the practical application of fullerene and their derivatives the intensity of studies of these materials is continuously increasing [1]. A systematic examination of the behavior of fullerene C₆₀ at high pressures and temperatures [2–7] showed that the transformations of C₆₀ under these conditions are accompanied with the formation of a family of new carbon states. Among them the crystalline phases based on dimers (C₆₀)₂ as well as linear (1D), planar (2D) and spatial (3D) polymerized phases of C₆₀, whose regions of the existence are illustrated with a generalized p–T diagram, are distinguished [5,7].

From the moment of the preparation of sufficient amounts of the substance samples the works on the calorimetric study of their thermodynamic properties are carried out [8–13]. However, in many earlier works [8–12] certain mixtures of polymerized C₆₀ phases of unknown fraction composition

rather than individual phases were examined by calorimetry methods. This circumstance calls for a consideration of the earlier data not as individual characteristics of various polymerized phases of C₆₀ but only as a qualitative illustration of the effect of HPHT-treatment parameters on the thermodynamic properties of the initial monomeric fcc phase of the fullerite. It is worth of note also that in our preceding works [8,10,13] the differential scanning calorimetry methods that permit to obtain only a qualitative picture of the temperature dependence of the heat capacity were used. The present work, as a part of complex investigations of the thermodynamic properties of the crystalline dimeric and polymerized phases of C₆₀, has been fulfilled for the samples of the highest purity degree of today. Standard thermodynamic properties of the crystalline dimer (C₆₀)₂ [14] and the polymerized phases - orthorhombic and rhombohedral phases based on linear (1D) and planar (2D) C₆₀ [15] - were considered earlier over the range from $T \rightarrow 0$ to 340 K, the data being obtained by precision adiabatic vacuum calorimetry.

In present paper the calorimetric data on the temperature dependences of isobaric heat capacity for the crystalline dimer and crystalline orthorhombic and rhombohedral

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polymerized phases of fullerene C_{60} between 300 and 650 K were discussed. A special attention was paid to the investigation of the known endothermic transformations of the polymerized phases of C_{60} at atmosphere pressure related to their depolymerization to the monomer fcc phase of C_{60} [3,4] and the analysis of thermodynamic characteristics of these processes. From the data on the heat capacity of the polymerized phases obtained earlier and in the present work, the standard thermodynamic functions $C_p^0(T)$, $H^0(T) - H^0(0)$, $S^0(T) - S^0(0)$ and $G^0(T) - H^0(0)$ of the substances were calculated first for the temperature range from $T \rightarrow 0$ to (380–490) K. The comparison of literature data and the experimental thermodynamic characteristics of the depolymerization process was made. A row of the relative thermodynamic stability at 298.15 K and atmosphere pressure of the tested crystalline polymerized phases of C_{60} was arranged.

2. Experimental procedure

Samples of orthorhombic (O), rhombohedral (R) phases and dimerized state of C_{60} (DS) were prepared by pressure-temperature initiated polymerization of C_{60} . As an initial material, twice sublimated fine-crystalline powder of fullerite (not more than 0.02 wt.% of impurities) produced by Term USA was used. The sample synthesis was carried out under conditions of quasi-hydrostatic compression in high pressure apparatus “Maksim” (piston-cylinder type) and “Toroid” [7]. The samples of DS, O and R phases were prepared at 1.5 GPa and 423 K, 1.3 GPa and 560 K, 6 GPa and 873 K, respectively. Time of isothermal holding was 1000, 20000 and 2000 s. The polymerized (dimerized) states formed by the treatment of C_{60} were kept under normal conditions, unloaded from the high pressure apparatus and characterized by X-ray diffraction and oscillation spectroscopy, as demonstrated in [7,16]. The X-ray diffractograms and structural parameters for the crystalline polymerized phases of C_{60} were recorded and described in detail by V. Davydov [5].

For the calorimetric study the samples with the maximum content of the main substance (~ 80 mol% for the DS sample and ca. 95 mol% for the samples of O and R phases) were chosen. According to the data [7,16,17], the dimerized state was a mixture of ~ 80 mol% dimer and ~ 20 mol% the initial C_{60} that was corroborated by subsequent calorimetric measurements [14]. Besides, it was suggested that the properties of the $(C_{60})_2-C_{60}$ mixtures were additive. It should be noted that the O and R phase samples contained, as impurities, small amounts of low-molecular polymerized C_{60} phases the unambiguous identification of which, unfortunately, failed.

The heat capacity, temperatures and enthalpies of transformations of the substances over the range 300–650 K were determined with using an ADKTTM automatic precision dynamic calorimeter operating by the principle of triple thermal bridge. The calorimeter design and the measurement

technique [18,19] enable the C_p^0 values of substances to be measured with an uncertainty of about $\pm 1.5\%$ and the transformation temperatures to be determined within to ± 0.5 K. The reliability of the calorimeter operation was checked by measuring the heat capacity of standard samples of copper and synthetic corundum and the thermodynamic characteristics of fusion of indium, tin and lead.

The low-temperature heat capacity of the substances was measured by us earlier in a BKT-3 completely automatic thermophysical device—an adiabatic vacuum calorimeter [14,15]. The uncertainty of C_p^0 measurements at helium temperatures is $\pm 2.0\%$. With rising temperature up to 40 K it decreases to $\pm 0.5\%$ and becomes about $\pm 0.2\%$ in the range 40–350 K.

3. Results and discussion

3.1. Heat capacity, thermodynamic characteristics of transformations

The heat capacity of the DS sample was determined between 310 and 650 K, O and R phases of C_{60} from 320 to 650 K at an average rate of heating of the calorimeter and substance 0.0133 K/s. The substance masses were 0.3995, 0.4290 and 0.4276 g, respectively. The heat capacity of the substances in the whole temperature interval was on the average 20 to 55% of the total heat capacity of (calorimetric ampoule and substance). A computer-assisting averaging of the experimental C_p^0 points was made by means of exponential and semi-logarithmic polynomials so that their root mean square deviation from the averaged $C_p^0 = f(T)$ curve did not exceed an experimental error of this value estimation.

Fig. 1a illustrates the experimental C_p^0 values and the averaging curves $C_p^0 = f(T)$ for DS while Fig. 2a shows them for O phase of C_{60} and Fig. 2b for R phase. The C_p^0 points (o) correspond to each third value of the heat capacity. The data on the heat capacity of DS in the range 6–340 K [14] are demonstrated in Fig. 1a by a solid line and of the polymerized O and R phases of C_{60} [15] in the same interval by a dotted line (Fig. 2a and b).

The first cycle of measurements was completed in the dynamic calorimeter after reaching temperature ~ 650 K. The samples were cooled down to $T = 320$ K and further a repeated cycle of C_p^0 measurements was conducted till 520–650 K. Then the samples were unloaded from the dynamic calorimeter and studied in the adiabatic vacuum calorimeter between 150 and 340 K. The $C_p^0 = f(T)$ relation for DS is shown in Fig. 1b (curve 1) and for O and R phases of C_{60} in Fig. 2a and b (curve 2), respectively. The C_p^0 values for all compounds were calculated per mole of C_{60} .

The regions of an anomalous change in the heat capacity, as temperature rises, are seen for DS on the $C_p^0 = f(T)$ curve (Fig. 1a). In the range 185–280 K a physical transformation, explained by the availability of 21 mol% the initial

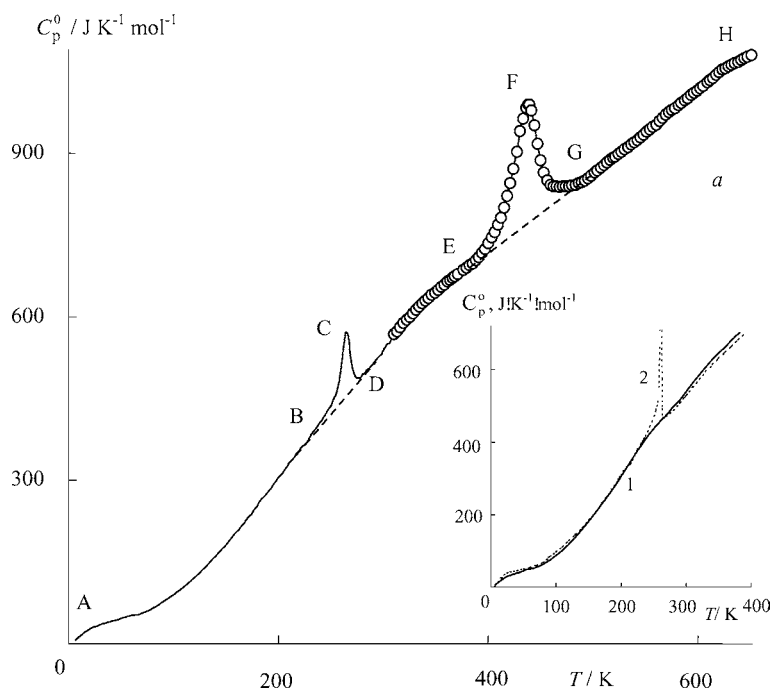


Fig. 1. (a) Temperature dependence of heat capacity of DS sample (mixture of 79 mol% dimer and 21 mol% fullerite C_{60}): AE and GH—before and after depolymerization, respectively; the crystalline dimer till the temperature of depolymerization onset (curve 1) and the initial C_{60} (curve 2). (b) Temperature dependence of heat capacity of depolymerization product of DS (1) and the initial C_{60} (2) [22,23].

fullerite in the DS sample, occurs (BCD section, Fig. 1a). The transition and the estimation of C_{60} content in DS from the calorimetric data were discussed in detail earlier [14]. The phase transition is reversible and its nature was quite completely interpreted [20,21]. It can be regarded as a combination of two transformations: the second-order transition

of order \rightleftharpoons disorder type and the first-order phase transition. The thermodynamic characteristics of the transition for DS are as follows: the transition temperature $T_{tr}^0 = 264.7 \pm 0.3$ K (it was taken to correspond to the maximum apparent heat capacity of DS ($C_{p,max}^0 = 571.2$ J/K mol) in the transition interval 185–280 K); the enthalpy of transition $\Delta_{tr}H^0 =$

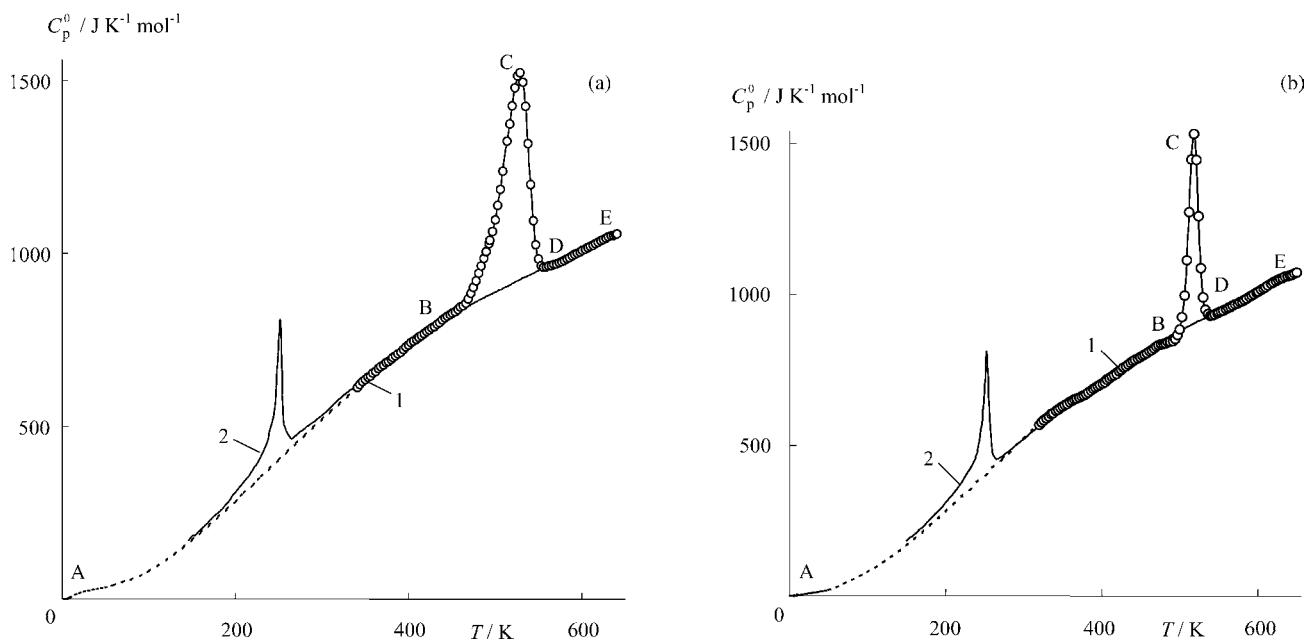


Fig. 2. Temperature dependence of heat capacity of orthorhombic (a) and rhombohedral (b) polymerized phases of C_{60} . In both cases; a dotted line and circles—the first scan, a solid line—a repeated scan; AB and DE—before and after the depolymerization of O and R polymerized phases.

1.56 ± 0.03 kJ/mol was determined graphically as the area bounded with BCDB curve (Fig. 1a). The interpolation heat capacity of the DS sample is denoted by a dotted line (BD section, Fig. 1a) while ABDE section is the relation $C_p^0 = f(T)$ for DS (an additive mixture of 79 mol% $(C_{60})_2$ and 21 mol% C_{60}) till the temperature of the subsequent transformation onset (E point, Fig. 1a). Thus, C_p^0 for $(C_{60})_2$ can be evaluated by the additive formula [14]:

$$C_p^0\{(C_{60})_2\} = \frac{C_p^0(\text{DS}) - 0.21 C_p^0(C_{60})}{0.79} \quad (1)$$

with using the appropriate data for the fullerite [22,23]. The temperature dependence of the heat capacity for the crystalline dimer determined by Eq. (1) is shown in Fig. 1a (curve 1) till the temperature of the following transformation beginning (385 K). The heat capacities of $(C_{60})_2$ and C_{60} [22,23] are close within the measurement and calculation uncertainty over the range 150–385 K, the C_p^0 values for the dimeric phase being somewhat larger in the above temperature interval than of the monomer phase of C_{60} . Considerable differences in the C_p^0 values of the monomeric and dimeric phases are seen at $T < 100$ K [14] that is brought about with the difference in heterodynamics of their structure.

The glass-like transformation (G-type transition) in the dimeric phase is observed between 46 and 56 K. Its $T_G^0 = 50 \pm 0.5$ K is substantially smaller than of the initial C_{60} [22]. The analysis and the thermodynamic characteristics of the DS transition are described in work [14]. It is worth that the G-transition similar to that of the fullerite is also related to the freezing of hindered motions of $(C_{60})_2$ molecules in a crystalline lattice.

In the interval 385–490 K the endothermic transformation as a consequence of the depolymerization of $(C_{60})_2$ is observed (section EFG, Fig. 1a). This process proceeds in a wide temperature range and the apparent heat capacity ($C_{p,\text{max}}^0 = 989.5$ J/K mol), corresponding to it, is shown with EFG curve (Fig. 1a). On cooling down to 319 K and repeated measuring till 520 K the temperature dependence of C_p^0 for DS was not reproduced (GG' section, curve 2, Fig. 1b), i.e. the endothermic effect was absent. The

enthalpy of depolymerization $\Delta_{\text{depol}}H^0$ was determined graphically as the area bounded with EFGE (Fig. 1a). The authors [10,13] determined the depolymerization of systems of the dimeric C_{60} phases from the differential scanning calorimetry data at average rates of scanning 0.167 and 0.334 K/s. Table 1 shows the thermodynamic characteristics of the depolymerization. As follows from the comparison of literature data and our thermodynamic characteristics of the process, the depolymerization of various samples of the dimeric phases proceeds virtually in the same temperature interval. However, temperatures corresponding to endothermic peak maxima (T_{max}) significantly differ. One of reasons is the fact that T_{max} values were determined at different rates of the sample heating and were not reduced to the zero rate of heating. It is known that the dependence of the transition temperature upon the heating rate can be fairly noticeable [24]. Another, possibly, more significant reason of the observed divergences is associated with that at atmosphere pressure the dimeric phase like other polymerized phases of C_{60} is a metastable state of the system relative to the monomeric fcc phase of C_{60} in the whole temperature interval. That is at atmosphere pressure the polymerized phases of C_{60} are kinetically stable phases without a distinct temperature of the transition to the monomeric state rather than thermodynamically stable ones. The transition temperatures in such cases are, perhaps, no longer definitive individual characteristics of the polymerized phases, those are apparent temperatures of transitions that depend on the thermal treatment conditions and, first of all, on the isothermal holding time of intermediate states [13]. The values of the enthalpies of transformation obtained by us and elsewhere [13], taking into account an unequal uncertainty of their estimation, practically coincide. Our enthalpies of transition and cited in work [10] are markedly distinguished and this is most likely explained by the different quality of the samples, although the influence of some methodics peculiarities of the measurements carried out by various groups cannot be ignored.

The depolymerization product of $(C_{60})_2$ was unloaded from the calorimetric ampoule of the dynamic calorimeter and afterwards studied in the adiabatic vacuum calorimeter (Fig. 1b). Judging by the $C_p^0 = f(T)$ relation, the product

Table 1
Standard thermodynamic characteristics of depolymerization of the studied objects (conventional mole: 720.66 g/mol)

Objects	Temperature interval (T_{max}), K	$\Delta_{\text{depol}}H^0$ (298.15), kJ/mol	$\Delta_{\text{depol}}S^0$ (298.15)*, J/K mol	$\Delta_{\text{depol}}G^0$ (298.15), kJ/mol	Reference
DS	385–490 (438)	9	47	5	Our paper [10] [13]
	500–570 (540)	57	–	–	
	400–500	7	–	–	
O C_{60}	460–560 (529)	22	87	4	Our paper [10] [13]
	520–570	19	–	–	
	(555)	20	–	–	
R C_{60}	490–540 (519)	10	115	24	Our paper [10] [13]
	–	14	–	–	
	512–565 (530)	10	–	–	

* Data in [14,15].

has more intensive orientation phase transition in the range 186–279 K as compared to the initial DS. The transition temperature $T_{tr}^0 = 255.89$ K was assumed to correspond to the maximum apparent heat capacity in the transition range ($C_{p,max}^0 = 854.0$ J/K mol). The enthalpy of transition $\Delta_{tr}H^0 = 6.75 \pm 0.05$ kJ/mol was determined graphically as the area bounded with BCDB curve of the apparent heat capacity (Fig. 2b). For the initial C_{60} [22] the values are the following: the transition interval 185–275 K, $T_{tr}^0 = 260.7$ K ($C_{p,max}^0 = 34747$ J/K mol), $\Delta_{tr}H^0 = 7.46 \pm 0.15$ kJ/mol (the area under BEE'FB curve in Fig. 1b). It is clear that the depolymerization products are mainly the monomer fcc phase of C_{60} (denoted C'_{60}) and the thermodynamic characteristics of C'_{60} transition are slightly lower than of C_{60} . This is likely to be explained with that the monomeric phase of C_{60} formed during the depolymerization of the dimerized state of C_{60} is more imperfect than the initial fcc phase of the fullerite. The quantity (n) of the fcc phase of C_{60} in the C'_{60} sample can be easily estimated by the equation

$$n(\text{mol}\%) = \frac{\Delta_{tr}H^0(C'_{60}) - \Delta_{tr}H^0(\text{DS})}{\Delta_{tr}H^0(C_{60})} \times 100 \quad (2)$$

It was found that $n = 69$ mol% and this value can be interpreted as the degree of crystallinity (α) of C_{60} as well. As seen from Eq. (2), on estimating the quantitative composition of the solid phase being formed during the thermal depolymerization, we did not take into consideration the amount of fcc C_{60} available in DS. The increase of the volume fraction of intergrain boundaries, associated with the change in C_{60} crystallite size as a result of successive dimerization and depolymerization, can exert a virtual effect on α . IR and Raman spectra of the samples produced by the depolymerization of DS show unambiguously that the samples are a monomeric C_{60} phase.

With orthorhombic and rhombohedral polymerized phases of C_{60} , the depolymerization occurs in the range 460–560 K and 490–540 K, respectively. On $C_p^0 = f(T)$ curves the process manifests itself as a well visible endothermic effect (BCD section, Fig. 2a and b). The maximal apparent heat capacities of O and R phases in the transition range were found to be $C_{p,max}^0 = 1523$ and 1531 J/K mol. On cooling to about 320 K and repeated measurement the relation $C_p^0 = f(T)$ till $T = 650$ K endothermic effect no was observed too (curve 2, Figs. 2a and b). The thermodynamic characteristics of the depolymerization process are summarized in Table 1. The enthalpy of depolymerization of O and R phases of C_{60} was determined as in the case of the DS sample. The depolymerization process of the samples of the orthorhombic and rhombohedral polymerized phases of C_{60} was studied earlier by DSC [10,13]. Literature data and our values of the depolymerization enthalpies agree quite satisfactorily within experimental uncertainties. In all cases, $\Delta_{depol}H^0$ was determined by the numerical integration of endothermic peaks. Meanwhile, temperatures corresponding to the endothermic peak maxima differ from each other because of the different kinetic stability of the phases and the methodics peculiarities of experiments as was stated above.

The depolymerization products of the crystalline O and R polymerized phases of C_{60} were studied by the procedure similar to that used for depolymerization products of DS sample (Fig. 3a and b). They are the partially crystalline monomer phase C_{60} . This is confirmed by the orientation phase transition that is seen on the $C_p^0 = f(T)$ relations in the interval from ~ 185 to 275 K (curve 1, Fig. 3a and b), as for the initial C_{60} . The thermodynamic characteristics of their transitions are as follows: $T_{tr}^0 = 251.50$ and 252.43 K ($C_{p,max}^0 = 808.0$ and 810.1 J/K·mol), $\Delta_{tr}H_0 = 6.21 \pm 0.05$ and 5.75 ± 0.03 kJ/mol. The transition enthalpies $\Delta_{tr,i}H^0$

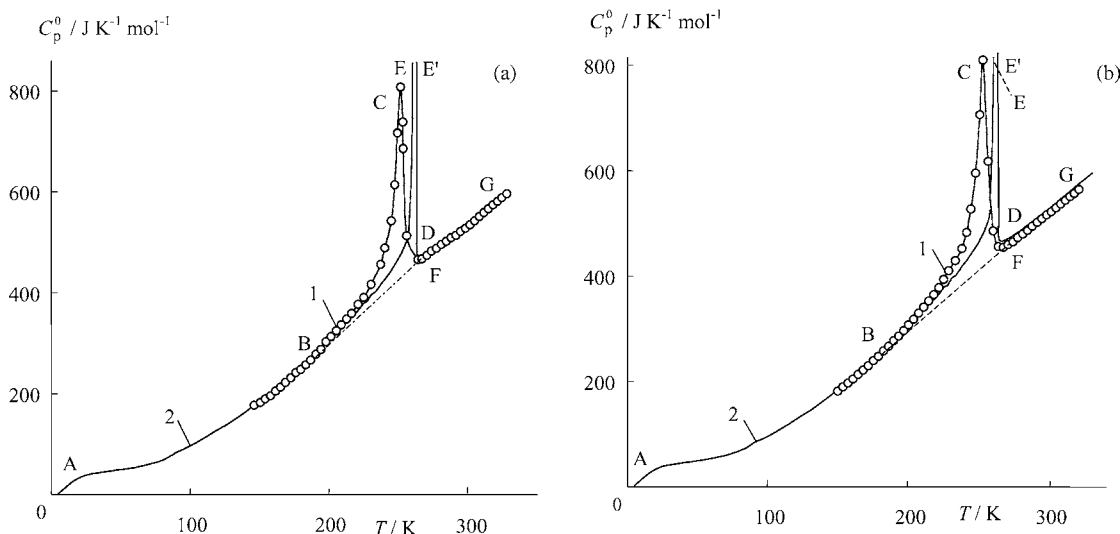


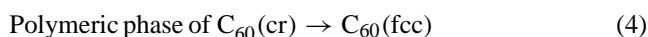
Fig. 3. Temperature dependence of heat capacity determined in adiabatic vacuum calorimeter for depolymerization products of O (a) and R (b) phases of C_{60} (curve 1) and initial C_{60} (curve 2) [22].

were determined graphically as areas bounded with BCDB curves (Fig. 3a and b). From the calorimetric data it is possible to evaluate the amount of fcc phase of C₆₀ in the depolymerization products of O phase (n_1) and R phase (n_2) of C₆₀ by the expression

$$n_i(\text{mol}\%) = \frac{\Delta_{\text{tr},i}H^0}{\Delta_{\text{tr}}H^0(\text{C}_{60})} \times 100 \quad (3)$$

It was found that $n_1 = 83 \text{ mol}\%$ and $n_2 = 77 \text{ mol}\%$; the proper values for the initial C₆₀ were taken from [22]. The depolymerization products of the crystalline O and R polymerized phases of C₆₀ were characterized by oscillation spectroscopy and their spectral data testify to that those are the monomeric fcc phase of C₆₀.

The depolymerization process can be provisionally described as a scheme



According to Eq. (4), the enthalpy of depolymerization is a energy effect of the transformation of 1 mole of polymer to 1 mole of monomer in certain conditions and with specific physical states of reagents. The enthalpy of polymerization $\Delta_{\text{pol}}H^0$ is equal to the value of the depolymerization enthalpy ($\Delta_{\text{depol}}H^0$) with an opposite sign. The polymerization of the fullerite proceeds through the mechanism of [2 + 2] cycloaddition between two orientated in parallel double C=C bonds of neighbouring C₆₀ molecules to form a four-membered cycle [25]. In the framework of a simple scheme of the process, namely the formation of intramolecular C–C bonds in the polymerization and their scission during the depolymerization, the largest energy effect should be in the depolymerization of R polymerized phase of C₆₀. However, as demonstrated in [13], we derived an absolutely different relation between the enthalpies of

depolymerization and the number of breaking bonds. This can be explained by the fact that the values of the polymerization enthalpies depend on many factors and $\Delta_{\text{pol}}H^0$ is the sum of contributions [26]

$$\Delta_{\text{pol}}H^0(T) = \Delta H_{\text{at}} + \Delta H_{\text{conj}} + \Delta H_{\text{s.s.}} + \Delta H_{\text{mol}} + \Delta[H^0(T) - H^0(0)] \quad (5)$$

here ΔH_{at} is the difference in average enthalpies of breaking and generating in the polymerization bonds, ΔH_{conj} is the difference of conjugation enthalpies of atomic links in the monomer and polymer, $\Delta H_{\text{s.s.}}$ is the difference of energies of steric stresses in the monomer and polymer, ΔH_{mol} is the difference of enthalpies of intermolecular interaction in the monomer and polymer, $\Delta[H^0(T) - H^0(0)]$ is the difference of enthalpies of heating of the polymer and monomer from 0 to T . The depolymerization of the polymerized (dimeric) phases of C₆₀ leads not only to the scission of carbon bonds between adjacent molecules of C₆₀ but also to the destruction of the crystalline structure of the corresponding phases and the formation of fcc fullerite crystals. The differences in average energies of destruction of O and R phases of C₆₀ and the formation of the fcc phase of the fullerite are, certainly, unequal.

The thermodynamic stability of the crystalline polymerized phases of C₆₀ with respect to the initial fullerite at 298.15 K and atmosphere pressure can be estimated using the values of Gibbs function of polymerization $\Delta_{\text{pol}}G^0_p$ which is the sum of enthalpy ($\Delta_{\text{pol}}H^0$) and entropy ($T \Delta_{\text{pol}}S^0$) contributions [26]. The values of entropies of the synthesis of crystalline polymerized phases of C₆₀ from the fcc fullerite, i.e. the entropies of polymerization $\Delta_{\text{pol}}S^0$, calculated at 298.15 K are given earlier in Refs. [14,15]. Since at $T > 250 \text{ K}$ the C_p^0 values of the fullerite and the samples

Table 2

Calculated thermodynamic functions of crystalline dimer (C₆₀)₂ per mole of C₆₀ ($M = 720.66 \text{ g/mol}$); $p = 101.325 \text{ kPa}$

T (K)	$C_p^0(T)$ (J/(K mol))	$H^0(T) - H^0(0)$ (kJ/mol)	$S^0(T) - S^0(0)$ (J/(K mol))	$-[G^0(T) - H^0(0)]$ (kJ/mol)
5	3.26	0.0043	1.15	0.0015
10	11.9	0.0437	6.25	0.0188
20	24.87	0.2288	18.57	0.1430
30	33.15	0.5228	30.38	0.3890
50	45.21	1.303	50.06	1.200
100	87.58	4.402	91.41	4.739
150	181.0	10.94	143.2	10.53
200	305.4	22.99	211.6	19.34
250	436.4	41.67	294.4	31.94
298.15	534.3	64.96	379.4	48.16
300	539.5	65.95	382.7	48.87
310	564.6	71.47	400.8	52.79
320	587.2	77.23	419.1	56.89
330	608.9	83.21	437.5	61.17
350	651	95.8	475	70.3
360	666	102	493	75.1
370	681	109	512	80.2
380	695	116	530	85.4
382	697	117	534	86.4

Table 3

Thermodynamic functions of O phase and R phase of C₆₀ per mole of C₆₀ ($M = 720.66$ g/mol); $p = 101.325$ kPa

T (K)	$C_p^0(T)$ (J/(K mol))		$H^0(T) - H^0(0)$ (kJ/mol)		$S^0(T) - S^0(0)$ (J/(K mol))		$-[G^0(T) - H^0(0)]$ (kJ/mol)	
	O	R	O	R	O	R	O	R
5	1.03	0.476	0.00130	0.00060	0.345	0.160	0.000431	0.000201
10	6.23	2.56	0.0180	0.00780	2.46	1.08	0.00654	0.00293
20	17.29	6.504	0.1393	0.05140	10.42	3.923	0.06918	0.02710
30	24.01	9.987	0.3481	0.1335	18.80	7.210	0.2158	0.08276
50	33.60	19.50	0.9270	0.4182	33.37	14.28	0.7416	0.2958
100	80.83	78.31	3.636	2.774	69.15	44.56	3.279	1.681
150	171.4	168.0	9.811	8.823	118.0	92.37	7.887	5.033
200	284.0	280.7	21.15	19.97	182.4	155.7	15.34	11.18
250	403.1	400.6	38.31	37.00	258.5	231.2	26.32	20.81
298.15	517.5	517.6	60.50	59.10	339.4	311.8	40.70	33.86
300	521.7	522.1	61.46	60.06	342.6	315.0	41.33	34.44
340	610.9	612.8	84.10	82.82	413.3	386.1	56.44	48.45
350	635	631	90.3	89.0	431	404	60.7	52.4
360	656	643	96.8	95.4	450	422	65.1	56.5
370	676	657	103	102	468	440	69.7	60.8
380	696	671	110	109	486	458	74.4	65.3
390	716	687	117	115	505	475	79.4	70.0
400	735	703	125	122	523	493	84.5	74.8
410	753	721	132	129	541	510	89.8	79.9
420	772	740	140	137	560	528	95.3	85.0
430	790	759	148	144	578	546	101	90.4
440	808	777	156	152	596	563	107	96.0
450	826	795	164	160	615	581	113	102
460	843	811	172	168	633	599	119	108
480	–	836	–	184	–	634	–	120
490	–	846	–	193	–	651	–	126

of the polymerized (dimeric) C₆₀ phases differ not more than by 2% it is quite reliable to assume that $\Delta_{\text{depol}}H^0(298.15) = \Delta_{\text{depol}}H^0(T)$ (T is temperature of the region where the depolymerization proceeds). Based on the above stated it is possible to arrange a row of the relative thermodynamic stability of some polymerized phases of C₆₀. The relative thermodynamic stability of the C₆₀ phases at 298.15 K and atmosphere pressure changes in the following sequence: C₆₀ (fcc) > O phase C₆₀ \approx dimerized phase (C₆₀)₂ > R phase C₆₀. Thus, fcc phase of fullerite C₆₀ is the most thermodynamic stable at 298.15 K and standard pressure while R polymerized phase of C₆₀ exhibits the least stability.

It is to be noted that our conclusions about the relative thermodynamic stability of the crystalline polymerized phases of C₆₀ under the above conditions were inferred first based on the value and the sign of the Gibbs function of depolymerization. The conclusions about the relative thermodynamic stability of C₆₀ phases in [10,13] qualitatively differ from those in the present work since the authors [10,13] did not take into account an entropy component in their estimates and used only the $\Delta_{\text{depol}}H^0$ values.

3.2. Thermodynamic functions

From the data on the relation $C_p^0 = f(T)$ in the present work and our previous results [14,15], the thermodynamic functions of the crystalline dimer between $T \rightarrow 0$ and

380 K (Table 2) and O and R phases of C₆₀ from $T \rightarrow 0$ to (460–490) K (Table 3) were calculated. The enthalpy $H^0(T) - H^0(0)$ and entropy $-S^0(T) - S^0(0)$ were evaluated by the numerical integration by the curves. The Gibbs function $G^0(T) - H^0(0)$ was estimated from the enthalpy and entropy values at the corresponding temperatures. The procedure for the function calculation was published elsewhere [26].

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