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Thermodynamics of 2D polymerized tetragonal phase of fullerene C_{60} in the range from $T \rightarrow 0$ to 650 K at standard pressure

A.V. Markin [a], N.N. Smirnova [a,*], B.V. Lebedev [a], A.G. Lyapin [b], V.V. Brazhkin [b]

[a] Chemistry Institute, Nizhny Novgorod State University, Gagarin Prospect 23/5, 603950 Nizhny Novgorod, Russia
[b] Institute for High Pressure Physics, Russian Academy of Sciences, 142190 Troitsk, Moscow, Russia

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Abstract

By dynamic calorimetry the temperature dependence of heat capacity for two-dimensional (2D) polymerized tetragonal phase of C_{60} has been determined over the 300–650 K range at standard pressure mainly with an uncertainty ±1.5%. In the range 490–550 K, an irreversible endothermic transition of the phase, caused by the depolymerization of the polymer, has been found and characterized. Based on the experimental data obtained and literature information, the thermodynamic functions of 2D polymerized tetragonal phase of C_{60}, namely, the heat capacity $C_p^\circ(T)$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T)$, and Gibbs function $G^\circ(T) - H^\circ(0)$, have been calculated over the range from $T \rightarrow 0$ to 490 K. From 150 to 330 K in an adiabatic vacuum calorimeter and between 330 and 650 K in a dynamic calorimeter the thermodynamic properties of the depolymerization products have been examined and compared with the corresponding data for the monomeric phase C_{60}.

Keywords: 2D polymerized tetragonal phase of C_{60}; Heat capacity; Calorimeter; Endothermic transition; Depolymerization

1. Introduction

The present work is devoted to the recent studies of the thermodynamic properties of crystalline polymerized phases of fullerene C_{60} which are performed at the laboratory of polymer thermodynamics of the Nizhny Novgorod State University [1–5]. It is obvious that the determination and accumulation of precise thermodynamic data for new polymers, synthesized by high-pressure high-temperature treatments (HPHTT) of fullerite C_{60} [6–13], are highly urgent.

A complex examination of thermodynamic properties of 2D polymerized tetragonal phase of C_{60} was conducted earlier with using high-precision adiabatic vacuum calorimeters in the range from $T \rightarrow 0$ to 350 K [1,14,15]. However, the numerical values of the heat capacity over the temperature interval studied were published only in [1]. Differential scanning calorimeters that are employed most often in the calorimetric study of based-on-C_{60} polymers between 200 and 650 K afford only a qualitative picture of the temperature dependence of the heat capacity [16–18].

The goal of the given work is to determine calorimetrically the heat capacity, temperatures, and enthalpies of possible transformations of 2D polymerized tetragonal phase of C_{60} in the range 300–650 K, to calculate the thermodynamic functions $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$, and $G^\circ(T) - H^\circ(0)$ between $T \rightarrow 0$ and 490 K from our experimental- and literature data, to disclose the depolymerization process of 2D tetragonal phase of C_{60} and to evaluate its thermodynamic characteristics, to study the thermodynamic properties of the depolymerization products by methods of adiabatic vacuum and dynamic calorimetry in the range 150–650 K and to compare them with the appropriate data for the monomeric phase C_{60}.

2. Experimental

2.1. Sample

To prepare the sample to be tested of 2D polymerized tetragonal phase of C_{60}, a small crystalline (100 μm) powder of fullerite C_{60} (with the C_{60} content not less than 99.9 mass%) synthesized at the Institute of Organometallic Chemistry of the Russian Academy of Sciences (Nizhny

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* Corresponding author. Tel.: +7-8312-65-64-50; fax: +7-8312-65-64-50.
E-mail address: smirnova@ichem.unn.runnet.ru (N.N. Smirnova).

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Novgorod) was used as an initial material. The compression of C_{60} was carried out in a “toroid” – type high-pressure chamber [19] with use of a platinum container. Temperature was measured with a chromium–aluminum thermocouple.

It is known that the formation of 2D tetragonal phase depends upon the selection of conditions of C_{60} treatment. The synthesis parameters of the examined 2D tetragonal phase of C_{60} ($p = 3.5\,\text{GPa}$, $T = 960\,\text{K}$, time of HPHTT $\tau = 600\,\text{s}$) were chosen in accordance with a tentative phase diagram demonstrated in detail elsewhere [10,11]. After the treatment, the samples were subjected to hardening, and under common conditions those were thermodynamically metastable phases.

The sample structure was characterized by X-ray diffraction spectroscopy with using Cu Kα and Cr Kα irradiation. According to the data obtained and literature data [6,10,11], the synthesized samples were a mixture of tetragonal and rhombohedral phases, the tetragonal phase being predominant and its content in the sample amounting to 60–80 mass%.

2.2. Apparatus and measurement procedure

To study the heat capacity, temperatures, and enthalpies of transformations in the range 300–650 K an automated dynamic calorimeter operating by the principle of triple thermal bridge was employed. The calorimeter design and the technique of measurements of the heat capacity, temperatures, and enthalpies of transitions were described earlier [20,21]. The reliability of the calorimeter operation was tested 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 C_p° values of corundum measured by us are distinguished from the literature data not more than ±1.5%. The measurement uncertainties of the melting temperatures for indium, tin, and lead are 0.2, 0.6, and 0.3 K, respectively. It is supposed that the calorimeter and the measurement procedure allow the determination of the heat capacity of substances with an error of ±1.5%, and the temperatures of physical transitions within about ±0.5 K.

The heat capacity in the 6–350 K range was measured in [1] in an automated thermophysical device (BKT-3), an adiabatic vacuum calorimeter. It should be noted that all measurements were automated and monitored by a computer-measuring system consisting of a computer, an analog-to-digital and a digital-to-analog converter and a switch. The calorimetric ampoule is made of a thin-walled cylindrical vessel from titanium of $1.5 \times 10^{-6}\,\text{m}^3$ in internal volume. Its weight is $1.48 \times 10^{-3}\,\text{kg}$. Temperature was measured with an iron–rhodium resistance thermometer (resistance $R \cong 100\,\Omega$) calibrated according to ITS-90). The reliability of the calorimeter operation was tested by the measurement of the heat capacity for copper of special purity grade and standard synthetic corundum and K-2 benzoic acid prepared at metrological institutions of the State Standard of RF. As the analysis of the results shows, an uncertainty of the heat capacity measurements of substances at helium temperatures is within to ±2%, with rising temperature up to 40 K it decreases down to ±0.5% and amounts to ca. ±0.2% between 40 and 350 K.

3. Results and discussion

3.1. Heat capacity, temperatures, enthalpies, and entropies of transformations

The mass of the substance placed in a calorimetric ampoule was 0.5149 g. The data on the heat capacity of the sample of 2D polymerized tetragonal phase of fullerene C_{60} over the 300–650 K range were obtained at an average rate of heating of the calorimeter and the substance 0.0133 K/s. The experimental C_p° values are given in Table 1. The heat capacity of the sample in the whole temperature interval under study was 18–35% of the total heat capacity of (calorimetric ampoule and substance). A computer-assisted averaging of the experimental C_p° points was made by means of degree and semi-logarithmic polynomials. The root mean square deviation of them from the smoothed $C_p^\circ = f(T)$ curve in the range 300–650 K did not exceed ±0.3%.

Fig. 1 illustrates the temperature dependence of the heat capacity for the sample of 2D polymerized tetragonal phase of C_{60}: our experimental data (○) between 300 and 650 K and the experimental data (- - -) over the range 6–340 K demonstrated earlier in [1]. Besides, the experimental data and an averaged curve of the second series of measurements (a solid line), obtained under conditions of the adiabatic vacuum calorimeter from 150 to 330 K and of the dynamic calorimeter between 320 and 570 K, are demonstrated in this figure. The heat capacity was calculated per mole of C_{60}. It is seen that in the studied temperature range the heat capacity of 2D polymerized phase of C_{60} gradually increases with temperature, except for the range 490–550 K (BCD section, curve 1, Fig. 1), where the endothermic transformation due to the polymer depolymerization is observed. The depolymerization of crystalline polymerized 1D and 2D phases of fullerene C_{60} was observed earlier [12,14–16] but the thermodynamic characteristics of transition were not given since its nature was not quite clear. This process occurs in a certain temperature interval and the apparent heat capacity, described with BCD curve (its maximum value $C_{p,\max}^\circ = 1626\,\text{J/(K mol)}$), corresponds to it. On cooling down to ∼320 K and repeated measuring the temperature dependence of the heat capacity was not reproduced (curve 2, Fig. 1), in other words, an endothermic effect was absent. The above transformation is irreversible. The enthalpy of transition $\Delta_{\text{tr}}H^\circ = 11.9 \pm 0.3\,\text{kJ/mol}$ was determined graphically as the area bounded with curve BCD. The entropy of transition $\Delta_{\text{tr}}S^\circ = 19.1 \pm 0.4\,\text{J/(K mol)}$ was estimated by the numerical integration of the relation

Table 1
Experimental values of heat capacity of 2D polymerized tetragonal phase of C_{60} per mole of C_{60}; $M = 720.66$ g/mol

Series 1		Series 2		Series 3	
T (K)	C_p° (J/(K mol))	T (K)	C_p° (J/(K mol))	T (K)	C_p° (J/(K mol))
310.6	541.8	323.8	597.3	152.23	190.1
312.2	546.4	326.0	602.8	156.55	200.8
314.1	551.4	328.4	607.6	160.14	209.0
316.0	555.9	330.7	611.2	163.73	218.3
318.1	559.9	332.5	613.8	167.32	229.0
320.1	565.4	334.6	617.2	170.91	236.2
322.1	570.1	336.2	618.8	174.48	243.3
324.0	575.6	338.2	621.7	178.05	251.3
326.2	579.8	340.8	624.4	181.62	262.8
328.3	584.1	342.0	625.8	185.18	273.1
330.1	588.0	344.2	628.6	188.73	282.5
332.1	591.9	346.1	631.5	192.28	293.0
334.0	597.6	347.8	633.2	195.83	301.9
336.1	601.1	350.2	638.8	199.37	312.1
338.2	605.6	352.6	643.9	202.90	323.9
340.1	613.6	353.8	645.4	206.42	334.9
342.3	621.1	356.0	649.9	209.90	346.6
344.2	623.0	358.0	653.4	213.41	359.6
346.0	629.0	360.1	655.9	216.90	372.1
348.1	634.1	362.0	656.9	220.39	389.4
350.1	637.0	364.0	660.9	223.89	402.9
352.2	639.7	366.1	664.4	227.39	418.4
354.1	643.5	368.0	667.4	230.85	441.8
356.1	647.1	370.0	669.4	234.31	468.1
358.1	651.5	372.1	673.4	237.76	498.4
360.0	655.7	374.1	677.6	241.19	540.1
362.1	659.0	376.0	680.7	244.62	588.1
364.1	663.3	378.1	684.8	248.05	634.5
366.2	667.3	380.1	688.2	251.47	641.1
368.0	670.9	382.0	691.7	254.94	573.5
370.1	674.7	384.1	695.1	258.44	495.5
372.2	679.1	386.2	699.2	261.90	467.1
374.0	682.7	388.0	701.6	265.24	464.7
376.1	684.1	390.2	704.7	268.64	467.9
378.0	688.7	392.2	709.0	272.02	474.7
380.0	691.6	394.0	713.2	275.40	482.6
382.1	696.6	396.1	715.9	278.76	487.3
384.1	700.6	398.0	717.8	282.12	497.3
386.1	703.4	400.0	719.1	285.47	505.6
388.0	707.6	402.0	722.2	288.82	514.6
390.1	711.1	404.1	724.2	292.15	519.5
392.2	714.5	406.0	726.9	295.46	525.8
394.1	717.9	408.1	730.5	298.76	536.1
396.0	720.1	410.0	732.6	302.02	542.5
398.2	723.5	412.1	737.5	305.28	549.5
400.0	725.9	414.0	741.7	308.54	558.5
402.1	730.2	416.1	744.9	311.78	567.5
404.1	735.4	418.0	748.4	314.98	574.6
406.1	738.3	420.0	751.7	318.02	582.6
408.1	741.3	422.1	755.6	321.24	590.6
410.1	744.2	424.3	759.6	324.44	598.4
412.1	748.4	426.1	763.0	327.64	604.7
414.1	749.9	428.0	766.0		
416.0	755.5	430.1	770.8		
418.1	759.1	432.1	772.8		
420.0	762.5	434.0	777.0		
422.1	766.5	436.2	780.1		
424.2	771.3	438.1	783.7		
426.0	774.9	440.1	787.4		
428.0	778.7	442.0	791.3		
430.0	781.1	444.1	795.5		

Table 1 (*Continued*)

Series 1		Series 2		Series 3	
T (K)	C_p° (J/(K mol))	T (K)	C_p° (J/(K mol))	T (K)	C_p° (J/(K mol))
432.0	785.9	446.1	798.5		
434.1	789.1	448.1	801.7		
436.3	791.6	450.0	804.5		
438.1	794.0	452.1	807.9		
440.1	798.1	454.0	811.4		
442.1	799.9	456.0	814.4		
444.1	803.3	458.0	818.1		
446.2	807.8	460.1	821.3		
448.2	808.1	462.1	822.7		
450.1	812.2	464.2	826.0		
452.1	815.6	466.0	829.7		
454.1	818.1	468.1	831.6		
456.1	819.7	470.2	833.4		
458.1	822.2	472.0	835.9		
460.0	824.7	474.1	839.4		
462.1	827.5	476.0	840.4		
464.0	825.7	478.0	841.9		
466.0	828.3	480.1	845.7		
468.0	829.7	482.0	848.5		
470.0	832.3	484.0	851.3		
472.0	833.3	486.2	854.9		
474.0	836.2	488.0	857.2		
476.2	840.0	490.0	858.8		
478.1	842.3	492.2	861.3		
480.0	844.0	494.0	863.0		
482.1	848.7	496.2	868.0		
484.0	849.2	498.1	871.1		
486.2	853.5	500.1	874.0		
488.1	854.8	502.1	876.8		
490.1	855.1	504.1	879.7		
492.0	856.3	506.1	882.3		
494.0	862.3	508.2	885.5		
496.8	868.8	510.0	888.1		
498.0	871.6	512.0	890.6		
500.1	879.2	514.1	892.1		
502.1	887.8	516.1	894.4		
504.1	898.6	518.0	896.9		
506.0	911.4	520.1	898.5		
508.0	931.8	522.1	901.9		
510.2	961.5	524.1	905.6		
512.6	1002	526.0	908.3		
514.9	1083	528.1	909.8		
516.8	1164	530.0	912.0		
518.6	1291	532.1	914.5		
520.2	1363	534.1	917.3		
522.0	1494	536.1	920.1		
524.2	1600	538.0	923.1		
526.1	1626	540.0	924.5		
528.0	1583	542.1	927.1		
530.0	1471	544.1	930.8		
532.0	1354	546.0	935.7		
534.0	1232	548.0	938.7		
536.0	1133	550.1	944.0		
538.0	1071	552.1	945.9		
540.0	1028	554.2	947.0		
542.0	999.5	556.0	948.4		
544.0	983.9	558.0	950.4		
546.1	971.7	560.0	953.1		
548.0	966.3	562.1	955.3		
550.1	963.5	564.0	958.6		
552.1	962.7	566.1	962.4		
554.2	963.4	568.0	964.7		

Table 1 (*Continued*)

Series 1		Series 2		Series 3	
T (K)	C_p° (J/(K mol))	T (K)	C_p° (J/(K mol))	T (K)	C_p° (J/(K mol))
556.1	963.5	570.1	966.5		
558.1	965.3				
560.0	967.3				
562.1	969.5				
564.1	973.2				
566.0	973.3				
568.1	973.5				
570.0	976.9				
572.1	978.6				
574.1	982.8				
576.1	984.4				
578.0	986.9				
580.0	989.0				
582.1	990.5				
584.1	991.4				
586.1	990.8				
588.1	993.1				
590.1	998.1				
592.0	999.1				
594.2	1000				
596.0	1000				
598.1	1002				
600.0	1004				
602.0	1005				
604.0	1006				
606.1	1006				
608.1	1006				
610.0	1007				
612.1	1007				
614.1	1008				
616.0	1011				
618.1	1014				
620.1	1015				
622.0	1017				
624.1	1020				
626.1	1020				
628.0	1020				
630.1	1022				
632.2	1024				
634.1	1027				
636.0	1030				
638.1	1033				
640.1	1035				
642.0	1038				
644.1	1040				

In series 1 and 2 each secondary experimental value of C_p° is given.

$C_p^\circ = f(T)$ by $\ln T$ (area under BCDB curve, Fig. 1). While evaluating the entropy of transition from its enthalpy and temperature by the known equation of the second law of thermodynamics, another numerical value was derived. In [15], the value of the enthalpy of depolymerization for 2D polymerized phase of C_{60} (mainly a tetragonal phase) was determined to be $\Delta_{tr}H^\circ = 55$ kJ/mol. The enthalpy was estimated assuming that an equilibrium phase transition of the polymerized C_{60} phase to the monomeric phase C_{60} takes place. As seen, the experimental value of $\Delta_{tr}H^\circ$ is smaller by a factor of some times than the calculated one. This, in turn, confirms again that the observed transition can't be classified as the equilibrium transformation of the polymerized phase of C_{60} to the monomeric phase.

The tested sample, unlike the initial fullerite C_{60}, does not show both the orientational phase transformation [22–24] and a G-type transition [22,25] (curve 1, Fig. 1). Considerable discrepancies of the values of the heat capacity and the different character of its temperature dependence of 2D polymerized phase of C_{60} and the initial fullerite are seen only at very low temperatures ($T < 100$ K), and this is due to the different heterodynamics of their structure, as was noted elsewhere [1]. At temperatures above 100 K and prior to the onset of the endothermic transition, the heat capacities of the

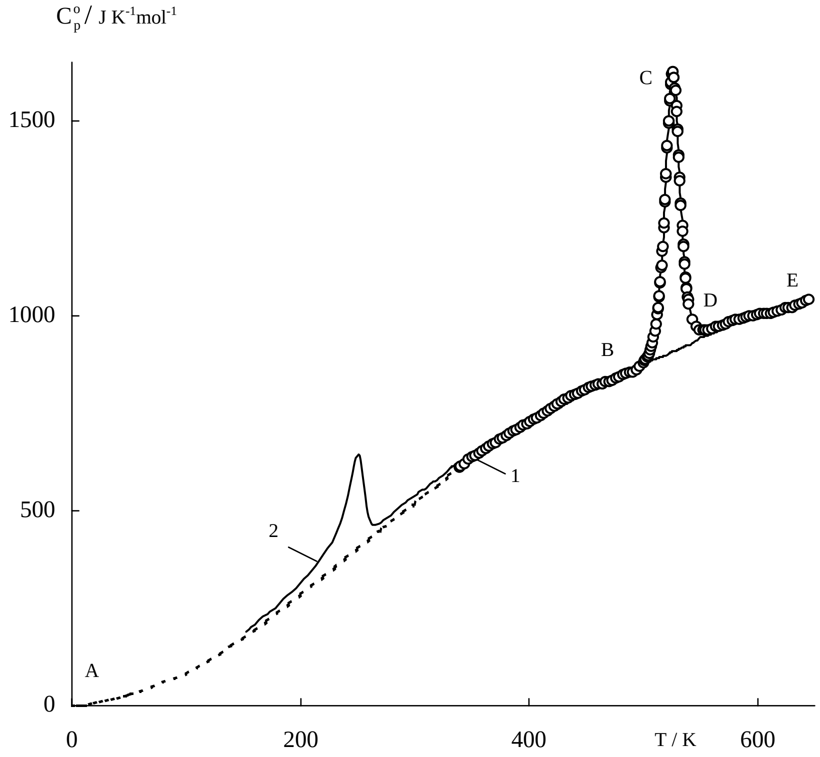

Fig. 1. Temperature dependence of heat capacity of 2D polymerized tetragonal phase of C_{60}; (- - -) and (○) the first trend of measurements; (—) a repeated trend of measurements; AB and DE – before and after depolymerization, respectively.

objects to be compared are close (differences do not exceed 1.5%), although the C_p° values of 2D polymerized phase of C_{60} are always smaller than those of the initial C_{60} [22,26].

The depolymerization product of 2D polymerized phase of C_{60} was drawn from a calorimetric ampoule of the dynamic calorimeter and further studied in the adiabatic vacuum calorimeter (Fig. 2). It is seen that on the relation $C_p^\circ = f(T)$ its orientational phase transition appears in the 185–275 K range as for the initial fullerite. However, judging by the ratio of the corresponding areas under the curves of apparent heat capacities (BCDB and BEE'FB) in the transition range (Fig. 2), the enthalpy of transition of the sample is some times smaller than that of C_{60}. The temperature corresponding to the maximum value of the apparent heat capacity in the transition interval 190–275 K ($C_{p,\max}^\circ = 641$ J/(K mol)) was regarded as the transition temperature $T_{\mathrm{tr}}^\circ = 251.5$ K. The enthalpy of transition $\Delta_{\mathrm{tr}}H^\circ$, determined graphically as the area bounded with curve BCDB (Fig. 2), was equal to 5.16 ± 0.05 kJ/mol. The appropriate values of the initial C_{60} [22] are the following: the transition range 185–275 K, $T_{\mathrm{tr}}^\circ = 260.7$ K ($C_{p,\max}^\circ = 34747$ J/(K mol)), $\Delta_{\mathrm{tr}}H^\circ = 7.46 \pm 0.15$ kJ/mol. It is obvious that the depolymerization products are chiefly the monomer phase of fullerite C_{60} (it is denoted C_{60}'). The values of thermodynamic characteristics of transition of the C_{60}' sample, produced by the depolymerization of 2D polymerized phase of C_{60} are somewhat smaller than those of the initial C_{60}.

This is, probably, caused by the fact that the high-pressure treatment of C_{60} in the course of the polymerized phase synthesis and further its thermal depolymerization resulted in the appearance of many defects in the molecular structure of C_{60}. The amount (n) of Van der Waals fcc. C_{60} phase in

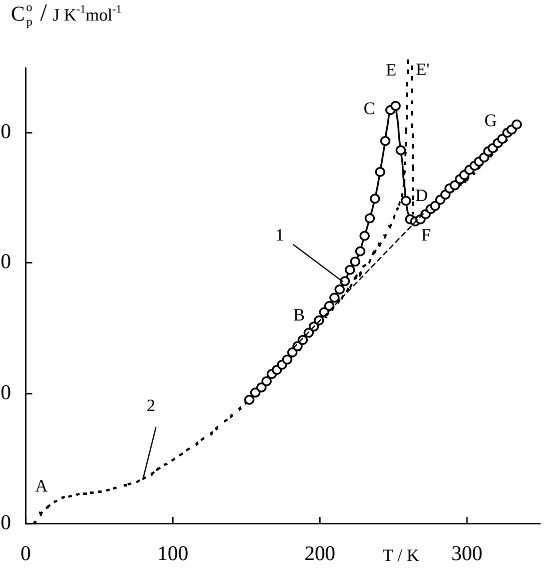

Fig. 2. Temperature dependence of heat capacity determined in adiabatic vacuum calorimeter of: (1) the depolymerization product of 2D polymerized tetragonal phase of C_{60}; (2) the initial fullerite C_{60} [22].

Table 2
Thermodynamic functions of 2D polymerized tetragonal phase of C_{60} per mole of C_{60} ($M = 720.66$ g/mol); $p = 101.325$ kPa

T (K)	$C_p^\circ(T)$ (J/(K mol))	$H^\circ(T) - H^\circ(0)$ (kJ/mol)	$S^\circ(T)$ (J/(K mol))	$-[G^\circ(T) - H^\circ(0)]$ (kJ/mol)
0	0	0	0	0
5	0.105	0.00010	0.0313	0.000030
10	1.330	0.00320	0.4027	0.000860
15	3.400	0.01480	1.322	0.00500
20	5.930	0.03800	2.638	0.01470
30	11.63	0.1251	6.090	0.05760
50	27.23	0.5062	15.49	0.2683
100	82.11	3.202	50.70	1.868
150	172.4	9.431	99.97	5.564
200	285.4	20.81	164.7	12.12
250	403.0	38.01	241.0	22.22
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	564.1	71.90	359.6	43.19
330	589.4	77.66	377.4	46.87
340	613.5	83.68	395.3	50.73
350	635.5	89.93	413.4	54.78
360	655.5	96.38	431.6	59.00
370	674.1	103.0	449.8	63.41
380	691.9	109.9	468.1	68.00
390	709.6	116.9	486.3	72.77
400	727.5	124.1	504.4	77.72
410	745.6	131.4	522.6	82.86
420	763.7	139.0	540.8	88.18
430	781.1	146.7	559.0	93.68
440	797.2	154.6	577.1	99.36
450	811.4	162.6	595.2	105.2
460	823.4	170.8	613.2	111.3
470	833.7	179.1	631.0	117.5
480	844.2	187.5	648.7	123.9
490	858.4	196.0	666.2	130.5

the C'_{60} sample can be easily evaluated by the expression:

$$n = \left[\frac{\Delta_{\rm tr} H^\circ(C'_{60})}{\Delta_{\rm tr} H^\circ(C_{60})}\right] \times 100\% \qquad (1)$$

It was found that $n = 70$ mol%. The difference in numerical values of enthalpies of the orientational phase transition in the initial C_{60} and the C'_{60} sample can be quite attributed to the availability in the latter of a certain portion of non-decomposed low-molecular dimers and oligomers of C_{60}, stable because of their interaction with other structural defects or due to a high degree of polymerization. So, it is known [9] that on exceeding a certain degree of polymerization with the formation of 3D, the polymer structure becomes resistant to depolymerization under common conditions. In addition, the increase in the volume fraction of intergranular boundaries, associated with the change in the specific size of C_{60} crystallites as a result of consequent polymerization and depolymerization, can exercise a noticeable influence on the enthalpy of transition.

3.2. Thermodynamic functions

From the data on the relation $C_p^\circ = f(T)$ obtained in the present work and given in [1], for 2D polymerized tetragonal phase of C_{60}, their thermodynamic functions were calculated over the range from $T \to 0$ to 490 K (Table 2). The enthalpy $H^\circ(T) - H^\circ(0)$ and entropy $S^\circ(T)$ were estimated by the numerical integration by curves. The Gibbs function $G^\circ(T) - H^\circ(0)$ was evaluated from the values of $H^\circ(T) - H^\circ(0)$ and $S^\circ(T)$ at the corresponding temperatures. The calculation procedure of the functions was demonstrated, for example, in [27].

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