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Thermodynamic properties of C_{60} and C_{70} fullerenes

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Contents

I.	Introduction	95
II.	Behaviour of fullerenes in thermodynamic studies	95
III.	Enthalpies of formation of C_{60} and C_{70}	96
IV.	Heat capacities in the condensed state and thermodynamics of phase transitions in C_{60} and C_{70}	97
V.	Saturated vapour pressures and enthalpies of sublimation of fullerenes	100
VI.	Thermodynamic properties of C_{60} and C_{70} in the ideal gas state	100
VII.	Conclusion	102

Abstract. The most reliable values of the basic thermodynamic parameters of the C_{60} and C_{70} fullerenes are recommended based on the analysis of the published data and original calculations, *viz*., enthalpies of formation in the solid and gaseous states, saturated vapour pressures, enthalpies of sublimation, enthalpies of phase transitions, heat capacities, entropies in the condensed state and heat capacities and entropies in the ideal gas state. The factors influencing the results of thermodynamic studies of fullerenes are discussed. Various aspects of crystal structure determination, PVT-relationships and frequencies of normal modes of the C_{60} and C_{70} fullerenes are considered in order to interpret and correlate the thermodynamic data and extend them to a wide temperature range. The bibliography includes 135 references.

I. Introduction

The need for the knowledge of thermodynamic properties of fullerenes arises not only from the interest in this unusual class of compounds or the quest for efficient ways of their preparation and practical use. The fullerenes have now become the 'proving ground' for testing virtually all the modern methods of predicting the structure and properties of solids, fluids and ensembles of particles. Therefore, the well-grounded and reliable values of the basic thermodynamic parameters of these compounds are of great importance. Although the extensive literature on fullerenes is available (including reviews [1 – 5]), their thermodynamic properties are known less reliably than those of many other 'ordinary' compounds. The publication of a specialised review [6] devoted to the studies of thermodynamic properties of fullerenes was followed by the appearance of many new communications. However, their results were often contradictory. The main reason for the contradictions seems to lie in the specific properties of fullerenes, which are more sensitive to the sample prehistory and conditions of the experiment than the properties of ordinary organic substances. Understanding of this fact came gradually in the course of thermodynamic and other studies, so that the lack of information at the time of publication of an article often did not enable the authors to assess the influence of various factors on the final result of their measurements. Therefore, any report on thermodynamic properties of fullerenes should be considered in the light of the overall information available on these compounds with the details of the experiment taken into account.

Based on such an analysis (the experimental data published between 1987 and 1998 have been surveyed), the present review recommends values for the most important thermodynamic parameters of the C_{60} and C_{70} fullerenes. The following criteria were used in selecting the experimental data and establishing the recommended values. The characterisation of samples and experimental procedures should be exhaustive in order to rule out the influence of known factors affecting the results of measurements. Preference was given to the results available for the sublimates whose purity and stability were confirmed by independent studies. The precision of the techniques used and reproducibility of the results were taken into account. Thus the heat capacity values measured by adiabatic calorimetry (AdC) were considered to be the most reliable. An agreement between the results obtained by various authors as well as between the thermodynamic parameters of each of the fullerenes were also taken into consideration.

II. Behaviour of fullerenes in thermodynamic studies

The effect of impurities and chemical instability of fullerenes are the factors that hamper the determination of their thermodynamic properties most seriously. Conventional purification procedures and methods of purity control applied to organic compounds appeared to be inefficient for fullerenes which show a tendency towards co-crystallisation with the solvent molecules. Even small amounts of impurities significantly affect various properties of fullerenes. Thus, the phase transition temperature [7] (T_{tr}) of C_{60} shifts from 260.7 K to 243 K or to 245 K in the presence of benzene [8] or toluene admixtures. Also an additional heat capacity anomaly appears at 232 or 239 K, respectively. Two additional heat capacity anomalies,[9] at 185 and 425 K appear in the C_{60} sample crystallised from carbon disulfide due seemingly to the presence of a CS_2 impurity. The anomaly observed at 185 K disappears after annealing the sample at 425 – 500 K. The C_{60} crystals grown from a solution of fullerene in carbon disulfide are monoclinic, the temperature of the 'ordinary' phase transition being shifted in such crystals to 242 K.[10] The rhombohedral C_{60} crystals grown from a toluene – hexane solution (the purity is 99.9% from mass spectrometric measurements) undergo a phase

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transition associated with a diffuse anomaly of the heat capacity at 239 K.[11] It was found that an adduct of the C_{70} fullerene with toluene ($C_{70}\cdot C_7H_8$) exhibits heat capacity anomalies at 195 and 430 K (the latter is due to an irreversible decomposition of the adduct).[12] After the decomposition of the adduct, a heat capacity anomaly[12] at 304 K and two phase transitions[13] at 277.4 and 340.0 K were observed in the sample. It was also found out that several heat capacity peaks observed upon phase transition in C_{60} are due to the C_{70} impurity present in the sample.[14]

It was found that fullerenes absorb (or adsorb) large amounts of oxygen and, probably, water.[15] Pellet-like samples were kept in a moist oxygen atmosphere under pressure of 30 bar. It was measured that C_{60} absorbs 30–60 g mol^{-1} in 0.5 h and C_{70}, more than 150 g mol^{-1} in ~24 h. Although these estimates[15] are seemingly overstated (the specific surface of the C_{60} samples measured with liquid nitrogen[16] was ~3 m^2 g^{-1}), the uncontrolled adsorption could affect the results of combustion experiments. Two maxima on the temperature curve of desorption of oxygen and other substances plotted for a C_{60} sample indicate[17] that impurities are absorbed by both the surface and the bulk of a substance. The location of impurities in polycrystalline fullerene C_{60} has been studied in detail;[16] it was found that the solvent molecules were mainly adsorbed on the surface of microcrystals, whereas upon thermal treatment, they could be fixed in cavities of the baked crystals. This may be a reason why it is difficult to purify fullerenes by heating *in vacuo*.

The thermodynamic properties of fullerenes were reported to depend on the size of crystals in a sample.[18–21] A finely crystalline C_{60} sample (**1**) of brown colour which contained 0.004 mol of C_{70} (from HPLC measurements) exhibited a fall in the phase transition temperature (T_{tr} = 258.6 K), a decrease in the enthalpy of combustion (Δ_cU° = −35 896 J g^{-1}) and incomplete yield of CO_2 in the combustion products (approximately 99.8%) as compared to similar characteristics (T_{tr} = 260.9 K; Δ_cU° = −36 030 J g^{-1}; the yield of CO_2 upon combustion is 100.00 ± 0.04%) exhibited by a chromatographically pure coarsely crystalline C_{60} sample (**2**) of black colour.[21] Both samples were dried under the same condi-tions: for several hours at 440–520 K and a pressure of 0.001 Pa. Kolesov *et al.*[21] suggest however that the changes in the properties of the sample **1** could be caused by impurities either occluded upon its fast crystallisation or adsorbed by its developed surface.

It was found[19,20] that the C_{60} crystals become progressively less capable of solid-state transitions as they are ground. Skokan *et al.*[16] examined this phenomenon in detail to conclude that this results from the defects accumulated in the crystals, the effect of solvent impurity not being involved.

At fairly high temperatures (700 K and above) at which most of the reported effusion measurements have been made, partial decomposition of samples can occur. Thus, a nonvolatile residue (8%) was detected in C_{60} after it had been sublimed at 1273 K in a nitrogen atmosphere and dried *in vacuo* at 700 K.[22] A sample of C_{60} purified by sublimation at 673 K (the sample purity was 99% from mass spectrometric measurements[23]) yielded 5% of a nonvolatile residue after it had been sublimed at 973–1073 K in a nitrogen or an argon atmosphere. After sublimation of the 99.98% pure C_{60} fullerene, 0.1%–0.3% of the substance still remained nonvolatile, the evaporation of the first half of the sample being followed by a not fully understood fall of the saturated vapour pressure.[24] It is suggested that partial transformation of fullerenes into nonvolatile amorphous carbon at 700–740 K may result from contamination of the initial sample with remains of organic solvents.[25] Fullerene C_{70} (98.5% pure, the main impurity being C_{60}) contained 6%–8% of nonvolatile deposit (amorphous carbon) after mass loss of 1% had been detected at 450 K and a cycle of effusive measurements had been performed.[26] A sublimed sample was evaporated nearly completely in a repeat run, although some pressure fall was observed in the effusive measurements in carbon cells at 800–900 K and a small amount of nonvolatile deposit was still detected. Destruction of the C_{60} and C_{70} fullerene molecules in the vapour phase[27] begins at 2650 and 2440 K, respectively, and in the condensed state,[28,29] above 1000–1073 K, the temperature limits depending on the nature and content of impurities.[25]

Therefore, the following strategies appear to be efficient in the preparation of pure specimens suitable for thermodynamic studies: growth of large-sized crystals[16,21] and sublimation of fullerenes *in vacuo*.[24,26,30,31] If, prior to sublimation, a sample is dried at a gradually increasing temperature, the major portion of the solvent is probably removed before the degradation (amorphisation) of the basic substance begins.

Experience gained by various researchers suggests[15,17] that the protection from traces of oxygen is particularly necessary in the sublimation. Fullerenes are known to be vigorously oxidised by oxygen at elevated (> 500 K) temperatures.[23,32–34] However, under exposure to either high-energy photons or visible light (0.5–5.0 eV), the photoinduced oxidation of the fullerenes by atmospheric oxygen becomes possible at room and even low (20 K) temperatures.[35] This imposes additional requirements for the preparatory conditions and purification of fullerenes intended for thermodynamic studies.

Methods of purity control of the samples used for thermodynamic measurements are of principal importance. HPLC is a traditional method which allows determination of the degree of separation of fullerenes with different compositions and the $C_{60}O$ content.[15] It is significant to establish to what extent the organic solvents used for the sample preparation (benzene, toluene, xylene, carbon disulfide, diethyl ether, *etc.*) have been removed. The presence of benzene impurity is determined using ^{1}H NMR,[36] although the sensitivity of the method may be insufficiently high.[37] The hydrogen content in a C_{60} sample is measured by activation analysis.[38] The C_{60} sample was heated in a sealed tube in a nitrogen atmosphere (673 K, 10 min) and the vapour phase was then analysed by GLC.[39] Unfortunately, total removal of impurities as well as their constant chemical composition are questionable under such conditions. Volatile substances released upon gradual heating of a C_{60} sample were analysed by mass spectrometry,[17] but no quantitative estimates of the impurity content were made. The phase transition temperatures and a proportion of nonvolatile deposit found after the sublimation may serve as indirect criteria of the sample purity.

The lack of details in some papers describing the prehistory of samples and methods of their study does not enable one to evaluate the effect of the above-listed factors on the results of measurements of thermodynamic properties.

III. Enthalpies of formation of C_{60} and C_{70}

The measured enthalpies of combustion and formation of C_{60} are listed in Table 1. The scatter in the standard combustion energies amounts to ~0.6% (from −35 914 to −36 124 J g^{-1}) which is

Table 1. The enthalpies of combustion and formation of C_{60}.

$-\Delta_cU^\circ$ /J g^{-1}	$-\Delta_cH^\circ$ /kJ mol^{-1}	Δ_fH° /kJ mol^{-1}	Ref.
35 914.0±(18.0)	25 881.8±(13.0)	2273.0±(13.0)	36
35 923.6±(16.8)	25 888.7±(12.1)	2278.1±(14.4)	38
35 929.5±19.4	25 893.0±14.0	2282±16	43
35 992±61	25 938±44	2327±44	15
36 004.6±(11.8)	25 947.1±(8.5)	2336.5±(8.5)	42
36 030±16	25 965±12	2355±15	21
36 036.7±16.7	25 970±12	2360±16	39
36 123.7±(19.4)	26 032.9±(14.0)	2422.3±(14.0)	37
36 017±17	**25 956±12**	**2346±12**	

Note. Here and in Table 2, the recommended values are printed in bold face. We estimated the uncertainties within the reliability interval of 95%. The errors given in parentheses are taken from the reference cited; they are most commonly twice the standard deviation.

Table 2. The enthalpies of combustion and formation of C_{70}.

$-\Delta_c U^\circ$ /J g^{-1}	$-\Delta_c H^\circ$ /kJ mol^{-1}	$\Delta_f H^\circ$ /kJ mol^{-1}	Ref.
35 587±(25)	29 921±(36)	2375±(36)	36
35 629.4±(10.6)	29 956.1±(8.9)	2410.4±(8.9)	42
35 664±44 [a]	29 985±37 [a]	2439±37 [a]	44
35 733±42 [b]	30 042.8±35.3 [b]	2497±35 [b]	
35 802±26	30 101±22	2555±22	15
35 828.4±15.8	30 123.5±13.4	2577.8±16.2	45
35 802±26	**30 101±22**	**2555±22**	

[a] From the mass of a substance; [b] from the mass of CO_2.

more than an order of magnitude higher than the experimental error of measurement by combustion calorimetry of organic substances without heteroatoms. The reasons for such a scatter may be the factors that counteract each other, *e.g.*, organic solvent impurities like toluene which are characterised by the heats of combustion of large absolute values (-42382 J g^{-1}) and adsorbed oxygen and water which increase the apparent weight of a sample. The problems of precise determination of the enthalpies of combustion of fullerenes are discussed in a review,[40] and the enthalpies of formation of carbon clusters in relation to their structures and sizes are analysed in a review.[41] The scatter of the reported enthalpies of combustion $\Delta_c H^\circ$ lies within 0.12%.[15, 21, 39, 42] The results of earlier publications lie outside this interval. Five experiments performed on presumably one of the best C_{60} samples (purified by sublimation) [15] gave, for unclear reasons, a wide dispersion of the results. Kolesov *et al.*[21] examined a specially prepared coarsely crystalline sample; an analysis of the combustion products gave the CO_2 yield of 100.00±0.04%. A similar result was obtained [39] (see Table 1) using large samples (of approximately 0.5 g) and an original GLC-analysis of organic solvent contaminations in fullerene (0.013 mass % of diethyl ether and 0.007 mass % of *o*-xylene). Later, An *et al.*[42] gave the enthalpy of C_{60} combustion which was slightly different from their previous result.[39] Therefore, the value $\Delta_f H^\circ(\text{cr}) = 2346 \pm 12$ kJ mol^{-1} which is an average of the published data [21, 42] is recommended for the enthalpy of formation of C_{60} in the crystalline state.

The enthalpy of formation in the gaseous state is $\Delta_f H^\circ(\text{g}) = 2530 \pm 13$ kJ mol^{-1}, the enthalpy of sublimation of C_{60} ($\Delta_{sub} H^\circ = 183.7 \pm 5.1$ kJ mol^{-1}) being taken into account.

The measured combustion energy values $\Delta_c U$ for the C_{70} fullerene (Table 2) are scattered even wider, over more than 0.7% (from $-35\,587$ to $-35\,828$ J g^{-1}). The reasons for the scatter are evidently similar to those for C_{60}. The uncertainty of the crystal composition of C_{70} at 298.15 K which is discussed below cannot have a notable effect on the error in determination of the enthalpy of formation, because the energy difference between different crystal modifications of C_{70} is two orders of magnitude smaller. It is likely that the best sample of this fullerene purified by sublimation was studied by Beckhaus *et al.*,[15] therefore their results are recommended as most reliable. Only in one publication [44] was the amount of CO_2 in the combustion products measured to find a yield of 99.81±0.02%. Assuming that the material balance on carbon [44] was upset due to the presence of inert impurities (adsorbed gases or water) in the C_{70} finely crystalline sample and relating the heat of combustion to the appropriate amount of CO_2, one obtains the value $\Delta_c U^\circ = -35\,732.5 \pm 42$ J g^{-1}, which is close to that given by Beckhaus *et al.*[15] The data by Diogo *et al.*[45] are also close to the latter value [15], but one cannot say, judging from the results of HPLC analysis of C_{70} fullerene,[45] whether toluene was completely removed from the sample. We cannot offer an explanation of a low absolute value of the enthalpy of C_{70} combustion reported by An *et al.*[42]

Thus, the recommended value for the enthalpy of formation [15] of C_{70} is $\Delta_f H^\circ(\text{cr}) = 2555 \pm 22$ kJ mol^{-1}. With the enthalpy of sublimation of C_{70} $\Delta_{sub} H^\circ_{298.15} = 200.3 \pm 6.1$ kJ mol^{-1} taken into account, the enthalpy of formation in the gaseous state at 298.15 K is $\Delta_f H^\circ(\text{g}) = 2755 \pm 23$ kJ mol^{-1}.

IV. Heat capacities in the condensed state and thermodynamics of phase transitions in C_{60} and C_{70}

It is now commonly accepted that the C_{60} fullerene crystallises at $T = 298.15$ K and pressure $P = 1$ atm in a face-centred cubic lattice with $a = 14.152$ Å and $d = 1.69$ g cm^{-3} (see Ref. 17). Molecular rotation in such a crystal results in an orientational disorder. Upon cooling below 260 K, a solid-state transition occurs. In the low-temperature modification,[46, 47] the C_{60} molecules have four different orientations in space making a simple cubic lattice. Some rotational degrees of freedom are retained in this case. The remaining rotational degrees of freedom freeze upon vitrification of the crystal [48] at around 90 K. From calorimetric measurements, the vitrification temperatures are $T_g = 86.8$ (see Ref. 49) and 86.0 K (see Ref. 7). The residual entropy of C_{60} at 0 K was estimated to be 4.7±0.5 (see Ref. 50) and 4.9 J K^{-1} mol^{-1} (see Ref. 7). Although the estimation procedures are not indisputable, we see little reasons for revising the results. As reported by Willart *et al.*,[51] no other transitions occur in an impurity-free C_{60} sample at atmospheric pressure.

Table 3 lists the measured enthalpies of phase transition $\Delta_{tr} H$ in C_{60} around 260 K. Probable reasons for the scatter in T_{tr} and

Table 3. Thermodynamic characteristics of a solid-state transition in C_{60}.

T_{tr} /K	$\Delta_{tr} H$ /kJ mol^{-1}	Sample	Method	Note	Ref.
249	4.8	purity 99.5%	DSC		52
255	6.7	dried *in vacuo* at 700 K	AdC	sample of small weight, 8% of a deposit detected after sublimation in nitrogen at 700 K	22
256	7.0	dried *in vacuo* at 475 K, purity 99.5% [a]	DSC		53
257.6	7.54	–	AdC		49
258	6.2	–	DSC	three peaks at 253, 258 (90%) and 260 K	54
259	3.2±0.2	–	DSC	peaks at 240 K (due to impurities) and 259 K; difficulty in baseline location	27
260	7	dried at 440 K (13 Pa, 5 days)	DSC		47
260.7	7.46±0.15	dried *in vacuo* at 400 K, purity 99.98% [b]	AdC		7
261.4	9.0±0.5	sublimed, single crystal	DSC	sample of small weight, the heat effect under the peak is 6.8 kJ mol^{-1} (see [c])	19

Note. DSC is differential scanning calorimetry, AdC is adiabatic calorimetry. [a] From mass spectra and Raman spectra; [b] from HPLC measurements; [c] the remaining part of the heat effect (2.2 kJ mol^{-1}) was found by integrating the difference between the heat capacity of a sample and the baseline in the temperature interval 150 – 290 K.

Table 4. Details of heat capacity measurements of C_{60} in the condensed state.

Sample	Method	Temperature range /K	Ref.
Not completely solvent-free	AdC	10 – 300	8
Extracted with benzene, chromatography, dried at 700 K, 8% of a deposit detected after sublimation	AdC	4.2 – 300	22
Extracted with a benzene – hexane mixture, chromatography, washed with ether, dried at 475 K, 99.5% pure [a]	DSC	120 – 560 [b]	53
Extracted with toluene, washed with ether, chromatography, dried at 450 K for 50 h, purity 99.99 mol.% [c]	DSC	300 – 800	37
–	thermal relaxation	1.4 – 20	56
–	AdC	13 – 300	49
Extracted with a benzene – hexane mixture, chromatography, dried at 523 K for 24 h, single crystal	MC	120 – 300	11
Extracted with toluene, chromatography, dried at 400 K, 99.98 % pure [d]	AdC	5 – 339	7

Note. MC is modulation calorimetry. [a] From mass spectra and Raman spectra; [b] no phase transitions occur upon further heating to 950 K; [c] from HPLC measurements; [d] from HPLC and X-ray diffraction.

$\Delta_{tr}H$ values were discussed in Section II. In addition, the transition is not isothermal (2N-type according to the classification of Westrum and McCullough [55]), which makes difficult both the interpretation of the calorimetric data and the choice of the heat capacity baseline in the calculation of the enthalpy of phase transition. This seems to account for the large value of $\Delta_{tr}H$ reported by Dworkin *et al.*[19] The values [7,49] of $\Delta_{tr}H$ measured by an adiabatic calorimetry are in good agreement with each other. The values measured in 1993 using differential scanning calorimetry (DSC) are fairly close to them.[19,47,54] For the calculation of the entropy of the crystalline C_{60}, one should know the value of $\Delta_{tr}H$ together with the heat capacity values, which rules out the use of $\Delta_{tr}H$ averaged over several published data. Therefore, we recommend the values [7] $T_{tr} = 260.7$ K and $\Delta_{tr}H = 7.46 \pm 0.15$ kJ mol^{-1} which are consistent with the heat capacity values recommended in the same publication.[7]

The heat capacities of C_{60} samples of different qualities measured by various methods are listed in Table 4. All the published results except for the data given in Refs 7, 37, 53 were presented only in a graphical form to show a fairly good agreement with each other (except for the data [37]). Thus, the recommended values of thermodynamic parameters for the solid C_{60} in the interval 0 – 1000 K (Table 5) were listed based on the heat capacities measured by AdC [7] in the range 5 – 340 K and by DSC [53] in the range 340 – 560 K. Because the Debye characteristic temperature of fullerenes is low, it is important to know their heat capacity below 5 K. Allowance is made in Table 5 for the heat capacities of C_{60} in the range 0 – 10 K which were measured by a thermal relaxation method (the graphical data [56]). We extended the heat capacity values to the interval 560 – 1000 K by a procedure described by Jin *et al.*[53] The heat capacity C_V of a crystal was represented by a sum of contributions of the lattice (C_{lat}) and intramolecular (C_{int}) vibrations

$$C_V = C_{lat} + C_{int} .$$

The contribution of the intramolecular vibrations was calculated by methods of statistical thermodynamics using the set of normal modes chosen as described in Section VI. The contribution of the lattice translational modes at $T > 298.15$ K was taken to be $3R$, whereas that of the librational modes (or molecular rotation in a crystal) was calculated for the hindered rotation of the C_{60} molecules using a harmonic potential. The effective value of the potential barrier to molecular rotation (5 kJ mol^{-1}) was chosen to provide the best fit of the calculated heat capacities with their measured values in the range 300 – 560 K. A relatively low value of the potential barrier is qualitatively consistent with both the spherical shape of the C_{60} molecule and the absence of heat capacity jump upon the solid-phase transition.[57]

Table 5. Recommended values of the thermodynamic parameters [C_P, S and $-(G-H_0)/T$ in J K^{-1} mol^{-1}; $H-H_0$ in kJ mol^{-1}] of the crystalline C_{60}.

T /K	C_P	S	$-(G-H_0)/T$	$H-H_0$
Vitreous crystal II				
0	0	4.9	4.9	0
5	2.37	5.7	5.1	0.0030
10	13.78	10.4	6.4	0.0399
20	33.41	26.9	12.4	0.2887
50	49.72	65.5	33.8	1.586
86.0	76.62	97.4	53.8	3.744
Crystal II				
86.0	76.62	97.4	53.8	3.744
100	96.60	110.6	60.8	4.974
150	185.5	165.4	86.2	11.88
200	303.3	234.5	114.3	24.04
250	423.1	315.1	146.3	42.20
260.7	446.8	333.3	153.6	46.85
Crystal I				
260.7	446.8	361.9	153.6	54.31
298.15	525.6	427.1	183.8	72.52
300	529.6	430.3	185.3	73.50
350	633.6	520.1	226.7	102.7
400	720.5	610.4	269.0	136.6
450	801.9	700.0	311.9	174.6
500	877.7	788.5	355.2	216.6
550	947.8	875.5	398.5	262.3
600	1009	960.6	441.8	311.3
650	1062	1044	485.0	363.1
700	1107	1124	527.7	417.3
750	1147	1202	570.1	473.7
800	1180	1277	611.9	531.9
850	1210	1349	653.2	591.6
860	1215	1363	661.4	603.8
900	1236	1419	693.8	652.8
950	1259	1487	733.8	715.2
1000	1281	1552	773.0	778.7

Table 6. The α and β parameters of the C_{60} fullerene.

T /K	$10^5\alpha$ /K^{-1}	$10^{10}\beta$ /Pa^{-1}	Method	Ref.
298	–	0.7	X-ray structural analysis	58
323 – 523	27 [a]	1.4 – 2.5 [a]	dilatometry of powder	59
298.15	–	1.47	dilatometry	60
260 – 300	4	–	capacitance dilatometry	48
298	6.2±0.2	–	X-ray structural analysis	61
298	3.5	0.70	calculation	62
300 – 900	4.57±0.04	–	X-ray structural analysis	63
298	–	1.5	the same	64

[a] A 3 : 1 mixture of C_{60} and C_{70}.

C_P was calculated from C_V by the relationship

$$C_P - C_V = \frac{\alpha^2}{\beta} V_m T,$$

where α is the volume expansion coefficient, β is the isothermal compressibility coefficient, V_m is the molar volume. The following values were accepted for α and β at 300 K: $\alpha = 4.6 \times 10^{-5}$ K^{-1}, $\beta = 1.55 \times 10^{-10}$ Pa^{-1} (Table 6). At this temperature, the difference $C_P - C_V$ was as low as 1.8 J K^{-1} mol^{-1}, which appeared to be much less than the value estimated by Jin *et al.*[53]. The difference $C_P - C_V$ was extended to $T = 1000$ K using the procedure described by the same authors

$$C_P - C_V = kC_V T, \quad (1)$$

the value of k (1.16×10^{-5} K^{-1}) was calculated from the data at 300 K.

The calculated heat capacities of the C_{60} crystal (Fig. 1) are in good agreement with those measured by DSC[53] in the interval 500 – 550 K, whereas at 300 K, they are 11 J K^{-1} mol^{-1} (or ~2%) less than the values measured by AdC.[7] We estimate the error of the entropy determination of C_{60} to be ±2 and ±13 J K^{-1} mol^{-1} at 298.15 and 860 K, respectively.

The Debye characteristic temperature of C_{60} estimated from the heat capacity measurements in the interval 0 – 5 K amounts to ~46 K, which is close to the value predicted based on the law of corresponding states with the inert gases (40 K).[5]

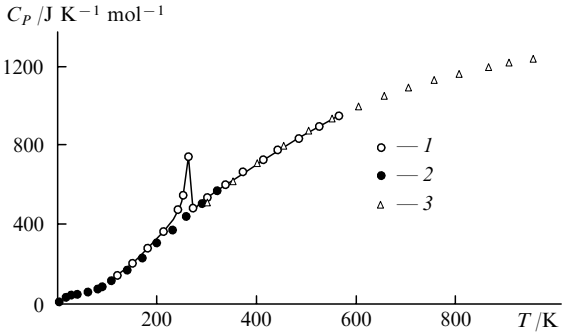


Figure 1. The heat capacity of the C_{60} fullerene *vs.* temperature. (*1*) the DSC data;[53] (*2*) the AdC smoothed data;[7] (*3*) our calculations.

In a recent paper,[13] the data reported on the heat capacity[65 – 67] and thermodynamics of phase transitions[12,68] in C_{70} were compared and commented. We are also aware of reports[69 – 72] the results of which require no revision.[13] The phase state of C_{70} fullerene is influenced by the sample prehistory.[73 – 79] A crystal I in the high-temperature phase characterised by an isotropic molecular rotation can form either a hexagonal or a face-centred lattice. With time, it transforms to a crystal having a face-centred lattice which however comprises 10% – 20% of a hexagonal phase. Upon cooling, the crystal I converts to the crystal II characterised by partially frozen rotational degrees of freedom and having either a rhombohedral or a distorted hexagonal ($c/a = 1.82$) structure with considerable admixture of hexagonal or rhombohedral phases, respectively. Upon further cooling, a monoclinic phase III arises which, unlike the low-temperature C_{60} fullerene crystal, does not undergo transition to the vitreous state. At increased pressure, the transition to the phase III splits into two phase transitions. Some researchers report that the double peak on the heat capacity curve is observed also at atmospheric pressure and explain this phenomenon by either a mixture of the crystal phases present in a sample or successively proceeding phase transitions. It might be suggested from the aforesaid that two modifications of the low-temperature monoclinic crystal are available and the residual entropy of C_{70} is not zero at 0 K. Unfortunately, the latter could not be estimated. Note that according to Ref. 13, the transformation of the crystal III to II (Table 7) is associated with one peak on the heat capacity curve.

We calculated the thermodynamic parameters of solid C_{70} in the range 0 – 340 K (Table 8) based on the heat capacities measured by AdC.[13] To our knowledge, the report[13] is the only one which gives the numerical values of heat capacities of C_{70} in this temperature range. In the range 340 – 560 K, we used the heat capacities measured by DSC.[13,65] The heat capacity of C_{70} was earlier extended to $T = 1000$ K (see Refs 26 and 65); we made an extension by a procedure identical to that for C_{60}. The contribution of intramolecular vibrations was calculated using the same set of frequencies as that accepted for the calculation of the thermodynamic properties in the ideal gas state (see Section VI). The translational contribution of the lattice heat capacity was accepted to be $3R$, the librational one was calculated for the hindered rotation of the C_{70} molecules using the harmonic potential. To give the calculated heat capacity the best fit to its measured values in the range 300 – 560 K, the effective potential barrier to molecular rotation was chosen to be 3 kJ mol^{-1}. The difference $C_P - C_V$ was estimated to be 2.6 J K^{-1} mol^{-1} at $T = 365$ K assuming $\alpha = 4.6 \times 10^{-5}$ K^{-1} and $\beta = 1.25 \times 10^{-10}$ Pa^{-1} (see Ref. 80). It was extended to a high-temperature region using Eqn (1). The value of k (9.44×10^{-6} K^{-1}) was calculated from the data at 365 K.

The calculated heat capacities of crystalline C_{70} (Fig. 2) are close to their experimental values at all the temperatures except for those around 400 K where they are 30 J K^{-1} mol^{-1} (~4%) larger than those measured by DSC.[65] In that region, the curve lies below the line connecting the adjacent regions, the reason being as yet unexplained. We estimate the error in the entropy determination of C_{70} to be ±3 and ±15 J K^{-1} mol^{-1} at 298.15 and 843.5 K, respectively.

Note that in the interval 100 – 1000 K, excluding the phase transition areas, the heat capacities per carbon atom of the C_{60}

Table 7. The thermodynamic characteristics of solid-state transitions in C_{70} (see Ref. 13).

T /K	$\Delta_{tr}H$ /kJ mol^{-1}	$\Delta_{tr}S$ J K^{-1} mol^{-1}	Note
29	0.0139	0.54	non-isothermal
38	0.0176	0.47	non-isothermal
277.4	3.22	11.6	cr. III → cr. II
340	2.7±0.4	8	cr. II → cr. I

Table 8. Recommended values of the thermodynamic parameters [C_P, S and $-(G-H_0)/T$ in J K^{-1} mol^{-1}; $H-H_0$ in kJ mol^{-1}] of crystalline C_{70}.

T/K	C_P	S	$-(G-H_0)/T$	$H-H_0$
Crystal III				
0	0	0	0	0
5	3.71	1.17	0.274	0.00448
10	16.46	7.44	2.109	0.0533
20	34.38	25.08	9.175	0.318
50	52.77	65.74	31.92	1.691
100	105.7	114.5	60.95	5.351
150	207.1	175.4	88.52	13.04
200	337.7	252.4	119.6	26.56
250	485.4	343.4	155.0	47.10
277.40	566.9	398.1	176.3	61.52
Crystal II				
277.40	566.9	409.7	176.3	64.74
298.15	625.6	452.7	194.0	77.12
300	630.7	456.6	195.6	78.28
340	727.0	541.7	231.3	105.5
Crystal I				
340	727.0	549.6	231.3	108.2
350	746.2	571.0	240.7	115.6
400	813.0	675.0	288.6	154.6
450	940.5	777.6	337.2	198.2
500	1040	882.3	386.5	247.9
550	1116	985.0	436.3	301.8
600	1186	1085	486.2	359.4
650	1247	1183	536.0	420.2
700	1300	1277	585.6	483.9
750	1346	1368	634.7	550.1
800	1386	1456	683.4	618.5
843.5	1417	1531	725.2	679.5
850	1421	1542	731.4	688.7
900	1451	1624	778.7	760.5
950	1478	1703	825.2	833.8
1000	1502	1779	871.0	908.3

and C_{70} fullerenes are similar to those of graphite, although these are markedly different in the molecular composition and the crystal structure. It is noteworthy that unlike most organic substances, the temperature dependence of the heat capacities of fullerenes exhibits two inflections, which are caused by low Debye temperatures ($\sim$46 K and $\sim$40 K for C_{60} and C_{70}, respectively) and low libration frequencies. When temperature increases from 0 to $\sim$30–50 K, both the Debye and librational contributions to the fullerene lattice heat capacity approach their limiting values $3R$, whereas the intramolecular contributions still remain small in this temperature range. In the range 30–50 K, the heat capacity remains relatively stable varying within 40–50 J K^{-1} mol^{-1} (close to $6R$), which indicates that the Debye and librational contributions to the heat capacity are saturated. For most of organic substances, such a saturation occurs at higher temperatures being masked by an increasing contribution of the intramolecular vibrations.

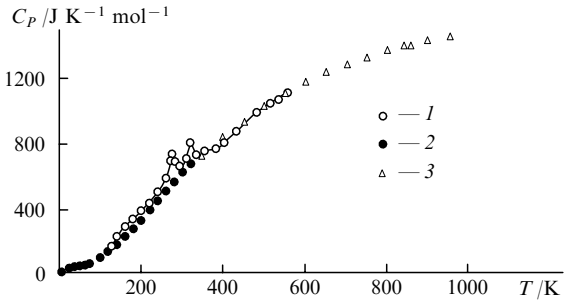


Figure 2. The heat capacity of the C_{70} fullerene *vs*. temperature; (*1*) the DSC data;[65] (*2*) the AdC smoothed data;[13] (*3*) our calculations.

Various computational approaches, from the Debye models with adjustable parameters[22,56] to those based on the examination[81,67] and integration[53,82] of phonon spectra of crystals may give a key to a more comprehensive interpretation of the heat capacities of fullerenes in the condensed state. Both theoretical[83–87] and experimental[88,89] data on the fullerene lattice vibrations can be found in the literature.

V. Saturated vapour pressures and enthalpies of sublimation of fullerenes

The results of a recent extensive study by Piacente *et al.*[24] gave the saturated vapour pressure (P) and the enthalpy of sublimation of C_{60} measured by the Knudsen method, which is one of the most precise methods for measuring low vapour pressures. The problems of sample purity and stability (see Section II) were closely examined, and earlier publications[23,25,90–96] were surveyed.[24] We are also aware of other reports.[97–103] Most of the results are merely consistent with those by Piacente *et al.*[24] in order of magnitude. The methods of measurement and preparatory procedures described[24] suggest that the following values of saturated vapour pressure and enthalpy of sublimation are most reliable:

$$\ln P(\text{kPa}) = (19.07\pm0.46) - (21\,078\pm350)/T \quad (T = 730-990\ \text{K}),$$

$$\Delta_{\text{sub}}H_{860} = 175.3\pm2.9\ \text{kJ mol}^{-1}.$$

It follows from these values and the data listed in Table 5 that at $T = 860$ K and $P = 1$ bar, the experimental magnitude of entropy of C_{60} in the gaseous state amounts to $S_{860}(\text{g}) = 1481\pm14$ J K^{-1} mol^{-1}. With the heat capacity of the crystal (see Section IV) and the results of statistical calculations of the heat capacity of a gas (see Section VI) taken into account, the enthalpy of sublimation of C_{60} at $T = 298.15$ K was recalculated:

$$\Delta_{\text{sub}}H^\circ = 183.7\pm5.1\ \text{kJ mol}^{-1}.$$

The saturated vapour pressure and enthalpy of sublimation of C_{70} were determined by Piacente *et al.* in their extended research.[26] In addition to the reports[25,92–94,104] discussed in Ref. 26, we are also aware of other publications (Refs 101 and 105). The values

$$\ln P(\text{kPa}) = (19.30\pm0.35) - (22\,835\pm370)/T \quad (T = 783-904\ \text{K}),$$

$$\Delta_{\text{sub}}H_{843.5} = 189.9\pm3.1\ \text{kJ mol}^{-1},$$

determined for the freshly sublimed C_{70} sample[26] are recommended as most reliable by the same reasoning as those for C_{60}.

Based on these values and the data listed in Table 8, one can deduce that the experimental value of the entropy of C_{70} in the gaseous state amounts to $S_{843.5}(\text{g}) = 1653\pm16$ J K^{-1} mol^{-1} at $T = 843.5$ K and $P = 1$ bar. With the crystal heat capacity (see Section IV) and the results of statistical calculations of the heat capacity of a gas (see Section VI) taken into account, the enthalpy of sublimation of C_{70} at $T = 298.15$ K was recalculated to be

$$\Delta_{\text{sub}}H^\circ = 200.3\pm6.1\ \text{kJ mol}^{-1}.$$

VI. Thermodynamic properties of C_{60} and C_{70} in the ideal gas state

Thermodynamic properties of fullerenes in the gaseous state were calculated by the methods of statistical thermodynamics.[6,24,26] All the calculated entropy values of C_{60} appeared to be lower than the experimental ones (see Section V). In our opinion, the most reasonable set of frequencies of normal modes was used by

Piacente *et al.*[24] They averaged the values measured using IR [106] and Raman spectroscopy,[107–109] inelastic neutron scattering [110, 111] and those derived from the calculations of the normal modes.[112] It appeared that the statistical calculation carried out using the average frequencies of normal modes gives the entropy of gaseous C_{60} which is closest to its experimental value. Schettino *et al.*[106] gave also a short survey of the spectroscopy and assignment of the C_{60} vibration frequencies. Later, other reviews on IR spectroscopy of fullerenes [113] and assignment of the C_{60} vibration frequencies [114–121] were published. To our knowledge, no contradictions exist at present as to the interpretation of the C_{60} molecular vibration frequencies.

In the present review, the thermodynamic parameters of fullerenes in the ideal gas state were calculated as described by Frenkel *et al.*[122] The translational contributions of C_{60} and C_{70} were calculated using their molecular masses equal to 720.66 and 840.77, respectively. In the calculation of rotational contributions, the symmetry numbers 60 and 10 and the products of the principal moments of inertia ($I_A I_B I_C$) equal to 1.00×10^{-129} and 2.50×10^{-129} kg^3 m^6 were used for C_{60} and C_{70}, respectively. The two latter values were calculated by the models fairly consistent with the X-ray structural results [123] (for C_{60}) and the electron diffraction data [124] (for C_{70}). The scatter in the entropy values of C_{60} in the gaseous state does not exceed 0.2 J K^{-1} mol^{-1}, although different estimates of the moments of inertia are available in different publications. The frequencies of normal modes of C_{60} (Table 9) were averaged over the measured values.[106] The contribution of the excited electronic states (assuming that all the remaining contributions are independent on the electronic state of molecules) was estimated from the relative energies of one-electron states (Table 10). According to the model used, the contribution of the excited electronic states to the heat capacity of C_{60} at temperatures above 3000 K amounts to 5 J K^{-1} mol^{-1}, whereas a similar contribution to the entropy is reached at 4500 K. The calculated value of S°_{860} (1463.8 J K^{-1} mol^{-1}, Table 11) is 17 J K^{-1} mol^{-1} smaller than that determined experimentally (1481±14 J K^{-1} mol^{-1}). Therefore, 17 J K^{-1} mol^{-1} can be considered as the error in calculation of the entropy of C_{60} in the gaseous state. This comprises ~1.5% of the vibrational contribution to the entropy, as in the case of the cage hydrocarbons $C_{11}H_{14}$ and $C_{14}H_{16}$ with rigid carbon skeletons.[129, 130] To make both the entropy of fullerenes in the gaseous state and the heat capacity of a crystal (see Section IV) consistent with the experimental data, we examined a possibility to revise the C_{60} vibration frequencies. In order for the calculated entropy of C_{60} in the gaseous state to be equal to its measured value, one has to reduce the wave numbers hence breaking the agreement of the calculated heat capacity of a crystal with the experiment. Therefore, the agreement currently available between the thermodynamic and molecular data on the C_{60} fullerenes seems to be the best at present.

Table 9. The frequencies of the C_{60} normal modes used in statistical calculations.

Type	Degeneracy	Wave number /cm^{-1}
A_g	1	491, 1458
H_g	5	266, 429, 710, 768, 1095, 1254, 1437, 1570
T_{1g}	3	565, 850, 1289
T_{2g}	3	535, 764, 805, 1334
G_g	4	484, 570, 738, 1135, 1314, 1515
A_u	1	973
T_{1u}	3	527, 578, 1184, 1439
T_{2u}	3	355, 714, 1040, 1187, 1565
H_u	5	403, 486, 669, 740, 1211, 1342, 1530
G_u	4	344, 760, 771, 967, 1321, 1415

Table 10. The low-lying excited electronic states of the C_{60} molecule.

Type	Energy /eV				Degeneracy
	I	II	III	IV	
$1\,^1T_{2g}$	2.58	2.29	1.88	1.88	3
$1\,^1T_{1g}$	2.61	2.33		2.33	3
$1\,^1G_g$	2.70	2.34		2.34	4
$1\,^1T_{2u}$	2.89	2.76		2.76	3
$1\,^1H_u$	3.15	3.01		3.01	5
$1\,^1H_g$	3.15	2.65		2.65	5
$1\,^1G_u$	3.21	3.11		3.11	4
$2\,^1H_u$	3.89	3.70		3.70	5
$2\,^1G_u$	3.90	3.38		3.38	4
$1\,^1T_{1u}$	4.08	3.36		3.36	3
$2\,^1T_{2u}$	4.12			4.12	3
$3\,^1G_u$	4.37			4.37	4
$3\,^1H_u$	4.39			4.39	5
$2\,^1T_{2g}$	4.41			4.41	3
$2\,^1T_{1u}$	4.51	4.00		4.00	3
$3\,^1T_{1u}$	6.19	4.26		4.26	3
$1\,^3T_{2g}$	2.06		1.6	1.60	3
$1\,^3T_{1g}$	2.40			2.40	3
$1\,^3G_u$	2.58			2.58	4
$1\,^3H_g$	2.59			2.59	5
$1\,^3T_{2u}$	2.59			2.59	3
$1\,^3T_{1u}$	2.61			2.61	3
$1\,^3G_g$	2.66			2.66	4
$1\,^3H_u$	2.98			2.98	5
$2\,^3T_{2u}$	3.66			3.66	3
$2\,^3H_u$	3.81			3.81	5
$2\,^3G_u$	3.84			3.84	4
$2\,^3G_g$	4.26			4.26	4
$2\,^3H_g$	4.28			4.28	5
$3\,^3G_u$	4.29			4.29	4
$2\,^3T_{2g}$	4.32			4.32	3
$3\,^3H_u$	4.32			4.32	5
$3\,^3T_{1u}$	4.34			4.34	3

Note. I, see Ref. 125; II, see Ref. 126; III, see Refs 127 and 128; IV, the energies used in the calculations of contributions of the excited electronic states to the thermodynamic parameters (Table 11).

The set of frequencies of the C_{70} normal modes (Table 12) was obtained by averaging the experimental values (the IR [114, 131, 132] and Raman [114, 131] spectroscopic data) based on the reported frequency assignment [133, 134] (see Ref. 26). The report [133] was followed by publication of the data [113] on IR spectroscopy of fullerenes and assignments of frequencies of the C_{70} normal modes [115, 117, 118, 121] which require no revision.[133, 134]

The calculated value of $S^\circ_{843.5}$ (1669.2 J K^{-1} mol^{-1}) is 16 J K^{-1} mol^{-1} larger than the experimental one (1653±16 J K^{-1} mol^{-1}). This difference can be considered as the uncertainty in the calculated entropy of C_{70} in the gaseous state. Unfortunately, we have no information on a reasonably complete set of the excited electronic state energies for the C_{70} molecule. The experiments [127, 135] provide evidence that the low-lying electronically excited states are expected to have slightly lower energies than those of C_{60}. Nevertheless, it is believed that only at temperatures above 3000 K does the neglect of the excited electronic state contributions increase significantly the error in the calculation of the entropy of C_{70} in the gaseous state.

Table 11. The thermodynamic properties of the C_{60} and C_{70} fullerenes [S°, C_P°, $(H-H_0)/T$ and $-(G-H_0)/T$ in J K^{-1} mol^{-1}; $\Delta_f H^\circ$ and $\Delta_f G^\circ$ in kJ mol^{-1}] in the ideal gas state at 101 325 Pa.

T/K	S°	C_P°	$\frac{H-H_0}{T}$	$-\frac{G-H_0}{T}$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
Fullerene C_{60}						
0	0	0	0	0	2534.6	2538.6
50	254.7	34.8	33.4	221.2	2535.8	2527.8
100	286.9	72.3	41.0	245.9	2535.2	2516.2
150	331.6	160.2	65.1	266.6	2533.6	2505.0
200	392.7	272.0	102.6	290.2	2532.0	2494.4
273.15	502.8	442.3	170.8	331.9	2530.4	2479.5
298.15	543.9	498.5	196.0	348.0	2530.0	2474.5
300	547.0	502.6	197.8	349.2	2530.0	2474.2
400	720.4	706.3	300.3	420.1	2529.4	2454.3
500	896.4	870.2	398.6	497.8	2528.9	2434.6
600	1066.7	996.1	488.1	578.6	2527.8	2415.0
700	1227.8	1091.3	567.8	659.9	2526.1	2395.7
800	1378.4	1163.3	638.0	740.4	2523.7	2376.6
860	1463.8	1198.0	675.9	787.9	2522.0	2365.3
900	1518.7	1218.3	699.5	819.2	2520.8	2357.9
1000	1649.4	1260.9	753.6	895.8	2517.5	2339.6
1100	1771.2	1294.3	801.3	969.9	2513.7	2321.6
1200	1885.0	1320.9	843.6	1041.5	2509.4	2304.0
1300	1991.6	1342.3	881.1	1110.5	2505.0	2287.0
1400	2091.7	1359.8	914.7	1177.0	2499.4	2269.5
1500	2186.1	1374.2	944.9	1241.2	2493.5	2252.8
1750	2400.0	1400.9	1008.3	1391.8	2477.1	2214.0
2000	2588.4	1418.9	1058.5	1529.8	2456.7	2176.9
2500	2907.6	1441.5	1133.1	1774.6	2406.5	2110.7
3000	3171.8	1456.2	1185.8	1986.1	2350.4	2058.1
3500	3397.2	1468.8	1225.3	2171.9	2266.0	2008.3
4000	3594.2	1481.3	1256.5	2337.7	2172.9	1968.1
4500	3769.4	1493.6	1282.2	2487.2	2086.0	1964.7
5000	3927.3	1504.2	1303.9	2623.4	1970.0	1943.1
Fullerene C_{70}						
0	0	0	0	0	2760.4	2760.4
50	275.6	36.4	33.7	241.9	2761.5	2748.6
100	312.5	86.2	44.9	267.6	2760.8	2736.2
150	365.4	188.3	74.5	290.8	2759.0	2724.3
200	436.9	317.7	118.8	318.1	2757.2	2712.9
273.15	565.6	518.3	199.0	366.6	2755.3	2697.1
298.15	613.9	585.1	228.5	385.3	2755.0	2691.8
300	617.5	589.9	230.8	386.7	2755.0	2691.4
400	821.4	831.9	351.7	469.7	2754.9	2670.3
500	1028.7	1025.4	467.9	560.8	2755.3	2649.1
600	1229.4	1172.8	573.7	655.7	2755.0	2627.8
700	1418.9	1283.5	667.6	751.3	2754.0	2606.7
800	1596.0	1366.9	750.0	845.9	2752.3	2585.8
843.5	1669.1	1396.6	782.6	886.5	2751.3	2576.8
900	1760.8	1430.4	822.3	938.5	2749.8	2565.1
1000	1914.1	1479.3	885.6	1028.5	2746.8	2544.8
1100	2057.0	1517.7	941.4	1115.6	2743.2	2524.7
1200	2190.4	1548.1	990.7	1199.7	2739.0	2505.1
1300	2315.3	1572.6	1034.6	1280.7	2734.4	2486.2
1400	2432.6	1592.6	1073.8	1358.9	2728.6	2466.5
1500	2543.1	1609.1	1108.9	1434.2	2722.3	2447.8
1750	2793.6	1639.4	1182.7	1610.9	2704.5	2404.2
2000	3013.9	1659.7	1241.1	1772.8	2681.8	2362.5
2500	3387.2	1684.2	1327.6	2059.6	2625.1	2287.9
3000	3695.5	1697.8	1388.2	2307.3	2560.0	2229.0
3500	3957.9	1706.1	1433.1	2524.8	2459.5	2173.6
4000	4186.1	1711.5	1467.6	2718.5	2344.9	2129.7
4500	4387.9	1715.2	1494.9	2893.0	2232.6	2130.0
5000	4568.8	1717.9	1517.1	3051.7	2081.1	2110.4

Table 12. The frequencies of the C_{70} normal modes used in statistical calculations.

Type	Degeneracy	Wave number /cm^{-1}
A_1'	1	258, 357, 457, 573, 678, 728, 1061, 1175, 1189, 1363, 1433, 1522
A_2'	1	501, 550, 651, 742, 817, 958, 1208, 1325, 1432
E_1'	2	310, 341, 424, 509, 535, 578, 642, 683, 750, 792, 820, 904, 1073, 1135, 1222, 1254, 1280, 1318, 1384, 1454, 1569
E_2'	2	227, 305, 426, 491, 519, 643, 697, 711, 728, 765, 785, 792, 933, 1069, 1164, 1224, 1280, 1314, 1336, 1452, 1496, 1570
A_1''	1	333, 545, 612, 768, 807, 917, 1223, 1322, 1536
A_2''	1	322, 458, 566, 716, 843, 1099, 1179, 1292, 1414, 1501
E_1''	2	232, 409, 479, 505, 537, 665, 703, 739, 771, 793, 1050, 1088, 1186, 1259, 1298, 1332, 1377, 1470, 1515
E_2''	2	300, 384, 471, 588, 641, 690, 738, 748, 780, 800, 988, 1062, 1143, 1231, 1301, 1328, 1384, 1442, 1500, 1548

VII. Conclusion

Based on the analysis of the published data, the values of the most important thermodynamic parameters are recommended for the C_{60} and C_{70} fullerenes in the crystalline state in the temperature range 0–1000 K and in the gaseous state in the range 100–5000 K. We believe that their further refinement will be made within the limits of error outlined in the present review.

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