THERMODYNAMIC PROPERTIES OF THE NEW CARBON STRUCTURES

Litvinenko V.F.
Frantsevith Institute for Problems of Materials Science of NAS of Ukraine,
3, Krzhizhanovsky Str., Kiev, 03142, Ukraine; *E-mail: bas@materials.kiev.ua*

New carbon structures (carbyne, fullerenes, nanotubes, etc.) discovered at the end of XX century have unique properties and are perspective for practical application. Comprehensive investigations of such various structures formed by the same chemical element, promote the development of new methods of structure and properties of a solid prediction. The urgency and importance of knowledge of fundamental thermodynamic properties of such substances is difficult to overestimate.

On the present paper on the basis of the analysis of the literature data on calorimetric investigations of C_{60}, C_{70} fullerenes in solid and gas states as well as C_{60} polymeric forms and linear polymer of carbon – carbyne, the most reliable values of thermodynamic properties have been selected and their basic thermodynamic functions at temperatures above 298 K have been calculated as polinomials. Peculiarities of heat capacity temperature dependences and other properties of mentioned above carbon forms have been discussed.

Thermodynamic properties of C_{60} and C_{70} fullerenes have been intensively investigated since 90 th years when the method of reception and secretion separate fullerenes in amounts sufficient for various investigations including calorimetric experiments was developed. Obtaining and identification of chemically pure, structurally homogeneous, single-phase preparations is still an important problem of the reliable thermodynamic data definition. Oblique attributes of purity calorimetric specimens are phase transformation characteristics and residue quantity after sublimation. Among methods of calorimetry adiabatic one is considered to be the most precise (measurement error of heat capacity is 1,5 - 3 % at helium, 0,2 - 0,4 % at nitrogen and room temperatures). Heat capacity of substance in gaseousness is determined with high precision by calculation methods on the basis of the spectroscopical data.

Generalization of investigations of fullerenes thermodynamic properties up to 1998 - 1999 and the necessary references are represented in surveys [1, 2]. Heat capacity of C_{60} solid fullerene (fullerite) specimens was widely examined in temperature range of 0,5 - 800 K. The results are shown for the most part as graphic charts. In all investigations $C_p(T)$ values are conformed far off phase transformation temperatures, except one or two. 3 modifications of C_{60} are rather clearly shown: glassy phase at $T < 86{,}0$ K, simple cubic at $86{,}0\ K < T < 260{,}7$ K, face-centered cubic at $T > 260{,}7$ K. Temperatures and enthalpies of C_{60} and C_{70} fullerenes transformations considerably differ in different works.

The investigations of heat capacity of C_{70} solid fullerene have been carried out less widely (~10 works). C_{70} phase state is strongly influenced with obtaining procedures, purification and storage. Temperature ranges of transformations in C_{70} and their enthalpies sufficiently differ in other works, which is connected with specimens purity and C_{70} polymorphism.

Enthalpies of formation of C_{60} and C_{70} solid fullerenes have been obtained from calorimetricly measured enthalpies of combustion of specimens in oxygen.

C_{60} and C_{70} calorimetric properties in ideal gas state have been calculated [1] by statistical thermodynamics method, using both sets of normal atom oscillations in C_{60} and C_{70} molecules and contributions of translational and rotary motions of molecules. In case of C_{60} the contribution of excited electronic states was taken into account as well.

Under pressure (up to 10 GPa) and temperature (up to 1000 K) the process of crystalline fullerene polymerization takes place. Different structures are being formed: dimer (cubic) $(C_{60})_2$, quasione-dimensional 1D (rombic), quasi-bidimensional 2D (rhombohedral and tetragonal). Heat capacity of C_{60} polymeric structures has been examined in simple investigations at temperatures of 4-350 K. At temperature increasing heat capacity of explored polymeric structures smoothly rises, herein phase transformations aren't observed. At temperatures higher then 298 K heat capacity of C_{60} and its polymeric structures, C_{70} solid fullerenes and graphite get rather close (Fig. 1).

Heat capacity at 80-300 K temperature range and standard enthalpy carbyne formation have been examined on sets of 9 and 4 nonsingle-phase and insufficiently full certificated specimens. Not strictly proved, the preference has been given to one sample values in each investigation: the highest on heat capacity and the lowest on enthalpy of

formation. Obtained negative enthalpy of formation value of carbyne proves that it is thermodynamicaly more stuble than graphite. Other proves of this statement are unknown to us. Thermodynamic properties of carbyne need further investigating.

Analytical representation of reduced Gibbs energy and other interdependent thermodynamic functions (Table) for C_{60} and C_{70} in crystalline and gas states, and $(C_{60})_2$, 1D-C_{60}, 2D$_R$-C_{60} (rhombohedral) and 2D$_T$-C_{60} (tetragonal) polymeric structures have been found on the basis of the most reliable values of standard entropy, enthalpy, heat capacity and heat capacities at temperatures higher then 298 K.

Background of knowledge of heat capacity, other physical properties fullerenes under consideration allows to make the understanding of energy distribution, microdynamic of these substances deeper.

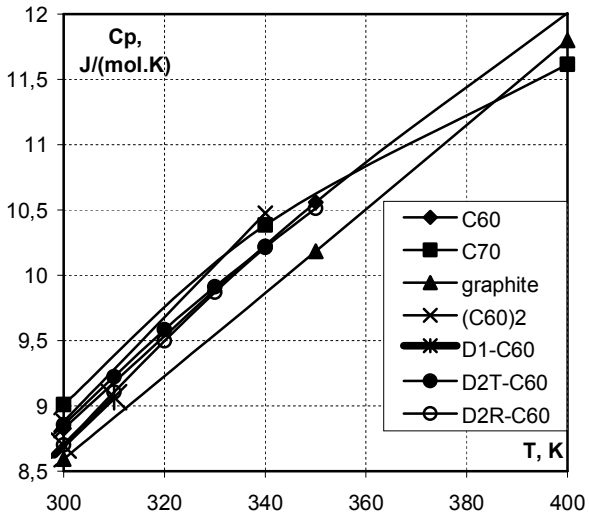

Fig. 1. Heat capacity of various fullerenes and graphite.

The table

Coefficients of reduced Gibbs energy $\Phi^*(T)$, heat capacity (J/(mole.K)) of fullerenes:

$\Phi^*(T) = \varphi_1 + \varphi_2 \ln x + \varphi_3 x^{-2} + \varphi_4 x^{-1} + \varphi_5 x + \varphi_6 x^2 + \varphi_7 x^3$,

$C_p(T) = \varphi_2 + 2\varphi_3 x^{-2} + 2\varphi_5 x + 6\varphi_6 x^2 + 12\varphi_7 x^3$, where $x = 10^{-4} T$.

Фуллерен	T, K	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6	φ_7
C_{60}(к)	298-600 600-1000	5598,28 -1793,93	1674,5 -437,384	-0,175649 -0,28719	39,3415 -3,14596	-27464 21081,7	204635 -61240	-652963 98516,5
C_{60}(г)	298-1000 1000-5000	-1743,44 3399,63	-475,772 1433,12	0,006235 -0,960144	-477942 88,1514	20919,2 111,93	-59399 -68,337	92981 46,6893
C_{70}(к)	298-340 340-400 400-1000 1000-6000	-15154,8 2103,64 1642,43 3736,68	-4200,36 883,251 741,637 1502,33	0,262944 -0,216472 -0,301307 0	-76,3869 37,2669 38,7989 59,3839	108413 530,95 6627,83 0	-418855 -45053 -8410,3 0	12372,1 39589 0 0
C_{70}(г)	298-1000 1000-5000	-504,372 931,782	-135,451 392,606	0,001298 -0,24947	-1,30484 23,6663	5952,34 68,531	-17098 -54,645	27019 22,325
$(C_{60})_2$(к)	298-340	-511581	-133739	6,18689	-2034	4393610	-3590.10^4	1568.10^5
1D-C_{60}	298-350	-121582	-31526,5	1,36476	-464,334	1068110	-88647	3950.10^4
2D$_T$-C_{60}	298-340	279895	73035,9	-3,31639	1102,4	-24132	2005.10^4	8839.10^4
2D$_R$-C_{60}	298-350	51034,5	13143,2	-0,54017	188,64	-456831	4116390	-1926.10^4

In solid C_{60} low-energy modes, connected with intermolecular interactions, and the high-energy modes, caused by intramolecular interactions are clealy separated. In solid C_{70} corresponding strips close.

At an increase of temperature higher than 100 K intensive magnification of heat capacity caused by filling of the high-energy phonon levels, connected with oscillations of carbon atoms in fullerene molecules is observed. $C_p(T)$ gaps with almost linear dependences bring in evidence of existence of corresponding sections with equal density of states in phonon spectrum.

References

1. Dikiy V.V., Kabo G.Y. Thermodynamic properties of C_{60} and C_{70} fullerenes // Chemistry Successes - 2000. - 69, №2. – pp. 107-117.
2. Lebedev B.V. Thermodynamic properties of fullerenes and their derivatives // Phys. Chem. J. - 2001. - 75, №5. – pp. 775-793.