Reviews

Thermodynamics of carbyne

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Published data on the thermodynamic properties of carbyne are analyzed and generalized. The thermodynamic properties of carbyne are compared with the properties of other allotropic modifications of carbon (fullerenes, diamonds, and graphite).

Key words: carbyne, heat capacity, enthalpy of formation, calorimetry, allotropic modifications of carbon, fullerenes, diamonds, graphite.

Carbyne is one of the allotropic modifications of carbon known to date. Having been discovered more than thirty years ago,[1–3] it still remains the object of various scientific and applied studies.[4,5] The unflagging interest in carbyne is caused by the great potential for its practical application.[6] This is due to the unique electronic structure of the linear macromolecules of carbyne, in which sp-hybridized carbon atoms are linked by σ- and π-bonds.[5,7] This is considered to be the reason for the semiconductor properties[8] and photoconductivity of carbyne,[9] high inertness against oxidants,[10] and the ability to be converted into diamond at high pressures and temperatures without any catalysts.[11] Defect-free filament crystals of carbyne should possess the highest tensile strength among all known filament materials.[12] Carbyne has demonstrated exceptionally useful properties as a material for medicine,[13] namely, the absence of toxicity, high biological compatibility, resistance to thrombosis, *etc.*

Polymeric molecules of carbyne are known to exist in two forms,[2,5,14] the polyyne $-C{\equiv}C-C{\equiv}C-$ (α-form or α-carbyne) and the cumulene $-C{=}C{=}C{=}C-$ (β-form or β-carbyne). β-Carbyne has a higher density than α-carbyne.[2] At a pressure of $9 \cdot 10^6$ kPa and $T = 2100$ K, the α-form undergoes a spontaneous solid-phase transition into the β-form. The enthalpies of formation of gaseous α- and β-carbynes from crystalline graphite (elemental carbon) at 298.15 K and standard pressure have been calculated[15] by a published procedure.[16] The enthalpy of formation of β-carbyne was found to be 32 kJ mol^{-1} greater than the corresponding value for α-carbyne. This means that, under the specified conditions, the hypothetical process of transformation of α-carbyne into β-carbyne in the gas phase would be accompanied by absorption of 32 kJ mol^{-1}.

The structure of the carbyne forms of carbon has been discussed previously.[3,17] Crystalline carbynes consist of carbon chains packed in crystals due to van der Waals forces. Both the polyyne (α-form) and polycumulene (β-form) chains are assumed to be linear in ideal structures. Figure 1, *a* and *b* shows schematically the structural models of the α- and β-carbyne molecules.[5] When the intermolecular valence bonds (cross-links) between chains are totally missing, carbyne should form an ideal crystal structure.[1,18] In order to confirm that carbyne does exist in this form, its single crystals should be obtained in an amount sufficient for comprehensive (including calorimetric) studies; however, this

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has not been done so far.[3,5] Carbon chains in real specimens are cross-linked by additional C—C bonds to some extent; the cross-links are arranged with a certain frequency and periodicity.[17,19] Therefore, the carbyne forms of carbon existing in reality are partially cross-linked three-dimensional crystalline or amorphous polymers in which extended fragments of linearly polymerized carbon predominate.[20] Figure 1, *a'* and *b'* shows the schemes of cross-linked macromolecules of α- and β-carbynes (each shows one cross-link of several possible variants). For example, the resonance Raman spectra of polyyne indicate that the chains are one-dimensional and the bonds alternate; a chain comprises 30±20 C≡C bonds.[21] When the linear carbon polymer chains are connected by valence cross-links, the carbon chains can be nonparallel. Previously,[22] a zigzag model for the structure of carbon chains of α- and β-carbynes has been proposed; according to this model, linear chain sections alternate with regular breaks. No rupture of chemical bonds takes place at the break points of polyyne chains, whereas in the structure of β-carbyne, unsaturated bonds are formed and cross-links between neighboring chains arise relatively easily. In particular, this model can account for the ease of transformation of β-carbyne into ultradispersed diamond.[5,11,23] The crystal structure of carbyne and differentiation of the unit cell in its structure have been discussed previously.[24]

The samples obtained by the conventional methods for the synthesis of carbyne (oxidative dehydropolycondendation of acetylene[3,25] or dehydrochlorination of polyvinylidene chloride[26] followed by evacuation of the reaction products at ~1300 K) contain mixtures of α- and β-carbyne crystals and amorphous α- and β-carbyne forms; the amorphous phase predominates.[25,27] The content of carbon in the product of carbyne synthesis is ~99.9%. The content of the crystalline material can be increased by keeping the samples at high pressure and at elevated temperatures.[3,14] Under these conditions, the carbon chains become cross-linked[17,27]; the number of cross-links cannot be easily controlled. In some cases, this number seems to be small; when such carbyne samples are used for investigations, the thermophysical characteristics thus determined correspond most closely to those of ideal carbynes.[28]

The temperature dependence of the heat capacity of carbyne can be studied using either amorphous or partially crystalline carbyne because the heat capacities of inorganic and organic chain polymers are known to be virtually independent of whether they occur in the vitreous, partially crystalline (at a temperature below the vitrification temperature), or crystalline state.[29] The differences in the C_p° values do not exceed the experimental error (~0.2% in the range of 40—340 K).

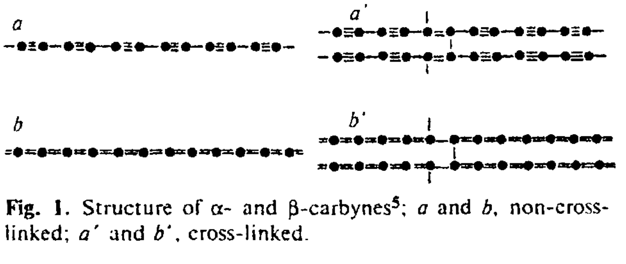

Fig. 1. Structure of α- and β-carbynes[5]; *a* and *b*, non-cross-linked; *a'* and *b'*, cross-linked.

The number of intermolecular cross-links in carbyne can also be estimated with a sufficient degree of reliability from the pattern of the temperature dependence of heat capacity. Virtually all the organic and inorganic linear polymers studied to date are characterized, irrespective of the composition and structure of the repeating monomeric units, by the presence of a broad temperature range in which the heat capacity C_p° varies linearly with temperature. This pattern of variation normally manifests itself in the range from 50—60 K up to the vitrification temperature for vitreous and partially crystalline polymers or up to the melting temperature for crystalline polymers.[29,30] The appearance of cross-links results in deflection of the heat capacity of chain polymers from the linear $C_p^\circ(T)$ dependence toward a higher exponent of temperature. In the case where the polymer structure has completely changed from a chain to a three-dimensional structure, the variation of C_p° *vs.* T becomes proportional to T^3.

The above empirical dependences are substantiated in terms of the Tarasov theory of heat capacity for solids with chain or layer structures[31] or a chain-layer structure.[32] When deriving the corresponding relations for the temperature dependence of heat capacity, the researchers[31,32] used the continual approach, by analogy with the Debye approach.[33] Chain and layer structures were treated as one- and two-dimensional continua, respectively. Debye has regarded objects with a three-dimensional structure as three-dimensional continua[33]; Tarasov considered that the greater part of eigen modes belongs to the layers and chains. Having omitted the details of derivation of the heat capacity function for chain structures with allowance for chain—chain interactions, stated in detail previously,[31,32] we present here the final expression

$$C_{1,3} = D_1\left(\frac{\theta_1}{T}\right) - \frac{\theta_3}{\theta_1}\left[D_1\left(\frac{\theta_3}{T}\right) - D_3\left(\frac{\theta_3}{T}\right)\right], \qquad (1)$$

where $C_{1,3}$ is the heat capacity of chain-structured objects (this is denoted by subscript "1") with allowance for chain—chain interaction (subscript "3"); D_1 and D_3 are the Tarasov and Debye heat capacity functions, respectively (the form of functions D_1 and D_3 is given, for example, in Ref. 31); $\theta_1 = h\nu_{max}/k$ and $\theta_3 = h\nu_1/k$ are the Tarasov and Debye characteristic temperatures; ν_{max} is the characteristic frequency; and ν_1 is the limiting frequency for the vibrations of a chain unit in the force field created by the surrounded chains.

The θ_3/θ_1 ratio is the chain—chain interaction parameter, which can vary from 0 to 1. When $\theta_3/\theta_1 = 0$, no interaction between the chains is involved (this is apparently a purely hypothetical case), while $\theta_3/\theta_1 = 1$ is the value typical of three-dimensional structures.

Analysis of the variation of $C_{1,3}$ *vs* T (Eq. (1))[31] shows that at the lowest temperatures ($T \ll \theta_{1,3}$, where

$\theta_{1,3} = \theta_1^{1/3} \cdot \theta_3^{2/3}$), $C_{1,3}$ is proportional to T^3. As the temperature increases, this pattern of variation switches to a linear $C_{1,3}(T)$ dependence for chain structures with relatively weak chain—chain interactions. As the θ_3/θ_1 ratio increases (the interaction between the chains is enhanced) in the same temperature range, the variation of heat capacity *vs* T can change from a linear dependence to one proportional to T^3. Further increase in the temperature results in the classical heat capacity value, stipulated by the Dulong and Petit law, irrespective of θ_3/θ_1. Thus, for most chain structures, the $C_p^\circ(T)$ dependence should be linear in a wide temperature range (from several tens to hundreds of degrees); as noted above, this is confirmed by analysis of the experimental data on C_p° for linear polymers.[30,34]

In this work, we consider published data on the thermodynamic properties of carbyne and compare them with the corresponding properties of other allotropic modifications of carbon (C_{60} and C_{70} fullerenes, graphite, and diamond).

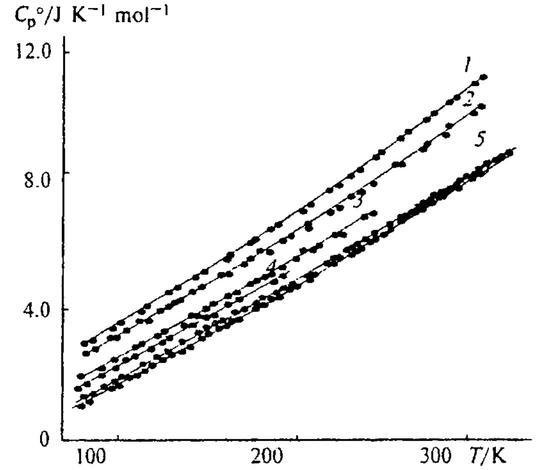

Fig. 2. Temperature dependence of the heat capacity of carbyne samples: (*1*) Cn-7; (*2*) Cn-6; (*3*) Cn-5; (*4*) Cn-4; (*5*) "Saratovskaya" acetylene black; (*6*) C-3 graphite[35] (the laboratory designations for the carbyne samples are given).

Heat capacity and thermodynamic functions

The temperature dependences of the heat capacity C_p° of the carbyne samples prepared in nine different experiments were measured[35] in the range of 80—300 K. The samples were synthesized by Yu. P. Kudryavtsev (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) using the known procedure.[36] Acetylene was passed into a heated solution of Cu_2Cl_2 in a methanol—pyridine mixture. The resulting black precipitate, which was a mixture of polyynes and copper acetylenides, was oxidized by an aqueous solution of $K_3Fe(CN)_6$ with heating. The product was treated successively with hot hydrochloric acid (for dissolution of CuO), ammonia, and water until the wash water became colorless. Then the solid residue was dried and annealed *in vacuo* for a long period with continuous evacuation and gradual increase in temperature to ~1300 K. The carbyne thus formed was a fine-grain somewhat hygroscopic black powder, which was stored in evacuated sealed glass tubes. The samples contained 99.0 to 99.5% (w/w) carbon, ~0.1% hydrogen, and traces of copper; they produced no ash upon combustion. It was shown that carbyne samples thus obtained were mainly amorphous and consisted of both polyyne and cumulene macromolecules; the polyyne structures predominated. They contained only small amounts of α- and β-carbyne crystals.

The heat capacity was measured using an adiabatic vacuum calorimeter, whose design, together with the operation procedure and the results of calibration and standardization, is documented.[37] The calorimeter allows the measurement of C_p° values of solids and liquids with an error of 0.2—0.3%. The results of these measurements are exemplified in Fig. 2, which presents all the experimental C_p° points and the averaging $C_p^\circ(T)$ curves for four of the nine carbyne samples. This figure also presents the results of heat capacity measurements for the "Saratovskaya" acetylene black and spectroscopy grade graphite C-3[35] in the same temperature range. The heat capacity of the acetylene black at 80—130 K is greater than that of graphite C-3 by 7%. As the temperature increases, the difference between their heat capacities diminishes; at 300 K, it is only 3%. This difference can be easily explained by the fact that acetylene black, which is a modification of graphite,[38] is substantially more polydisperse.

It can be seen in Fig. 2 that the heat capacity of all the carbyne samples studied is much higher than that of graphite, while the heat capacities of different carbyne samples are markedly dissimilar. The greatest heat capacity was found for the carbyne sample designated by Cn-7 (curve *1*) and the lowest value was found for sample Cn-4 (of those presented in Fig. 2, curve *4*). The heat capacity of sample Cn-6 (curve *2*) is ~10% lower than that of Cn-7. The heat capacity of sample Cn-7 at 80 K is 1.5 times greater and at 300 K, it is 40% greater than that of graphite C-3. The value found for the carbyne sample Cn-3 at 80 K is higher than that of graphite by 45%, while at 200 K, it is higher by 10%. The heat capacities of the other five samples of carbyne are arranged between curves *4* and *5* (they are not shown in Fig. 2).

The fact that the heat capacities of different graphite samples are unequal is apparently due to different numbers of cross-links between the macromolecules. An increase in the number of cross-links should increase the rigidity of the oscillating framework, which, in turn, should decrease the heat capacity, similarly to the trend observed in the carbyne—graphite—diamond sequence. Thus at 100 K, $C_p°$ of carbyne is 3.623 J K^{-1} mol^{-1} and those of graphite and diamond are 1.659 and 0.2444 J K^{-1} mol^{-1}, respectively.[39] The characteristic temperature θ_{max} can serve as a parameter describing the rigidity of the allotropic modifications of carbon in this series (this value for carbyne is 102 K [39] and those for graphite and diamond are 950 [40] and 1890 K,[41] respectively). The elasticity constants (force constants) vary in the same order; for the materials considered, they are 10^9, 10^{10}, and 10^{11}, respectively. The values for graphite and diamond were taken from the literature[41]; that for carbyne was estimated relying on the fact that the force constant is proportional to the characteristic temperature squared.[42]

In the case of the carbyne samples Cn-7 and Cn-6, possessing the greatest heat capacities, the $C_p°(T)$ dependence proved to be linear for the temperature range of 80—240 K. Hence, the $C_p°$ values of Cn-7 (J K^{-1} mol^{-1}) are described by the equation

$$C_p° = -0.0402 + 3.674 \cdot 10^{-2} T. \qquad (2)$$

The root-mean-square deviations of $C_p°$ from the heat capacity values calculated from Eq. (2) are ±0.2%.

Analysis of the $\log C_p° = f(\log T)$ curves indicates that the exponent n at T in the equation $C_p° = A \cdot T^n$ for other carbyne samples varies from 1.5 to 1.2 in different sections of the curves. For the graphite C-3, the n value in the temperature range of 80 to 240 K amounts to 1.8—1.3.

The results of calorimetric measurements of the heat capacity of carbyne Cn-7, graphite, and diamond in the temperature range of 50—300 K has been presented in the previous publication as $C_p°$—T plots.[43] The experimental data obtained in the study cited[43] coincide with the published values[41] for all the compounds studied (the deviations do not exceed 0.3%). However, no data for carbyne Cn-7 can be found in the monograph[41]; hence, when mentioning carbyne Cn-7, the authors[43] meant, apparently, the results given in another publication,[35] which they also refer to at the beginning of the paper.

Thus, the experimental data concerning carbyne Cn-7, which has the greatest heat capacity among the carbynes studied and exhibits a linear pattern of the temperature variation of heat capacity, permit the conclusion that the cross-links connecting the carbon chain macromolecules are few in number or totally missing. Thus, the C_p value of this sample is brought most closely to the heat capacity of ideal amorphous carbyne.

It has been shown previously[31,41] that, in the general case at low temperatures ($T < 0.1\ \theta_1$, where θ_1 is the Tarasov characteristic temperature), the heat capacity of chain polymer is described as the sum of contributions of skeletal vibrations of macromolecules (bending vibrations of chains), which is reproduced adequately as the Tarasov two-parameter function of heat capacity for chain structures[31] (Eq. (1)). At these temperatures, the $C_p°(T)$ dependence for polymers is not complicated by the contribution of stretching vibrations of atoms (*e.g.*, along the C≡C or C—C bonds); this contribution is well described by the Einstein heat capacity function, which does not provide a linear dependence of heat capacity on temperature.[30]

In the case of carbyne, the range in which $C_p°$ is proportional to T should apparently be substantially wider because the contribution of atom vibrations along the —C≡C—, =C=C=, and ≡C—C≡ bonds to the heat capacity becomes evident only at T values exceeding ~200 K due to the high frequencies and, correspondingly, higher Einstein characteristic temperatures θ_E. Based on the experimental $C_p°$ values for carbyne Cn-7 in the 80—100 K temperature range and using the heat capacity tables for chain structures,[44] we selected the values θ_1 = 512 K and θ_3 = 102 K for this substance. Equation (1) with these parameters reproduces the experimental $C_p°$ values of carbyne Cn-7 at 80—100 K with an error of 0.2 to 2%. Assuming that at $T < 80$ K, it reproduces $C_p°$ of ideal carbyne with the same accuracy, we determined the numerical values for heat capacity at 0—80 K. With allowance for these data, Fig. 3 presents the heat capacity of carbyne for the 0—300 K range. As was to be expected, $C_p°$ of carbyne is a linear function of T over a broad temperature range (40—240 K) because no contribution of the atomic vibrations along the conjugated —C≡C— and =C=C= bonds is involved. In the indicated temperature range, the heat capacity is described by Eq. (2). As the temperature varies from 240 to 300 K, the heat capacity of carbyne does not follow a linear dependence on the temperature

$$C_p° = 9.667 - 4.331 \cdot 10^{-2} T + 1.659 \cdot 10^{-4} T^2. \qquad (3)$$

The root-mean-square deviation of the experimental $C_p°$ values from those calculated by Eq. (3) does not exceed 0.2%. The appearance of the term depending on T^2 in Eq. (3) is apparently due to the contribution to the

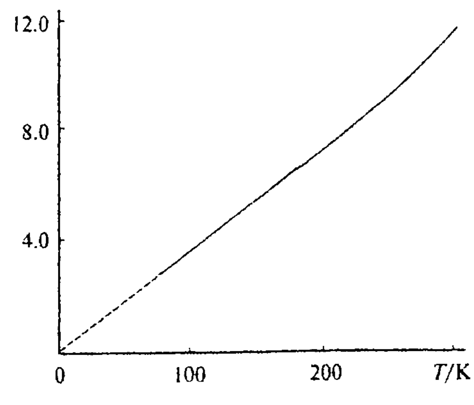

Fig. 3. Heat capacity of carbyne (sample Cn-7)[35].

heat capacity of atomic vibrations along the —C≡C—, =C=C=, and ≡C—C≡ bonds; at $T < 240$ K, they are not excited yet but at $T > 240$ K, they are partially excited and make a contribution, which increases at higher temperatures. At $T < 30$ K, the heat capacity is well described by the polynomial

$$C_p{}^\circ = 2.587 \cdot 10^{-5} + 0.0029 \cdot T - 4.754 \cdot 10^{-5} \cdot T^2 + \\ + 1.063 \cdot 10^{-5} \cdot T^3 - 1.952 \cdot 10^{-7} \cdot T^4 + \\ + 1.209 \cdot 10^{-9} \cdot T^5 - 2.31 \cdot 10^{-12} \cdot T^6. \quad (4)$$

The deviation of $C_p{}^\circ(T)$ from linearity in this temperature range can apparently be explained by the enhancement of chain—chain interaction at lower temperatures. According to published data,[31] the contribution to the heat capacity of chain structures, caused by the vibrations of macromolecules in the chain—chain interaction force field, starts to predominate at $T \ll \theta_{1,3}$; at the lowest temperatures, $C_p{}^\circ$ is proportional to T^3. At those temperatures where $C_p{}^\circ$ of carbyne is proportional to T, the ratio $\theta_3/\theta_1 = 0.2$, which points to the presence of pronounced chain—chain interactions and agrees with the estimates made by other methods.[25]

The thermodynamic functions of carbyne (enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T) - S^\circ(0)$, and the Gibbs energy $G^\circ(T) - H^\circ(0)$) (Table 1) were calculated by a known procedure.[45]

Enthalpies of combustion and thermodynamic parameters of formation

The results of calorimetric determination of the combustion energy of carbyne have been published previously.[27] Calculations of the enthalpies of combustion $\Delta_c H^\circ(\mathrm{a})$ and formation $\Delta_f H^\circ(\mathrm{a})$ and the entropy $\Delta_f S^\circ(\mathrm{a})$ and the Gibbs function $\Delta_f G^\circ(\mathrm{a})$ of the formation of carbyne from the element (graphite) at 298.15 K under standard pressure, carried out using the data of Refs. 27 and 35, have been reported.[27]

The enthalpy of combustion corresponds to the reaction

$$\mathrm{C_{carb}(a) + O_2(g) = CO_2(g)}, \quad (5)$$

and the thermodynamic parameters of formation, to the process

$$\mathrm{C_{gr}(cr) \rightarrow C_{carb}(a)} \quad (6)$$

under the indicated conditions. In Eqs. (5) and (6), $\mathrm{C_{carb}}$ is carbyne; $\mathrm{C_{gr}}$ is graphite; the letters in parentheses denote the physical states of the reactants: cr is crystalline, a is amorphous, and g is gaseous.

The presented thermodynamic characteristics of carbyne are not standard values because amorphous carbyne is thermodynamically metastable. The state of carbyne that is thermodynamically stable at the temperatures in question and at the standard pressure is the crystalline state.

The carbyne samples studied here were prepared by the procedure reported previously.[36] According to XRD data, they were mainly amorphous mixtures of macromolecules of polyyne and cumulene structures with an admixture of crystals formed by polyyne and cumulene chains. It was also shown that different samples contained different ratios of the α- and β-forms of carbyne. The researchers cited[27] did not rule out the possibility that a minor portion of C atoms in the macromolecules forms intermolecular cross-links, which transform a portion of carbyne into a carbonaceous substance with an aromatic structure. In the study under consideration,[27] the content of carbon in the material was not determined;

Table 1. Thermodynamic functions of carbyne (Mol. weight = 12.011 g mol^{-1}; p = 101.325 kPa)[35,39]

T/K	$C_p{}^\circ(T)$ /J K^{-1} mol^{-1}	$H^\circ(T) - H^\circ(0)$ /kJ mol^{-1}	$S^\circ(T) - S^\circ(0)$ /J K^{-1} mol^{-1}	$-[G^\circ(T) - H^\circ(0)]$ /kJ mol^{-1}
10	0.294	0.00146	0.276	0.00131
20	0.620	0.00600	0.578	0.00556
30	1.01	0.0141	0.899	0.0129
40	1.41	0.0260	1.24	0.0236
50	1.83	0.0427	1.60	0.0378
60	2.24	0.0626	1.97	0.0557
70	2.62	0.0869	2.35	0.0773
80	2.895	0.1145	2.713	0.1026
100	3.623	0.1796	3.436	0.1641
120	4.360	0.2595	4.163	0.2400
140	5.079	0.3537	4.888	0.3305
160	5.774	0.4624	5.612	0.4355
180	6.569	0.5824	6.337	0.5550
200	7.322	0.7240	7.065	0.6890
220	8.075	0.8761	7.799	0.8377
240	8.828	1.047	8.534	1.001
260	9.623	1.231	9.271	1.179
280	10.54	1.433	10.02	1.372
298.15	11.46	1.631	10.70	1.558

however, it has been shown previously[25] that carbyne samples obtained by this procedure contain 99% (w/w) carbon.

The combustion energies were measured using a KU-2 calorimetric setup.[7] The completeness of combustion of substances was checked by analyzing gaseous products. Unfortunately, the researchers[27] did not cite the results of these analyses, which hampers the objective appraisal of the results. However, judging by the enthalpies of combustion of several other carbon materials, in particular, graphite, measured using the same setup, the error of measurements did not exceed 0.05—0.10%.[47]

The enthalpies of combustion found using a calorimetric bomb for three carbyne samples designated in the study cited[25] by letters "a," "b," and "c" were $\Delta_c U$ = −353.7, −356.5, and −371.5 kJ mol^{-1}, respectively. One carbyne sample was heated to about 3000 K prior to burning. As shown by XRD, this sample was thus converted into nongraphitizing carbon[27] (its structure is described in Ref. 17). The energy of combustion of the heated sample was found to be −394.3 kJ mol^{-1}, which is close to the energy of combustion of graphite, −393.5 kJ mol^{-1}, measured using the same setup. It follows from the experimental data that an increase in the carbon fraction in the carbyne samples results in higher absolute magnitudes of $\Delta_c U$. Thus, sample "a" appears to have the smallest number of cross-links between macromolecules; it can be assumed that its $\Delta_c U$ value corresponds to the energy of combustion of ideal carbyne (having no cross-links). The $\Delta_c U$ value of sample "a" was used to estimate the combustion energy at the standard pressure, $\Delta_c U°$; this was used to calculate the enthalpy of combustion of carbyne.

Below we present the thermodynamic parameters of formation of amorphous carbyne at 298.15 K, determined from the data of Ref. 27.

$-\Delta_c H°$(a)	$-\Delta_f H°$(a)	$-\Delta_f S°$(a)	$-\Delta_f G°$(a)
kJ mol^{-1}		/J K^{-1} mol^{-1}	/kJ mol^{-1}
353.7	39.8	5.3	38.3

The enthalpy of formation of amorphous carbyne ($\Delta_f H°$(a)) was calculated from the enthalpies of combustion of carbyne and graphite; the standard value for graphite was taken from Ref. 49. The entropy of formation ($\Delta_f S°$(a)) was calculated from the entropies $S°$(298.15) of carbyne[6] and graphite[25]. The $S°$(298.15) − $S°$(0) values (see Table 1) were used as $S°$(298.15) of amorphous carbyne; the $S°$(0) value, *i.e.*, the residual entropy in the amorphous state, was neglected. This undoubtedly introduced some inaccuracy to the $\Delta_f S°$(a) value. Thus it was shown[50] that the zero-point entropy of a linear polymer in the vitreous state is normally ~10% of its entropy at 298.15 K. For carbyne, this means that the residual entropy $S°(0) \approx 1$ J K^{-1} mol^{-1} and $S°(298.15) \approx 11.7$ J K^{-1} mol^{-1}.

The Gibbs function of formation of amorphous carbyne $\Delta_f G°$(a) was calculated from the $\Delta_f H°$(a) and $\Delta_f S°$(a) values for 298.15 K.

The data presented above, first of all, the enthalpies of combustion and formation and the Gibbs functions of formation of carbyne need to be determined more precisely in the future, because determination of the combustion energy of carbyne can prove inaccurate. In any case, the published experimental data on the measurement of $\Delta_c U$ do not allow one to judge the reliability of the resulting values. The negative $\Delta_f G°$(a) values for carbyne indicate that at 298.15 K and the standard pressure, process (6) should go toward the formation of carbyne. However, this does not occur in reality, possibly due to kinetic reasons.

The results of theoretical estimates of the enthalpy of carbyne in the gaseous state have been published.[15,51] At 298.15 K and the standard pressure, the value $\Delta_f H°$(g) = 113.4 kJ mol^{-1} was obtained.[51] The $\Delta_f H°$(g) values found for α-carbyne and β-carbyne under the same conditions are 97.53 kJ mol^{-1} and 129.1 kJ mol^{-1}, respectively.[15] Calculations for α- and β-carbyne chains consisting of 100 carbon atoms were reported in the same publication.[15] In both studies,[15,51] the enthalpies of formation are referred to 1 mole of carbon atoms. It is of interest that the $\Delta_f H°$ value found in Ref. 51 is equal to the arithmetic mean of the enthalpies of formation of α- and β-carbyne determined in Ref. 15. Note that the calculation procedures used[15,16] were appreciably dissimilar. In addition, the Gibbs functions for the formation of α- and β-carbynes in the gaseous state at 298.15 K and p = 101.325 kPa were reported to be $\Delta_f G°$ = 94.39 and 127.8 kJ mol^{-1}, respectively.[15]

Comparison of the thermodynamic properties of carbyne and other allotropic modifications of carbon

The three valence states of carbon stipulate three types of spatial structure in elemental carbon[1—4]: the sp^3 state corresponds to a three-dimensional structure (diamond), the sp^2 state accounts for a planar configuration (graphite), and the sp state implies a linear structure (carbyne). Fullerenes, discovered relatively recently,[52,53] constitute a new allotropic modification in which the valence state of carbon is similar to that in graphite. The possibility of existence of yet another modification of carbon having a planar structure formed by sp^2- and sp-hybridized C atoms and termed graphyne has been predicted.[54]

Before we compare thermodynamic properties of carbyne with the properties of diamond, graphite, and C_{60} and C_{70} fullerenes, let us consider briefly the published calorimetric data for the above-listed modifications (the corresponding data for carbyne are considered above). All the results that we present have been obtained by adiabatic vacuum calorimetry, which is the most accurate method for measurements of heat capacity and the temperatures and enthalpies of physical transformations of substances at low and medium temperatures (5—340 K).[55]

The results of calorimetric studies of the temperature dependence of heat capacity of several samples of natural diamonds have been generalized, and the numerical values of the averaged heat capacities have been summarized in a table.[41] The most probable errors in the determination of $C_p°$ are equal to ±20% at 13 K, ±6% at 20 K, ±8% at 100 K, ±0.2% at temperatures from 200 to 280 K, and ±0.5% in the temperature range from 280 to 300 K. In another publication, the $C_p°$ values for natural diamond were studied in the 17—300 K temperature range. At $T < 70$ K, the error of determination was ±30%, while at $T > 70$ K, it was ±5%.[56] The temperature dependence of the heat capacity of a commercial synthetic diamond sample has been studied in the 9—340 K temperature range[46] (according to the certificate, the sample contained ~1% impurities). The root-mean-square deviations of the experimental points from the averaging curve $C_p° = f(T)$ were about ±1% in the 9—40 K temperature range, ±0.8% at 80—160 K, and ±0.5% at 160—340 K. The absolute errors of measurements for samples of natural diamond are apparently the same.[56]

Figure 4 shows the deviations of heat capacity $\Delta C_p°$ of diamond samples[46,56] from the average data[41] for diamond. It can be seen that the maximum deviation[56] (curve *2*) is observed in the 200—300 K range and is equal to 0.05 J K^{-1} mol^{-1} at 280 K; at any other temperature, it does not exceed 0.01 J K^{-1} mol^{-1}. The greatest deviation for synthetic diamond also occurs in the 280—300 K range; $\Delta C_p°$ = 0.18 J K^{-1} mol^{-1} at 298.15 K. At other temperatures, the deviation is much smaller; it is +0.04 J K^{-1} mol^{-1} in the 50—90 K temperature range and −0.04 J K^{-1} mol^{-1} at temperatures of 90—130 K.

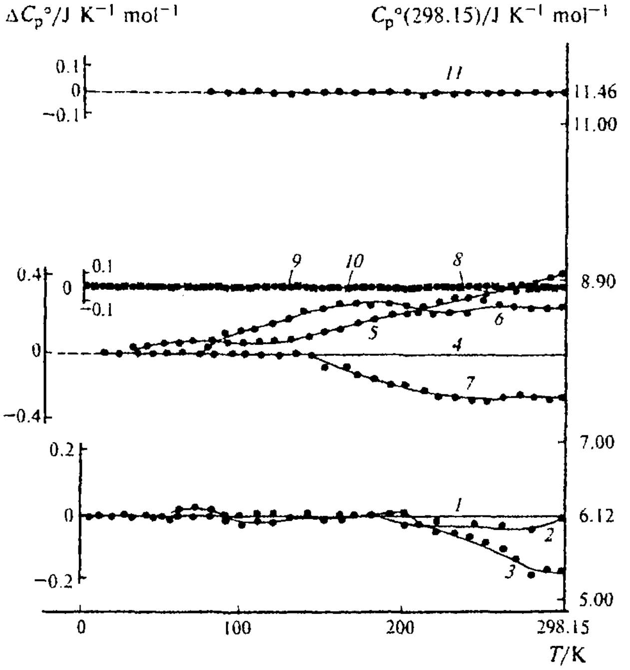

Fig. 4. Deviation of heat capacity $\Delta C_p°$ of individual samples of various allotropic modifications of carbon from the corresponding averaged $C_p°$ values for each modification in the 0—300 K temperature range. Straight horizontal lines *1*, *4*, *8*, and *11* are averaged values for diamonds,[41] graphites,[57] fullerenes, and carbyne,[35] respectively; (*2*) natural diamond[46]; (*3*) synthetic diamond[46]; (*5*) vitreous carbon[62]; (*6*) acetylene black[35]; (*7*) Acheson natural graphite[61]; (*9*) C_{60} fullerene[63]; (*10*) C_{70} fullerene.[64]

Despite these small absolute differences between the heat capacities of different diamond samples, the relative difference can amount to several tens of percent, especially at low temperatures, which is mainly due to the relatively small absolute values of $C_p°$ of diamond. For example, for synthetic diamond, the greatest deviation in the 280—300 K temperature range is ~−3% (see Fig. 4, curves *3* and *1*) and that for natural diamond at 200—300 K is ~1%. Yet another factor decreasing the accuracy of measurements of the diamond $C_p°$ values is a rather unfavorable relationship between the heat capacity of the diamond samples and the total heat capacity of a calorimetric tube with the material. However, all the heat capacity values known to date for various diamond samples are close at the corresponding temperatures.

Data on the heat capacities of various types of graphite, carbon-black, coke, and natural flake graphites, are presented in a monograph.[41] It was shown that $C_p°$ depends appreciably on the type of graphite and is determined by the degree of perfection of its crystal structure. It has been noted[41] that the degree of perfection of a graphite structure increases from carbon-black to coke graphite and from coke to natural graphite. Only 1/3 of planes in carbon-black graphite are parallel to neighboring planes. The structure of natural graphite resembles most closely that of a single crystal; it consists of 100—400-Å-thick planes.[41] As a consequence, the heat capacity of, for example, carbon-black graphite at 2 K is more than 200% greater than $C_p°$ of natural graphite. The error of measurements of $C_p°$ of graphites is estimated as 5 to 2% at $T < 20$ K and as 0.5 to 0.1% in the region of 20—340 K.

The averaged values of heat capacity of graphite were determined[57] using the results of experimental measurements for various samples of natural graphite, namely, the Madagascar,[58] Canadian,[59] Ceylon,[60] Acheson,[61] Taiginsk, and artificial pyrolytic graphite.[57] The data presented in Fig. 4 (curves *4*—*7*) permit comparison of the averaged values with the $C_p°$ values for glassy carbon[62] and acetylene black[35] (the most disordered graphite structures), on the one hand, and with the heat capacity of the natural Acheson graphite (the most perfect structure among natural graphites[62]), on the other hand. It can be seen that the $C_p°$ values of glassy carbon and acetylene black are higher than the average values over the whole temperature range ($\Delta C_p°$ varies from 0.03 J K^{-1} mol^{-1} at 30 K to 0.50 J K^{-1} mol^{-1} at 298.15 K). At temperatures of 8—210 K, the heat capacity of acetylene black is greater than that of glassy carbon, and at 210—300 K, it is smaller; the difference reaches ±0.24 J K^{-1} mol^{-1}. The heat capacities of the Acheson graphite (see Fig. 4, curve *7*) in the 10—145 K range are close to the averaged values (straight line *4*), while those at 145—300 K are smaller. Thus, the data on the heat capacity of various samples of graphite do not differ by more than 0.50 J K^{-1} mol^{-1}, which is ~6% at 298.15 K.

The numerical values of the heat capacities of C_{60} and C_{70} fullerenes, found using an adiabatic vacuum calorimeter in the temperature range of 5—390 K, have been published.[63,64] The error of measurements was ~2% at 5 K, 0.4% at 40 K, and 0.2% in the region of 40—340 K. The heat capacities of various fullerenes per mole of C atoms are close to one another (see Fig. 4). The arithmetic mean C_p° values for C_{60} and C_{70} are lower than C_p° of C_{60} fullerene and higher than the heat capacity of C_{70} over the whole temperature range. These differences are ±(8—5)% in the 5—50 K range, ±(4—3)% at temperatures of 50—210 K, and ±(2—0.2)% at 210—340 K.

The temperature dependences of the heat capacity of carbyne, C_{60} and C_{70} fullerene, graphite, and diamond are presented in Fig. 5. For each allotropic modification, C_p° is related to 1 mole of C atoms. The heat capacities of diamond, graphite, and carbyne smoothly increase with an increase in the temperature. The $C_p^\circ = f(T)$ curves for fullerenes display abnormal patterns of dependence of C_p° on T in some temperature ranges; this is due to transformations occurring in crystalline fullerenes on heating and cooling. The corresponding thermodynamic characteristics and discussion of the nature of these transformations appear in several studies.[63—65] In the 80—160 K temperature range, the C_p° values of different fullerenes are close both to one another and to the heat capacity of graphite (the difference does not exceed 8%). It is noteworthy that the heat capacity of C_{70} fullerene is somewhat lower than that of C_{60} and is closer to the heat capacity of graphite. Apparently, this is due to the fact that the surface curvature of C_{70} fullerene is less pronounced than that of C_{60} and, hence, the bond angles are less distorted, *i.e.*, the carbon cage is less strained.

At 80 K, the heat capacity of carbyne is 16 times greater than that of diamond and ~9 times greater than those of graphite and fullerenes; at 300 K, these factors are 1.7 and 1.3, respectively. This can be due to the fact that the rigidity of the vibrating frameworks of the modifications in question increases successively on passing from the one-dimensional chain structure of carbyne to the two-dimensional layered structure of graphite and then to the three-dimensional cage structure of diamond.

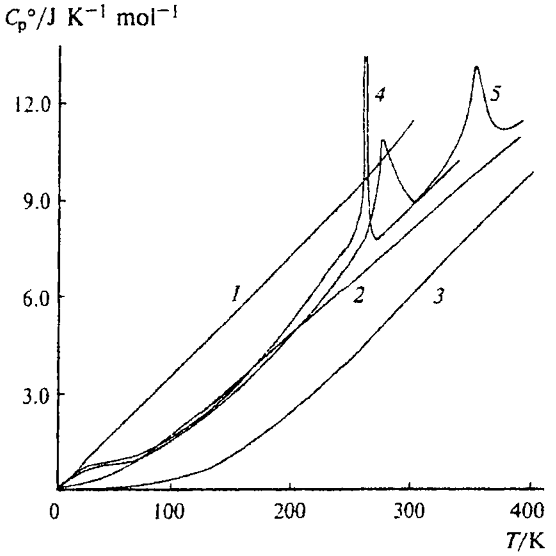

Fig. 5. Temperature dependence of the heat capacity of allotropic modifications of carbon: (*1*) carbyne[35]; (*2*) graphite[57]; (*3*) diamond[41]; (*4*) C_{60} fullerene[63]; (*5*) C_{70} fullerene.[64]

Analysis of the temperature variation of the heat capacity of allotropic modifications showed that C_p° of diamond in the range of 25—50 K is described by the Debye T^3 heat capacity law,[33] which is typical of three-dimensional structures. The graphite heat capacity in the 10—100 K range obeys a T^2 law in accordance with the Tarasov theory of heat capacity for layer structures.[31] Finally, the heat capacity of carbyne in the 40—240 K range is described by a T^1 dependence, which is also consistent with the Tarasov theory of heat capacity for chain structures with weak intermolecular interactions.[31,32]

Table 2 contains[39] thermodynamic functions for allotropic modifications of carbon, calculated from the patterns of temperature variation of their heat capacities. The calculation procedures were similar to those described previously.[29] The numerical values of the heat capacity $C_p^\circ(T)$, enthalpy $H^\circ(T) - H^\circ(0)$, and entropy

Table 2. Thermodynamic functions of allotropic modifications of carbon per mole of C atoms at 298.15 K and standard pressure[39,46]

Allotropic modification	Physical state*	$C_p^\circ(T)$ /J K^{-1} mol^{-1}	$H^\circ(T) - H^\circ(0)$ /kJ mol^{-1}	$S^\circ(T)$ /J K^{-1} mol^{-1}	$-[G^\circ(T) - H^\circ(0)]$ /kJ mol^{-1}
Carbyne	a	11.46	1.631	10.70**	1.558
C_{60} fullerene	cr I	8.747	1.207	7.108	0.912
C_{70} fullerene	cr II	8.911	1.102	6.467	0.826
Graphite	cr	8.109	1.008	5.508	0.634
Diamond	cr	6.117	0.5236	2.348	0.176

* Hereinafter, a is amorphous: cr is crystalline.

** Calculated without allowance for the zero-point entropy $S^\circ(0)$.

$S^\circ(T)$ diminish on going from carbyne to diamond; conversely, the Gibbs functions $G^\circ(T) - H^\circ(0)$ increase.

Table 3 presents thermodynamic characteristics of formation of allotropic modifications of carbon, calculated from calorimetric data. The calculation procedures are similar to those described previously.[29,45,66] Experimental data for carbyne were taken from Ref. 27, those for fullerenes were taken from Refs. 63—65, and the values for graphite were borrowed from Ref. 49. The $\Delta_c H^\circ$ and $\Delta_f H^\circ$ values for diamond were also taken from the literature;[67,49] the $\Delta_f S^\circ$ value was calculated from the $S^\circ(298.15)$ values for diamond and graphite.[49]

According to the magnitudes and the signs of the standard Gibbs function (see Table 3), the allotropic modifications of carbon can be arranged in the following sequence of thermodynamic stability: carbyne (a) > graphite (cr) > diamond (cr) > C_{70} fullerene (crII) > C_{60} fullerene (crI).

Thus, carbyne is thermodynamically the most stable allotropic modification of carbon at 298.15 K and standard pressure. The enhanced thermodynamic stability of carbyne is mainly due to two factors[27]: the greater energy of conjugation of the carbon—carbon multiple bonds in carbyne compared to graphite (~42 kJ mol^{-1}) and greater chain—chain interaction energy in carbyne compared to the energy of interaction between the layers in graphite (~111 kJ mol^{-1}). The latter is in good agreement with the fact that the distance between the neighboring carbon chains in crystalline carbyne is relatively small (l_{C-C} = 2.95 Å)[68] with respect to the distance between the neighboring layers of C atoms in crystalline graphite (l_{C-C} = 3.34 Å).

Conclusion

The review summarizes all the thermodynamic characteristics of carbyne published to date, namely, the temperature dependences of the heat capacity $C_p^\circ(T)$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T) - S^\circ(0)$, and the Gibbs function $G^\circ(T) - H^\circ(0)$ for the 0—300 K temperature range. The enthalpies of combustion $\Delta_c H^\circ$ and formation $\Delta_f H^\circ$ and the entropies $\Delta_f S^\circ$ and Gibbs functions $\Delta_f G^\circ$ of formation for T = 298.15 K and standard pressure (p = 101.325 kPa) are also covered. Unfortunately, these data still cannot be regarded as full-value thermodynamic constants of carbyne due to the following reasons.

All the values, except for the thermodynamic parameters calculated theoretically,[4,51] were found from the data of calorimetric measurements carried out for samples that were mixtures of α- and β-forms of carbyne in the amorphous state with minor portions of crystals of both forms.

In the calculation of the $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T) - S^\circ(0)$, and $G^\circ(T) - H^\circ(0)$ functions for carbyne in the 0—300 K temperature range, its heat capacity at 0—80 K was determined by extrapolation of experimental data on C_p° using the Tarasov heat capacity function[31] for chain structures with allowance for chain interaction. The reliability of the results obtained in this way is rather high; nevertheless, extrapolation introduces some uncertainty into the calculated thermodynamic functions (possibly, up to several percent).

The energies of combustion found from calorimetric data can be regarded only as estimates because the results of analysis of the combustion products were not published,[27] although this is necessary for precise determinations.[48] The calculated data on the enthalpies of combustion and thermodynamic parameters of formation are also rough estimates.[69]

The relative arrangement of the heat capacity curves (see Fig. 5) for the allotropic modifications of carbon considered here (carbyne, C_{60} and C_{70} fullerenes, graphite, and diamond) reflects objectively the difference between their physicochemical characteristics; apparently, this would not be revised in the future. However, due to the uncertainty of the $\Delta_c H^\circ$, $\Delta_f H^\circ$, and $\Delta_f G^\circ$ values, the position of carbyne in the series of thermodynamic stability of various allotropic modifications of carbon might be corrected subsequently.

The most important tasks for further studies of the thermodynamic characteristics of carbyne include high-precision calorimetric elucidation of the temperature variations of the heat capacities of individual α- and β-forms in the crystalline and amorphous states over a broad temperature range (from 1—2 K to 1000 K or higher) and the calculation of thermodynamic functions from the data of these measurements; measurement of the energies of combustion of these substances and calculation of thermodynamic parameters of formation for 298.15 K and standard pressure from the results of measurements. The parameters thus found would be the standard thermodynamic characteristics, which could be widely used in various thermodynamic and thermophysical calculations for processes involving carbyne.

Table 3. Enthalpies of combustion ($\Delta_c H^\circ$) and enthalpies ($\Delta_f H^\circ$), entropies ($\Delta_f S^\circ$), and Gibbs functions ($\Delta_f G^\circ$) of formation of allotropic modifications of carbon at 298.15 K and standard pressure

Allotropic modification	Physical state	$-\Delta_c H^\circ$ /kJ mol^{-1}	$\Delta_f H^\circ$ /kJ mol^{-1}	$\Delta_f S^\circ$ /J K^{-1} mol^{-1}	$\Delta_f G^\circ$ /kJ mol^{-1}	Reference
Carbyne	a	353.7	−39.8	5.3	−38.3	27
C_{60} fullerene	cr I	432.8	39.25	1.54	38.79	63, 65
C_{70} fullerene	cr II	430.0	36.50	0.959	36.21	64, 65
Graphite	cr	393.51	0	0	0	49
Diamond	cr	395.34	1.83	−3.372	2.83	49, 67

These data are required even now because carbyne has found wide practical application; to extend the fields of application, thermodynamic calculations are undoubtedly required.

A fundamental difference in obtaining thermodynamic constants of carbyne is due to the difficulty of preparation of individual forms of carbyne in amounts sufficient for classical calorimetric experiments.

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