Thermodynamic properties of carbynoid structures in the 0—340 K range

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The temperature dependences of the heat capacity ($C_p°$) of carbynoid structures prepared by alkaline dehydrochlorination of poly(vinylidene chloride) and 1,1,2- and 1,2,3-polytrichlorobutadienes were studied by adiabatic vacuum calorimetry between 5 and 340 K with an accuracy of ~0.2%. The low-temperature relaxation transitions and abnormal patterns of the $C_p°$ *vs.* T dependences were identified and characterized. The experimental results were used to calculate the thermodynamic functions $C_p°(T)$, $H°(T) - H°(0)$, $S°(T) - S°(0)$, and $G°(T) - H°(0)$ for 0—340 K. These data were compared with the corresponding data for carbyne produced by oxidative dehydropolycondensation of acetylene, which is a mixture of amorphous α- and β-forms with a minor impurity of crystals of both forms.

Key words: carbynoid structure, carbyne, heat capacity, enthalpy, entropy, Gibbs function, calorimetry, thermodynamics.

Carbyne is one of the four currently known allotropic modifications of carbon. Although it was discovered more than 40 years ago,**[1]** it still remains an object of scientific and applied research, first of all, due to good prospects for its practical application.**[2]** The polymeric carbyne molecules are known to exist in two forms,**[2,3]** namely, the polyyne ~C≡C—C≡C~ (α-form or α-carbyne) and cumulene ~C=C=C=C~ (β-form or β-carbyne) ones. The crystalline α- and β-carbynes consist of the respective carbon chains packed into crystals due to van der Waals forces. Without valence bonds between the linear chains, such crystals would represent the perfect carbyne.**[3—5]** Unfortunately, this form of carbyne has not been prepared yet in amounts sufficient, in particular, for calorimetric measurements. The usual method for carbyne synthesis by oxidative dehydropolycondensation of acetylene**[6]** followed by heating the reaction products *in vacuo* at $T \approx 1300$ K gives samples containing a mixture of amorphous α- and β-carbynes with a minor impurity of the crystals of both forms.**[7]** Recently, more than thirty-year-long studies on the thermodynamic properties of carbyne have been summarized.**[8]** Meanwhile, attempts at developing new methods of carbyne synthesis are made, especially, those to prepare samples with predominance of a particular carbyne form. Alkaline dehydrochlorination of poly(vinylidene halides)**[9]** and 1,1,2- and 1,2,3-polytrichloropolybutadiene isomers (1,1,2-PTCB and 1,2,3-PTCB, respectively**[10]**) is the most available and convenient method for this purpose. Complete dehydrochlorination of 1,1,2-PTCB is expected to give α-carbyne, while 1,2,3-PTCB should be converted into β-carbyne. Dehydrochlorination of poly(vinylidene halides), in particular, poly(vinylidene chloride) (PVDC) was suggested to produce β-carbyne. However, it was found that, together with β-carbyne,**[10]** up to 30% of α-carbyne can be formed. The processes of dehydrochlorination of these compounds are far from being perfect; in addition to dehydrochlorination, partial oxidation of the products takes place. The initial PTCB isomers contain not only the repeating monomer units with the 1,4 structure but also ~10% units with the 3,4 structure.**[11]** The 1,4 units are readily dehydrochlorinated, while the 3,4 units react with difficulty. In the case of 1,1,2-PTCB, the 3,4 units accout for the formation of products containing the $=C=CCl_2$ side groups, whilst in the case of 1,2,3-PTCB, the —C≡CCl side groups are formed. In all cases, the dehydrochlorination products contain a major amount of carbon along with hydrogen, oxygen, and chlorine.**[10]** Analysis of the products by NMR, IR, X-ray photoelectron, and Auger spectroscopy showed the presence of carbon chains corresponding to β- and α-carbynes in the case of PVDC, α-carbyne in the case of 1,1,2-PTCB, and β-carbyne in the case of 1,2,3-PTCB.**[2,10]** The products of dehydrochlorination of the polymers contain H, O, and Cl atoms, and those obtained from PTCB isomers contain additionally the $=C=CCl_2$ and —C≡CCl groups and some cross-links between the macromolecules. Therefore, the products are rather far in composition and structure from the perfect carbyne.

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Hence, we called them carbynoid structures (CS) and denoted by CS-β(PVDC), CS-β(1,2,3-PTCB), and CS-α(1,1,2-PTCB), where α and β are the carbyne forms, while the designations of the initial polymers used to prepare the corresponding CS are given in parentheses. Some of the CS considered here have already found practical application,[2] and some other have been recommended for use. Thermodynamic properties of these CS have not been studied. It is clear, however, that these properties would be very useful in the research concerning the synthesis and practical applications of the carbynoid structures.

The purpose of this work was to study the temperature dependence of the heat capacity of the carbynoid structures CS-β(PVDC), CS-β(1,2,3-PTCB), and CS-α(1,1,2-PTCB) in the temperature range of 5—340 K by calorimetry; to identify the physical transformations that take place during heating and cooling of the substances under study over the above-mentioned temperature range; to calculate the thermodynamic functions $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T) - S^\circ(0)$, and $G^\circ(T) - H^\circ(0)$; and to compare the thermodynamic properties of these carbynoid structures with those of carbyne.

Experimental

Samples. The CS-β(PVDC) sample was prepared (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) by dehydrochlorination of poly(vinylidene chloride) with an ethanolic solution of KOH containing a THF additive by a procedure similar to that described previously.[12] This gave a polymer with mainly the cumulene structure and only a minor fraction of the polyyne structure. The CS-β(1,2,3-PTCB) and CS-α(1,1,2-PTCB) samples were prepared by dehydrochlorination of 1,2,3-PTCB and 1,1,2-PTCB, respectively, with a mixture of an ethanolic solution of KOH and THF by a previously described procedure.[10] The polymers contained >90% 1,4 monomer units and also 3,4 units. Some characteristics of the resulting carbynoid structures are given in Table 1.

The structure of the CS was proved by vibrational, electronic, and NMR spectroscopy[10]. The presence of abnormal (3,4) units in the initial 1,1,2-PTCB and 1,2,3-PTCB polymers accounted for the presence of the $-C{\equiv}CCl$ and $=C{=}CCl_2$ groups in the dehydrochlorination products CS-β(1,2,3-PTCB) and CS-α(1,1,2-PTCB), respectively.

Instrumentation and procedure. The heat capacity values were measured on a BKT-3 fully automated adiabatic vacuum calorimeter designed and manufactured at the Termis company (Mendeleevo, Moscow region, Russia). The calorimeter design and the procedure of measurements were similar to those described previously.[13] Liquid helium and nitrogen were used as refrigerants, and special purity grade helium was used as the heat exchange gas. The calorimeter was verified by measuring the heat capacity of special purity grade copper and reference synthetic samples of corundum and K-2 benzoic acid prepared at the metrology laboratories of the Gosstandart of Russia. The results showed that the experimental error in C_p° measurement at liquid helium temperature was within ±2%. As the temperature increased to 40 K, the error reduced to 0.5%, and at $T > 40$ K, it was ~0.2%.

The main characteristics of the measurements. The heat capacity of CS-β(PVDC) was measured at 5.2—335 K, that of CS-β(1,2,3-PTCB) was determined at 7.9—325 K, and that of CS-α(1,1,2-PTCB), at 8.5—328 K. Samples of the above substances weighing 0.2095, 0.2344, and 0.2895 g, respectively, were placed into a calorimetric tube. The pressure of the heat-exchange gas (helium) in the tube with a sample was 40 Pa at ambient temperature. The heat capacity of the CS samples amounted to 15—20% of the total heat capacity of the tube with the substance at 8—90 K, or 10—15% at 90—330 K.

For CS-β(PVDC), 126 experimental C_p° values were obtained in twelve series of measurements; for CS-β(1,2,3-PTCB), 206 values were found in seven series; and for CS-α(1,1,2-PTCB), 214 values were obtained in eight series. The experimental C_p° points were averaged using a computer. The mean square deviation from the averaging $C_p^\circ = f(T)$ curves was 0.11% at 5—40 K, 0.08% at 40—90 K, and 0.05% at 90—340 K.

Results and Discussion

Heat capacity. Figure 1 shows the temperature dependences of the heat capacity (experimental values and $C_p^\circ = f(T)$ averaging curves) for the carbynoid structures under study (curves *1—3*) and, for comparison, the $C_p^\circ = f(T)$ curve for a carbyne sample[14] close in heat capacity to perfect carbyne.[8] Like most chain polymers studied, the carbynoid structures are characterized by a broad temperature range where C_p° is proportional to *T*. However (see Fig. 1), in the 170—260 K range for CS-β(PVDC) (curve *1*), 90—140 K range for CS-β(1,2,3-PTCB) (curve *2*), and 120—170 K range for CS-α(1,1,2-PTCB) (curve *3*), positive deviations from the linear C_p° *vs.* *T* dependence looking like

Table 1. Results of elemental analysis and gross formulas of the averaged repeating monomeric units in the carbynoid structures

Substance	Elemental composition (% w/w)				Gross formula	M/g mol^{-1}
	C	H	Cl	O		
CS-β(PVDC)	69.18	2.38	8.17	20.27	$CH_{0.41}Cl_{0.04}O_{0.22}$	17.361
CS-β(1,2,3-PTCB)	62.42	4.37	9.05	24.18	$CH_{0.83}Cl_{0.05}O_{0.29}$	19.260
CS-α(1,1,2-PTCB)	61.22	4.30	12.05	22.43	$CH_{0.84}Cl_{0.07}O_{0.28}$	19.819

Note. CS-β(PVDC) is a carbynoid structure containing sequences of β-carbyne and produced from PVDC; CS-β(1,2,3-PTCB) is the same produced from 1,2,3-PTCB; CS-α(1,1,2-PTCB) is a carbynoid structure containing sequences of α-carbyne and produced from 1,1,2-PTCB.

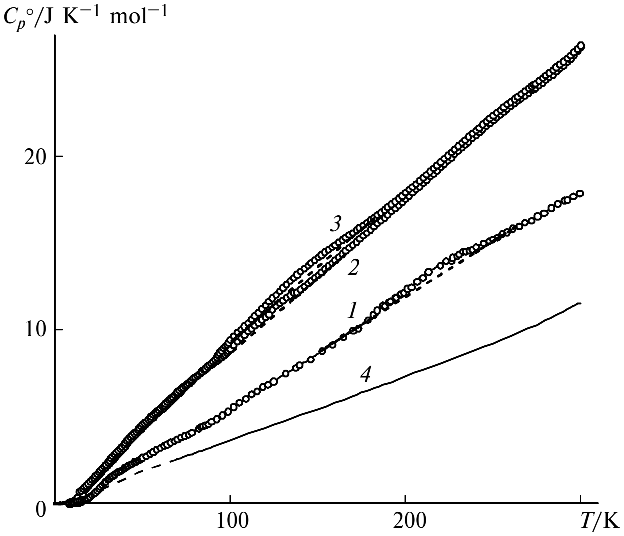

Fig. 1. Temperature dependences of the carbynoid heat capacity: (*1*) CS-β(PVDC), (*2*) CS-β(1,2,3-PTCB), (*3*) CS-α(1,1,2-PTCB), (*4*) carbyne.[2,8]

diffuse "humps" are observed. The greatest deviations of $C_p°$ from the linear dependence (dashed line) are found at 220 K (0.7 J K^{-1} mol^{-1}) in curve *1*, at 130 K (0.4 J K^{-1} mol^{-1}) in curve *2*, and at 140 K (0.3 J K^{-1} mol^{-1}) in curve *3*. Similar deviations have been observed previously[15] for chain polymers containing side atomic groups capable of hindered rotation about the macromolecule backbone. In the CS-β(1,2,3-PTCB) and CS-α(1,1,2-PTCB), this type of motion might be executed by the $—C{\equiv}CCl$ and $=C=CCl_2$ groups, respectively, present in these polymers.[10] Perhaps, the complex process of CS-β(PVDC) dehydrochlorination yields side groups capable of this type of motion and thus responsible for the deviation of $C_p° = f(T)$ dependence from linearity.

An interesting feature of the carbynoid structures considered is their ability to undergo low-temperature relaxation transitions, which are similar to devitrification regarding the pattern of $C_p°(T)$ variation near the transition. The same transformations have been found, for example, in tri(perfluorophenyl)germane[16] and polyvinylbenzyldimethylsilane.[17] They are explained in terms of excitation of hindered rotations of the perfluorophenyl and benzyl groups about the Ge—C and Si—C bonds, respectively. The manifestation of relaxation transitions in the $C_p°$ *vs.* T dependences for the carbynoid structures can be readily seen in Fig. 2. The thermodynamic characteristics of the transitions are presented in Table 2. The $\Delta T°_{tr}$ ranges, the transition temperatures $T°_{tr}$, and the increase in the heat capacity $C_p°(T°_{tr})$ at $T°_{tr}$ were determined graphically. As an example of determination of the above parameters, Fig. 3 shows the corresponding graphical analysis of the transition for CS-β(PVDC). The transition temperature was found by the graphical method of Alford and Dole[18] from the break in the entropy *vs.* temperature plot. The increase in the heat capacity upon this transition was found from the plot (CD segment); the transition range corresponds to the difference between the temperatures at the end ($T_f°$) and at the beginning ($T_i°$) of the transition. The increase in the configurational entropy during the transition, $\Delta S°_{conf}$, was calculated from our calorimetric data using the following relation[19]:

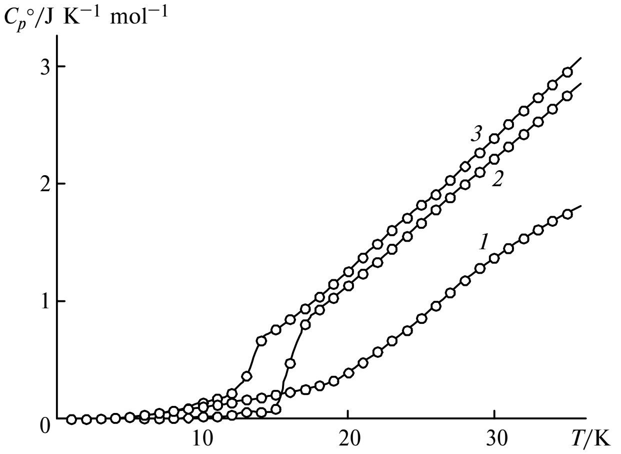

Fig. 2. Relaxation transitions in the $C_p°$ *vs.* T curves: (*1*) CS-β(PVDC), (*2*) CS-β(1,2,3-PTCB), (*3*) CS-α(1,1,2-PTCB).

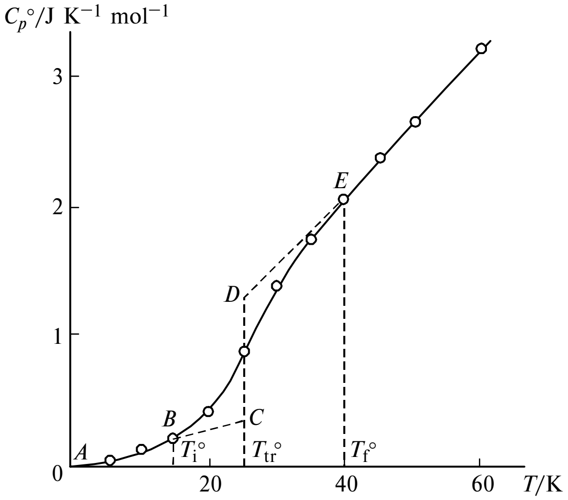

Fig. 3. Graphical analysis of the transition in CS-β(PVDC).

$$\Delta S°_{conf} = \Delta C_p°(T_{tr}°)\ln 1.29. \qquad (1)$$

Table 2. Parameters of relaxation transitions in the studied CS under standard pressure

Substance	T	$T_{tr}°$	$\Delta C_p°(T_{tr}°)$	$\Delta S°_{conf}$
	K		J K^{-1} mol^{-1}	
CS-β(PVDC)	15—40	25±0.5	0.93	0.24
CS-β(1,2,3-PTCB)	14—18	16±0.5	0.59	0.15
CS-α(1,1,2-PTCB)	11—15	13±0.5	0.37	0.09

The small values of $\Delta C_p^\circ(T^\circ_{tr})$ and ΔS°_{conf} indicate apparently that the number of the corresponding atomic groups responsible for the transitions in the polymers studied here is relatively small; this is consistent with the data published previously.[10]

The presence of cross-links between the macromolecules can be judged to a certain extent by the values of fractal dimension D, which can be found, according to published data,[20] from experimental values of the heat capacities of substances at low temperatures, *i.e.*, in the range where it can be assumed that $\Delta C_p^\circ \cong C_v$. In the case of polymers studied here, this approximation can be considered to hold with no essential error at $T < 100$ K. Then, it follows from the expression for the heat capacity function in the fractal variant[21] of the Debye heat capacity theory that

$$C_v = 3D(D+1)kN\gamma(D+1)\xi(D+1)(T/\theta_{max})^D, \qquad (2)$$

where D is the fractal dimension, k is the Boltzmann constant, N is the number of atoms in a repeating monomer unit, γ is a gamma function, ξ is the Riemann psi-function, and θ_{max} is the Debye characteristic temperature. The D values can be obtained from the plot for the $\ln C_v$ *vs.* $\ln T$ and the θ_{max} values can be calculated from Eq. (2). The values of these parameters are given below:

Substance	D	θ_{max}/K	δ (%)
CS-β(PVDC)	1.0	543.1	0.57
CS-β(1,2,3-PTCB)	1.1	492.5	0.38
CS-α(1,1,2-PTCB)	1.2	454.6	1.2

Here, δ is the error to which Eq. (2) reproduces the experimental C_p° values for carbynoid structures with the found values of D and θ_{max} in the 25—50 K temperature range.

According to previous publications,[20—22] $D = 1$ corresponds to chain structures, an increase in D from 1 to 2 corresponds to transition from chain to layer structures, and variation of D from 2 to 3 implies the transition to three-dimensional structures. The D values found here for CS may indicate that CS-β(PVDC) is a chain non-cross-linked polymer, while CS-β(1,2,3-PTCB) and CS-α(1,1,2-PTCB) are also chain polymers but having a very small number of intermolecular cross-links, whose formation during dehydrochlorination is quite possible.[10,12]

Let us note in conclusion that the heat capacity of the polymers considered is well reproduced by the Tarasov two-parameter heat capacity equation for chain structures,[22] which takes into account inter-chain interactions.

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

where $C_{1,3}$ is the heat capacity of solids with chain structure (this is indicated by the subscript "1") with allowance for the interaction of chains (the subscript "3"); D_1 and D_3 are designations of the Tarasov and Debye heat capacity functions, respectively (the form of the D_1 and D_3 functions is given, for example, in Ref. 22); $\theta_1 = h\nu_{max}$ and $\theta_3 = h\nu_1$ are the Debye and Tarasov characteristic temperatures, respectively; ν_{max} is the characteristic frequency of vibrations normal to the chain; and ν_1 is the limiting vibration frequency for chain units in the force field of the surrounding chains.

The θ_3/θ_1 ratio is a parameter of interchain interaction, which can vary from 0 to 1; when $\theta_3/\theta_1 = 0$, no chain interactions are involved (this case seems to be purely hypothetical), while $\theta_3/\theta_1 = 1$ is typical of three-dimensional solids.

In the 0—150 K temperature range, Eq. (3) reproduces well the heat capacities of CS-β(PVDC) with $\theta_1 = 675$ K and $\theta_3 = 175$ K; of CS-β(1,2,3-PTCB) with $\theta_1 = 627$ K and $\theta_3 = 124$ K; and of CS-α(1,1,2-PTCB) with $\theta_1 = 584$ K and $\theta_3 = 117$ K. The chain interaction parameter θ_3/θ_1 is the same for all these polymers and equals 2, pointing to substantial chain interactions.

The heat capacity values for CS-β(1,2,3-PTCB) and CS-α(1,1,2-PTCB) are close to each other and are about 1.5 times as great as those for CS-β(PVDC) almost over the whole range studied. This is due, on the one hand, to the similarity of compositions and gross formula masses for the former two CS and, on the other hand, to substantial difference between these values and that for CS-β(PVDC). The C_p° dependence on the gross formula mass is especially pronounced. For example, a calculated molar heat capacity equal to 12, *i.e.*, the same as for carbyne (see Fig. 1, curve *4*), leads to coincidence of curves *1* and *4*. This may imply that the major contribution to the heat capacity of CS-β(PVDC), as in the case of carbyne,[8] is made by the skeletal vibrations of the C atoms, while the contribution of atomic vibrations of other elements present in the CS is relatively small. However, this contribution is significant in the case of CS-β(1,2,3-PTCB) and CS-α(1,1,2-PTCB), as they contain greater numbers of atoms of elements other than carbon than CS-β(PVDC) does.

Thermodynamic functions. To calculate the thermodynamic functions (Table 3), the $C_p^\circ(T)$ dependences were extrapolated from 5—8 K, which is the lower limit of C_p° measurements, down to 0 K using the Debye heat capacity function:

$$C_p^\circ = nD(\theta_D/T), \qquad (4)$$

where D is the Debye heat capacity function, n and θ_D are specially adjusted parameters. For CS-β(PVDC), these are $n = 1$ and $\theta_D = 190.3$ K; for CS-β(1,2,3-PTCB), $n = 1$ and $\theta_D = 293.6$ K; and for CS-α(1,1,2-PTCB), $n = 1$ and $\theta_D = 167.9$ K. With these parameters, Eq. (4) describes the variation of C_p° *vs.* T at 5—12 K with an accuracy of 3.5, 2.8, and 3%, respectively. When calculating the thermodynamic functions, we suggested that

Table 3. Thermodynamic functions of the carbynoid structures

T/K	$C_p^\circ(T)$	$S^\circ(T) - S^\circ(0)$	$H^\circ(T) - H^\circ(0)$	$-[G^\circ(T) - H^\circ(0)]$
	J K^{-1} mol^{-1}		kJ mol^{-1}	
		CS-β(PVDC), M = 17.361 g mol^{-1}		
5	0.017	0.0058	0.00002	0.00001
10	0.1026	0.0424	0.0003	0.0001
15	0.2051	0.1028	0.0011	0.0005
20	0.3946	0.1828	0.0025	0.0012
25	0.8600	0.3170	0.0055	0.0024
30	1.370	0.5201	0.0112	0.0045
40	2.074	1.016	0.0285	0.0121
50	2.644	1.542	0.0522	0.0249
60	3.210	2.074	0.0815	0.0429
70	3.680	2.606	0.1161	0.0663
80	4.350	3.138	0.1560	0.0950
90	4.938	3.686	0.2025	0.1292
100	5.521	4.235	0.2548	0.1688
150	8.753	7.118	0.6157	0.4519
200	12.15	10.08	1.135	0.8814
250	15.20	13.14	1.824	1.462
298.15	17.66	16.01	2.610	2.162
330	20.10	17.93	3.211	2.705
		CS-β(1,2,3-PTCB), M = 19.260 g mol^{-1}		
5	0.0032	0.0011	0	0.000001
10	0.0263	0.0082	0.0001	0.000002
15	0.0840	0.0313	0.0004	0.0001
20	1.135	0.2410	0.0041	0.0007
25	1.667	0.5502	0.0111	0.0026
30	2.208	0.9023	0.0208	0.0063
40	3.306	1.686	0.0483	0.0191
50	4.391	2.542	0.0869	0.0402
60	5.340	3.428	0.1356	0.0701
70	6.292	4.322	0.1938	0.1088
80	7.259	5.226	0.2616	0.1565
90	8.062	6.130	0.3383	0.2133
100	8.928	7.019	0.4228	0.2791
150	13.17	11.47	0.9789	0.7419
200	17.55	15.86	1.746	1.425
250	22.09	20.26	2.738	2.328
298.15	26.08	24.48	3.893	3.406
330	34.60	27.45	4.827	4.231
		CS-α(1,1,2-PTCB), M = 19.819 g mol^{-1}		
5	0.0171	0.0057	0	0.000001
10	0.1390	0.0463	0.0003	0.00012
15	0.7600	0.1830	0.0022	0.0006
20	1.255	0.4704	0.0072	0.0022
25	1.818	0.8124	0.0149	0.0054
30	2.387	1.192	0.0254	0.0104
40	3.511	2.034	0.0549	0.0265
50	4.560	2.933	0.0954	0.0513
60	5.490	3.847	0.1456	0.0852
70	6.434	4.765	0.2053	0.1282
80	7.289	5.681	0.2740	0.1805
90	8.202	6.589	0.3512	0.2418
100	9.437	7.516	0.4393	0.3123
150	14.18	12.28	1.034	0.8070
200	17.90	16.85	1.834	1.536
250	22.34	21.32	2.841	2.491
298.15	26.20	25.58	4.007	3.620
330	30.80	28.44	4.907	4.480

at $T < 5-8$ K, Eq. (4) reproduces the heat capacity values of CS with the same accuracy. The functions (see Table 3) were calculated using the known equations:

$$H^\circ(T) - H^\circ(0) = \int_0^T C_p{}^\circ(T)\mathrm{d}T, \quad (5)$$

$$S^\circ(T) - S^\circ(0) = \int_0^T C_p{}^\circ(T)\mathrm{d}\ln T, \quad (6)$$

$$G^\circ(T) - H^\circ(0) = H^\circ(T) - H^\circ(0) - T[S^\circ(T) - S^\circ(0)]. \quad (7)$$

In Eqs. (5)—(7), $H^\circ(T) - H^\circ(0)$ is enthalpy, $S^\circ(T) - S^\circ(0)$ is entropy without the residual (zero-point) $S^\circ(0)$ value; $C_p{}^\circ(T)$ is the corresponding temperature dependence of the CS heat capacity; and $G^\circ(T) - H^\circ(0)$ is the Gibbs function. The calculation of the thermodynamic functions was described previously (*e.g.,* in Ref. 23).

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