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Reviews

Thermodynamics of copper, silver, gold, and mercury acetylenides

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Thermodynamic characteristics of the copper, silver, gold, and mercury acetylenides obtained from the data of precise calorimetric measurements in the region from 5 to 340 K are considered. Tables of the thermodynamic functions $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$, and $G^\circ(T) - H^\circ(0)$ at 0—340 K, standard enthalpies of combustion ΔH_c°, and thermodynamic characteristics of formation of the acetylenides from simple substances ΔH_f°, ΔS_f°, ΔG_f°, and $\log K_f^\circ$ at 298.15 K and standard pressure are presented. Temperature plots of the heat capacity of the acetylenides were analyzed in the framework of Tarasov's theory and the fractal version of Debye's theory of heat capacity. The values of heat capacity of several acetylenides yet unstudied were estimated.

Key words: copper, silver, gold, and mercury acetylenides; heat capacity; enthalpy of formation; calorimetry; thermodynamics.

Introduction

Interest in copper, silver, gold, and mercury acetylenides composing broad class of organometallic compounds[1] is due first of all to their application in organic synthesis.[2,3] For example, copper acetylenide was successfully used for the synthesis of $Cu(C{\equiv}C)_{20}Cu$,[4] carbyne derivative, *viz.*, the third allotropic carbon modification,[5] which is of great scientific and practical interest.[5—7] In addition, acetylenides possess semiconducting properties,[5,8] which makes them promising for practical use. Chemistry of copper and silver acetylenides is described in the book[5] and reviews.[9,10]

The thermal stability of copper and silver acetylenides increases[11] in the order silver butylacetylenide < copper butylacetylenide < silver phenylacetylenide < copper phenylacetylenide. Acetylenides were shown[12—14] to be coordination polymers. The thermodynamic functions[15] of several acetylenides at 298.15 K and thermochemical parameters of formation[16] of acetylenides have previously been determined. For some thermodynamic characteristics of acetylenides, see also the monograph.[17] A calorimetric study of gold and mercury acetylenides have recently been carried out at the Laboratory of Polymer Thermodynamics at the Research Institute of Chemistry at the Nizhnii Novgorod State University. Thus, the results of calorimetric studies have been reported in various publications but have never been generalized. Meanwhile, available data are sufficient for generalization and analysis, which seems fruitful for the formation of general views about acetylenide thermodynamics and revealing possible relations of their thermodynamic properties to the composition, structure, and temperature.

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Table 1. Some characteristics of acetylenides studied

Compound	Molecular weight	Found / Calculated (%) C	H	M	Empirical formula	Reference
Copper vinylacetylenide (**1**)	144.614	41.83 41.92	2.72 2.64	55.45 55.44	$C_2H_2C_2Cu$	21
Copper butylacetylenide (**2**)	144.680	49.72 49.81	6.58 6.27	43.70 43.92	$C_4H_9C_2Cu$	22
Copper hexylacetylenide (**3**)	172.730	55.63 54.16	7.59 7.89	36.78 36.98	$C_6H_{13}C_2Cu$	23
Copper phenylacetylenide (**4**)	164.670	58.81 58.31	3.24 3.04	62.05 61.29	$C_6H_5C_2Cu$	24
Silver phenylacetylenide (**5**)	208.991	45.57 45.70	2.35 2.40	52.08 51.90	$C_6H_5C_2Ag$	25
Фенилацетиленид золота (**6**)	298.094	32.07 32.23	1.67 1.69	65.75 66.07	$C_6H_5C_2Au$	26
Gold phenylacetylenide (**7**)	178.701	60.64 60.49	4.14 3.95	35.92 35.56	$C_7H_7C_2Cu$	21
Copper phenylethynylacetylenide (**8**)	188.696	63.15 63.65	3.11 2.67	33.60 33.68	$C_8H_5C_2Cu$	21
Mercury diphenylacetylenide (**9**)	402.845	47.46 47.70	2.48 2.50	49.77 49.79	$(C_6H_5C_2)_2Hg$	27

In this work, we examined and generalized the results of calorimetric studies of the thermodynamic properties of metal acetylenides. Using our and published data, we found relations of their properties to the composition, structure, and temperature under a standard pressure.

Experimental

Characteristics of samples. Samples of copper, silver, gold, and mercury acetylenides were prepared by previously described procedures.[18—20] Some published characteristics are presented in Table 1. According to X-ray analysis data, all the acetylenides are crystalline compounds. More detailed characteristics of the studied samples can be found in original works cited in Table 1.

Calorimetric apparatus. For measuring the heat capacity in the 5—340 K region, we used partially or completely automated calorimeters UUNT and TAU-1, whose designs and working procedures have previously been described.[28—30] Note that these calorimeters allow the determination of C_p° values of solid and liquid substances with an error of 1.5—2% at helium temperatures, 0.5% in the 10—40 K interval, and 0.2% in a region of 40—340 K. The main characteristics of experiments on measuring the heat capacities of acetylenides are presented in Table 2.

The combustion energy of acetylenides was measured using a V-08 calorimeter with a static bomb and an isothermic shell. The calorimeter was improved[32] at the Research Institute of Chemistry at the Nizhnii Novgorod State University. The calibration of the calorimeter with burning of succinic acid prepared at the D. I. Mendeleev Research Institute of Metrology (St. Petersburg) gave the standard enthalpy of combustion of the acid that coincided with the passport value with an error of 0.017%. The energies of combustion of acetylenides were determined under the calorimetric bomb conditions at 298.15 K (Table 3). Combustion was complete in all experiments. On calculating $\Delta\bar{U}_c$, standard thermochemical corrections for the combustion of auxiliary substances used in acetylenide combus-

Table 2. Parameters of experiments on measuring the heat capacity C_p°/J K^{-1} mol^{-1}) of acetylenides

Compound	T*/K	N**	Scatter*** ΔT/K	Deviation (%)	Reference
1	14.3—315	79	14.3—50	1	21
			50—330	0.3	
2	14—334	81	14—50	1	22
			50—330	0.3	
3	6.5—340	171	6.5—80	1.1	23
			80—250	0.3	
			250—330	0.2	
4	11.6—330	73	11.6—50	1	24
			50—330	0.3	
5	5—330	76	5—10	1	25
			10—30	0.5	
			30—330	0.2	
6	13—330	90	13—80	1	26
			80—330	0.2	
7	13.9—333	88	13.9—50	1.2	21
			50—330	0.2	
8	11.6—327	80	11.6—50	1	21
			50—327	0.2	
9	5—340	161	5—80	1	31
			80—340	0.2	

* Temperature region of heat capacity measurement.

** Number of experimental points C_p°.

*** Scatter of experimental C_p° values near the corresponding averaging curves of C_p° *vs.* T.

Table 3. Data of experiments on acetylenide combustion at $T = 298.15$ K and $p = 101.325$ kPa

Compound	Number of entries	m /g	Q /J	$[m^{\exp}(CO_2)/m^{\mathrm{calc}}(CO_2)] \cdot 100\%$	$\Delta\bar{U}_c$ /J g^{-1}	Reference
1	8	0.1673—0.2323	27403—29087	99.15—99.30	21246±18	33
2	7	0.2509—1.1043	20586—30364	99.81±0.03	26763±18	22
3	6	0.2026—0.7695	14778—21712	98.51—100.1	29298.4±19.2	23
4	8	0.2035—1.1531	25204—30260	100.11±0.02	26198±8	24
5	8	0.4694—1.2191	21957—29136	96.64±0.07	20136±7	25
9	5	1.3771—1.4376	29929—31490	—	20707±6	27

Note. Designations: m is the weight of the sample, Q is the total amount of energy released when the substance is burnt in a calorimetric bomb, $\Delta\bar{U}_c$ is the mean value of the combustion energy, and $[m^{\exp}(CO_2)/m^{\mathrm{calc}}(CO_2)] \cdot 100\%$ is the ratio of CO_2 weights found in the combustion products to calculated by its chemical formula.

tion were applied. The $\Delta\bar{U}_c$ values are given with the doubled root-mean-square error calculated by the formula

$$\delta = 2[\sum x^2/n(n-1)^{1/2}], \quad (1)$$

where x is deviation from the mean value, and n is the number of experiments.

Results and Discussion

Heat capacity. The found temperature plots of the heat capacity $C_p^\circ = f(T)$ for the studied acetylenides (Figs. 1 and 2) have no specific feature for all acetylenides: the heat capacity increases smoothly with temperature in the whole temperature region.

The heat capacity of copper phenylacetylenide is invariably lower than those of silver and gold phenylacetylenides (see Fig. 1). The heat capacities of the latters virtually coincide at $T < 70$ K, and at $T > 70$ K the C_p° values of gold acetylenide are somewhat higher than the corresponding values for silver acetylenide. It has previously been mentioned[26] that the heat capacities of the phenylacetylenides are proportional to the atomic masses of the incorporated Au, Ag, and Cu atoms. At $T = 298.15$ K the C_p° values of these acetylenides are described by the equation

$$C_p^\circ = 149.87 + 0.0645x, \quad (2)$$

and at 200 K

$$C_p^\circ = 109.87 + 0.0488x, \quad (3)$$

where x is the atomic mass of Au, Ag or Cu. Equations (2) and (3) reproduce the experimental data on C_p° at the corresponding temperatures with an error within 0.02 and 0.03%, respectively.

At $T > 70$ K the plots of C_p° *vs.* T for copper acetylenides are arranged in the following sequence: vinylacetylenide < phenylacetylenide < butylacetylenide < benzylacetylenide < phenylacetylenide < hexylacetylenide (see Fig. 2, curves *1—6*).

For many compounds the contribution of methylene groups to the thermodynamic properties is additive,[32,34—38] and the corresponding values are usually proportional to the number of C atoms in the alkyl group. It can be assumed the same is valid for alkylacetylenides. Then, based on the experimental data for C_p° of copper butyl- and hexylacetylenides, we can

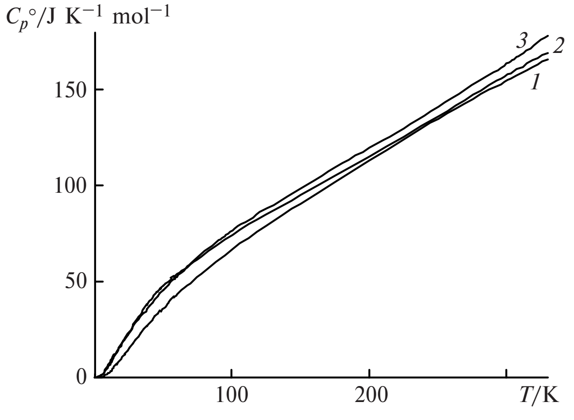

Fig. 1. Heat capacity of copper (*1*), silver (*2*), and gold (*3*) acetylenides.

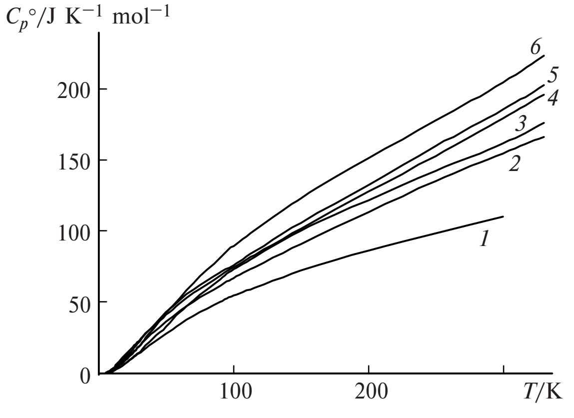

Fig. 2. Heat capacity of copper vinyl- (*1*), phenyl- (*2*), butyl- (*3*), benzyl- (*4*), phenylethynyl- (*5*), and hexylacetylenides (*6*).

obtain the equation of the plot, *e.g.*, for the heat capacity of copper alkylacetylenides *vs.* number of C atoms, which enables the estimation of the heat capacity of yet unstudied alkylacetylenides. Using the C_p° values for copper butyl- and hexylacetylenides at 298.15 K (see section *Thermodynamic functions*), we obtained

$$C_p^\circ\ (298.15\ \text{K}) = 32.8 + 21.3n, \qquad (4)$$

where n is the number of C atoms in a copper alkylacetylenide molecule. Equation (4) reproduces the numerical values of heat capacity (J K^{-1} mol^{-1}) of these compounds with an error within ±0.02%. In the general case, at any temperature

$$C_p^\circ = a + bn, \qquad (5)$$

where a and b are the coefficients at the corresponding temperatures. Equation (5) is valid for the temperature region in which the heat capacity of alkylacetylenides is a linear function of temperature: $C_p^\circ(T) \sim T$. For butyl- and hexylacetylenides, this is the region of $T > 150$ K. For the estimation of C_p° of alkylacetylenides with n from at least 2 to 10, the a and b coefficients can easily be obtained using the heat capacities of butyl- and hexylacetylenides at the corresponding temperatures (the data on them are presented in section *Thermodynamic functions*). Below we present C_p°/J K^{-1} mol^{-1} at 298.15 K of alkylacetylenides for n = 1—3, 5, and 7—10 for methyl-, ethyl-, propyl-, amyl-, heptyl-, octyl-, nonyl-, and decylacetylenides, respectively, calculated from Eq. (4).

n	1	2	3	5	7	8	9	10
C_p°	54.1	75.4	96.7	139.3	160.6	203.2	224.5	245.8

Equations of the type (4) and (5) can likely be applied for the estimation of other thermodynamic properties (enthalpy, entropy, Gibbs's function, and others) of acetylenides, as it is possible for some classes of organic and organoelement compounds.[32,34—38] Equations of the type (2) and (3) allow the determination to which extent the contribution of the Ag and Au atoms to the heat capacity of phenylacetylenides is higher than the contribution of the Cu atoms. At 298.15 K the corresponding differences are 2.80 and 5.80 J K^{-1} mol^{-1}. It can be assumed that this is valid for other acetylenides. Then, based on the C_p° values for copper acetylenides (they are presented in section *Thermodynamic functions*), we can easily find C_p° for silver and gold acetylenides, the analogs of copper acetylenides. The calculations give the following values of C_p°/J K^{-1} mol^{-1} at 298.15 K for the corresponding silver and gold compounds: 112.2 and 118.0 for vinylacetylenides, 163.4 and 169.2 for butylacetylenides, 206.0 and 211.8 for hexylacetylenides, 181.3 and 187.1 for benzylacetylenides, and 187.2 and 193.0 for phenylethynylacetylenides.

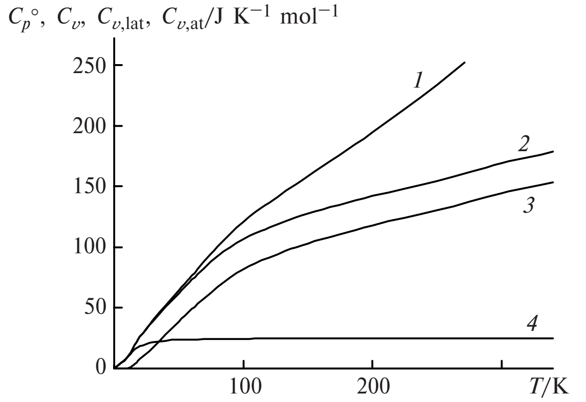

Fig. 3. Heat capacity of mercury diphenylacetylenide[31]: isobaric C_p° (*1*), isochoric C_v (*2*), lattice $C_{v,\text{lat}}$ (*3*), and atomic $C_{v,\text{at}}$ (*4*).

The isobaric (C_p°) and isochoric (C_v) heat capacities of mercury diphenylacetylenide and terms of the heat capacity: the lattice ($C_{v,\text{lat}}$) and atomic ($C_{v,\text{at}}$) contributions[31] are presented in Fig. 3. The isochoric heat capacity was calculated[31] by the Nernst—Lindeman formula[39] using the experimental values of C_p° and melting point of copper diphenylacetylenide $T_{\text{fus}}^\circ = 397.6$ K:[27]

$$C_p^\circ - C_v = A_0 C_v^2 T/T_{\text{fus}}^\circ, \qquad (6)$$

where $A_0 = 0.00512$ mol K^{-1} J^{-1} is a universal constant. Assuming that at $T < 30$ K $C_p^\circ = C_v = C_{v,\text{lat}}$, taking into account Debye's function for the heat capacity

$$C_p^\circ = nD(\Theta_\text{D}/T) \qquad (7)$$

(D is the symbol of Debye's function of heat capacity, Θ_D is the characteristic temperature, and n is the number of freedom degrees of vibrations of a molecule in the nodes of the crystalline lattice), we calculated $C_{v,\text{lat}}$ for the 0—340 K region. The Θ_D value found from the experimental data on C_p° at $T < 30$ K was used for the calculation of $C_{v,\text{lat}}$ in the whole indicated interval.

The atomic contribution was calculated from the equation

$$C_{v,\text{at}} = C_v - C_{v,\text{lat}}, \qquad (8)$$

because $C_v = C_{v,\text{lat}} + C_{v,\text{at}}$. The plot $C_{v,\text{lat}}(T)$(see Fig. 3) is a curve with saturation, and the $C_{v,\text{lat}}$ value becomes constant already at $T = 70$ K. The atomic component of the heat capacity $C_{v,\text{at}}$ increases smoothly with temperature. The contribution of atomic vibrations appears at 20 K, and $C_{v,\text{at}} = C_{v,\text{lat}}$ already at 35 K. The ratio $C_p^\circ/C_v = \gamma$ varies for the compound in question from 1 (at temperatures close to 0 K) to 1.8 (at 340 K), which is typical, in general, of organic crystals.[39]

It was of interest to obtain the values of fractal dimensionality D for the acetylenides, which is the most important magnitude in the fractal theory of heat capacity of solids,[40,41] because it allows conclusions about the character of heterodynamicity of solids.[42] According to

Table 4. Fractal dimensionality (D) and characteristic temperature (Θ_{max}) in Eqs. (9) and (10) for the studied acetylenides in the 25—50 K range

Compound	D	Θ_{max} /K	δ* (%)
1	1.9	210.1	0.59
2	2.0	232.2	0.74
3	1.8	271.4	0.19
4	1.7	235.5	0.26
5	1.3	206.8	0.44
6	1.0	285.0	0.80
7	1.5	218.8	0.39
8	1.7	232.5	0.15
9	1.0	331.0	0.60

* The error with which Eqs. (9) and (10) reproduce the heat capacity of acetylenides using the D and Θ_{max} parameters found for them in the temperature range from 25 to 50 K.

previous data,[40] D can be found from the plot $\ln C_v = f(\ln T)$, which follows from the formula

$$C_v = 3D(D+1)kN\gamma(D+1)\xi(D+1)(T/\Theta_{max})^D, \tag{9}$$

where k is the Boltzmann constant, N is the number of atoms in a molecule, $\gamma(D+1)$ is the γ-function, $\xi(D+1)$ is the Rieman ξ-function, and Θ_{max} is the maximum characteristic temperature. For a specific solid $3D(D+1)kN\gamma(D+1)\xi(D+1) = A$ is the constant value, and Eq. (9) can be written as

$$\ln C_v = \ln A + D\ln(T/\Theta_{max}). \tag{10}$$

Assuming[43] that at $T < 50$ K for the studied organoacetylenides $C_p{}^\circ = C_v$, then using the corresponding experimental data on the heat capacity, we obtain D (Table 4).

For solids with the chain, laminated, and spatial structures, the D values are[40,44] 1, 2, and 3, respectively. The fractional D values indicate the mixed heterodynamic structure of the solids. For the acetylenides under study. D range from 1.0 to 2.0, *i.e.*, they have the chain ($D = 1$), laminated-chain ($1 < D < 2$), and laminated ($D = 2$) structures. The fractal dimensionality D for gold and mercury phenylacetylenides is 1, *i.e.*, they possess the chain structure. Vinylacetylenide and, most likely, butylacetylenide are characterized by the laminated structure because for them $D = 2$. Other acetylenides have the laminated-chain structure with predomination of layers or chains, depending on the D layers: for $D > 1.5$ layers predominate, and for $D < 1.5$ chains predominate.

The heat capacity of solids with the laminated structure is described[42,44] by Tarasov's biparametric function for heat capacity taking into account the interaction of the layers

$$C_{2,3} = D_2(\Theta_2/T) - (\Theta_3/\Theta_2)[D_2(\Theta_3/T) - D_3(\Theta_3/T)], \tag{11}$$

where $C_{2,3}$ is the heat capacity of the interacting layers, D_2 is Tarasov's function for heat capacity, D_3 is Debye's function for heat capacity, and Θ_2 and Θ_3 are Tarasov's and Debye's characteristic temperatures, respectively. The Θ_3/Θ_2 ratio characterizes the interaction of the layers (interaction parameter). It changes within 0 and 1, and $\Theta_3/\Theta_2 = 0$ corresponds to hypothetical laminated substances without interaction between layers, whereas $\Theta_3/\Theta_2 = 1$ corresponds to substances, whose energies of interaction between the layers and inside the layers are the same, *i.e.*, in this case, we deal with a spatial structure.

The heat capacity of solids with the chain structure is described by Tarasov's biparametric function for heat capacity[42,44] taking into account the chain interaction

$$C_{1,3} = D_1(\Theta_1/T) - (\Theta_3/\Theta_1)[D_2(\Theta_3/T) - D_3(\Theta_3/T)], \tag{12}$$

where $C_{1,3}$ is the heat capacity of interacting chains, D_1 is Tarasov's one-dimensional function for heat capacity, D_3 is Debye's function for heat capacity, Θ_1 and Θ_3 are Tarasov's and Debye's characteristic temperatures, respectively, and the Θ_3/Θ_1 ratio is the chain interaction parameter (as in the case of solids with the laminated structure, it changes from 0 to 1).

The heat capacity of solids with the laminated-chain structure is described by the equation

$$\begin{aligned} C_{1,2,3} = {} & D_1(\Theta_1/T) - (\Theta_2/\Theta_1)[D_1(\Theta_2/T) - D_2(\Theta_2/T)] - \\ & - [\Theta_3{}^2/(\Theta_1\Theta_2)][D_1(\Theta_3/T) - D_3(\Theta_3/T)]. \end{aligned} \tag{13}$$

The specific form of the D_1, D_2, and D_3 functions is presented in several works.[42,44—46] Starting from the experimental data on $C_p{}^\circ$ for the acetylenides studied (see section *Thermodynamic functions*) and Eqs. (11)—(13), we can select the Θ_1, Θ_2, and Θ_3 parameters, estimated the interaction parameter of layers (Θ_3/Θ_2) and chains (Θ_3/Θ_1) for acetylenides under consideration. The heat capacity functions $C_{2,3}$ and $C_{1,3}$ are tabulated[47,48] and, hence, the selection of the Θ_1, Θ_2, and Θ_3 values in Eqs. (11) and (12) is not difficult. Tables for $C_{1,2,3}$ are not available, and this impedes the selection of the corresponding parameters for Eq. (13). Therefore, to estimate the interaction parameters of layers and chains in laminated-chain acetylenides with $1.5 < D < 2$, we used Eq. (11), and for those characterized by $1 < D < 1.5$, Eq. (12) was used. The Θ_1, Θ_2, and Θ_3 parameters were selected for the 25—30 K temperature interval. As a result, we obtained the following values of interaction parameters: for the chain gold and mercury phenylacetylenides Θ_3/Θ_1 are 0.5 and 0.9, respectively; for the laminated copper butylacetylenide and vinylacetylenide Θ_3/Θ_2 is 0.8 and 0.3, respectively; for laminated-chain copper hexyl-, phenyl-, and benzylacetylenides it is 0.3; and for silver phenylethynylacetylenide and phenylacetylenide it is 0.6 and 0.8, respectively.

Thermodynamic functions. The values of enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T)$, and the Gibbs function $G^\circ(T) - H^\circ(0)$ for the studied acetylenides are presented in Table 5. For the calculation of thermodynamic functions, the $C_p{}^\circ$ values of acetylenides were extrapolated

Table 5. Thermodynamic functions of the studied acetylenides under standard pressure

T /K	C_p°	$S^\circ(T)$	$H^\circ(T) - H^\circ(0)$	$-[G^\circ(T) - H^\circ(0)]$
	J K^{-1} mol^{-1}		kJ mol^{-1}	
Copper vinylacetylenide (**1**)[21]				
5	0.1604	0.0533	0.00021	0.00005
10	1.271	0.4281	0.0032	0.00104
15	3.800	1.382	0.0154	0.0053
20	6.960	2.903	0.0423	0.0158
25	10.53	4.835	0.0859	0.0349
50	27.62	17.51	0.5679	0.3078
100	54.26	45.71	2.679	1.893
200	86.00	93.86	9.807	8.966
298.15	109.4	133.3	19.62	20.38
315	114.2	138.8	21.30	22.42
Copper butylacetylenide (**2**)[22]				
5	0.1920	0.0460	0.0002	0.00003
10	1.554	0.4932	0.0038	0.0011
15	4.032	1.565	0.0175	0.0060
20	6.935	3.105	0.0045	0.0175
25	10.89	5.063	0.0888	0.0377
50	32.80	19.29	0.6339	0.3306
100	72.66	55.38	3.351	2.188
200	121.8	122.1	13.25	11.16
298.15	160.6	178.3	27.19	25.97
330	175.8	195.3	32.53	31.92
Copper hexylacetylenide (**3**)[23,49]				
5	0.3370	0.1128	0.0004	0.000141
10	2.018	0.8112	0.0059	0.00218
15	5.010	2.149	0.0230	0.00927
20	9.000	4.134	0.0579	0.02476
25	13.97	6.670	0.1152	0.05152
50	42.10	24.89	0.8131	0.4313
100	89.21	69.43	4.163	2.780
200	151.3	151.6	16.38	13.95
298.15	203.2	221.6	33.75	32.33
340	230.2	250.0	42.79	42.20
Copper phenylacetylenide (**4**)[24]				
5	0.2887	0.0658	0.00029	0.00004
10	2.218	0.7302	0.0056	0.00165
15	6.080	2.320	0.0259	0.00888
20	10.56	4.715	0.0681	0.0262
25	14.66	7.510	0.1311	0.0566
50	35.95	24.58	0.7775	0.4516
100	66.90	59.80	3.406	2.574
200	113.0	120.7	12.45	11.68
298.15	154.0	173.8	25.65	26.17
330	166.1	190.0	30.73	31.97
Copper benzylacetylenide (**7**)[21]				
5	0.4440	0.1428	0.0006	0.00016
10	3.355	1.053	0.0078	0.0027
15	8.320	3.325	0.0367	0.0132
20	13.16	6.382	0.0904	0.0372
25	18.27	9.865	0.1689	0.0777
50	40.72	29.79	0.9199	0.5694
100	74.44	69.26	3.862	3.064
200	127.6	137.4	13.99	13.48
298.15	178.5	197.6	28.96	29.95
330	119.6	216.6	34.98	36.50
Copper phenylethynylacetylenide (**8**)[21]				
5	0.3550	0.1061	0.0004	0.00009
10	2.688	0.9196	0.0069	0.0022
15	6.950	2.784	0.0307	0.0110
20	11.52	5.384	0.0765	0.0312
25	16.56	8.489	0.1466	0.0657
50	42.62	28.33	0.8999	0.5163
100	76.03	69.37	3.956	2.981
200	132.3	139.9	14.46	13.52
298.15	184.4	202.7	30.06	30.38
330	202.3	222.3	36.21	37.14
Silver phenylacetylenide (**5**)[25]				
5	1.345	0.6494	0.00233	0.00092
10	5.645	2.738	0.0187	0.00872
15	11.52	6.102	0.00612	0.0304
20	13.00	10.30	0.1350	0.0711
25	23.89	14.96	0.2399	0.1341
50	47.53	39.47	1.158	0.8148
100	74.51	81.52	4.268	3.883
200	115.1	145.7	13.76	15.38
298.15	156.8	199.3	27.08	32.14
330	169.3	215.9	32.28	38.97
Gold phenylacetylenide (**6**)[26]				
5	1.168	0.3918	0.0015	0.00049
10	6.827	2.745	0.0201	0.0074
15	12.69	6.652	0.0697	0.0303
20	17.62	11.01	0.1454	0.0748
25	23.12	15.52	0.2470	0.1410
50	45.27	38.77	1.117	0.8214
100	76.56	80.59	4.225	3.834
200	119.5	147.2	14.08	15.36
298.15	162.6	202.9	27.91	32.58
330	178.4	220.2	33.34	39.32
Mercury diphenylacetylenide (**9**)[31,49]				
5	1.744	0.5908	0.0022	0.00074
10	8.67	3.801	0.0273	0.0107
15	17.44	8.953	0.0924	0.0419
20	26.22	15.18	0.2016	0.1020
25	32.54	21.74	0.3492	0.1944
50	64.20	54.14	1.563	1.144
100	120.8	116.9	6.259	5.435
200	194.4	223.6	22.06	22.67
298.15	276.8	315.9	45.01	49.17
340	319.4	354.9	57.47	63.21

from T (the lower limit of measurements, see Table 2) to 0 K by Debye's function of heat capacity (Eq. (7)) using the specially selected parameters n and Θ_D (Table 6). For this n we accepted that in the studied temperature interval Eq. (7) reproduces the heat capacity with the same error as that presented in Table 6. The enthalpy and entropy were calculated by the numerical integration from the curves $C_p^\circ = f(T)$ and $C_p^\circ = f(\ln T)$, and the Gibbs function was calculated from the enthalpy and entropy at the corresponding temperatures. The procedure of calculation of the functions has been described previously (see, *e.g.*, Ref. 49). We believe that the error of the calculated functions is from 2 to 1%, 0.5%, and 0.2—0.3% at $T < 30$ K, in an

Table 6. Selected parameters n and Θ_D in Eq. (6)

Compound	n	Θ_D	T*	δ** (%)
		K		
1	3	115.2	14—19	1
2	2	94.20	14—19	1
3	3	107.4	14—19	0.3
4	3	94.50	11—16	1
5	3	65.68	14—20	1.2
6	3	59.09	14—18	0.6
7	4	91.04	14—19	3
8	3	88.30	14—19	1
9	3	51.45	6—9	1.7

* The temperature interval for which n and Θ_D in Eq. (7) were selected.

** The error with which Eq. (7) describes experimental values of heat capacity in the indicated T interval with the selected n and Θ_D values.

Table 7. Enthalpy of combustion and thermodynamic parameters of formation of the copper, silver, gold, and mercury acetylenides in the crystalline state at T = 298.15 K and p = 101.325 kPa

Compound	$-\Delta H_c°$	$-\Delta H_f°$	$-\Delta G_f°$	$-\Delta S_f°$ /J K^{-1} mol^{-1}	$\log K_f°$	Reference
	kJ mol^{-1}					
1	2456.0±1.7	−296.0±2.8	−331.8±1.0	119.3±1.0	58.12	33
2	3877.0±2.6	−73.2±3.5	−214.6±3.7	474.3±0.7	37.59	22
3	5067.7±3.3	100.4±3.3	101.5±3.4	677.1±0.6	−17.8	23, 49
4	4316.0±1.3	−296.0±2.1	−365.0±2.3	231.6±0.7	63.94	24
5	4209.0±1.7	−346.0±1.7	−410.0±1.9	215.4±0.8	71.91	25
6	—	—	—	216.7±1.3	—	26
7	—	—	—	344.0±1.0	—	*
8	—	—	—	214.2±0.6	—	*
9	8344.6±4.8	−621.3±5.2	−771±6	504.5±2.3	−135.3	31, 49

* This work.

interval of 30—80 K, and from 80 to 330 K, respectively.

Enthalpies of combustion and thermodynamic parameters of formation. Table 7 contains the thermodynamic characteristics of formation for all studied acetylenides. The enthalpies of combustion $\Delta H_c°$ were calculated from the energies of combustion of the studied samples at the standard pressure $\Delta U_c°$, and they were calculated in turn by the average energies of combustion $\Delta \bar{U}_c$ (see Table 3). The calculation procedure has previously been described in detail.[50] The enthalpies of formation $\Delta H_f°$ of copper vinyl-, butyl-, hexyl-, and phenylacetylenides and silver phenylacetylenide were calculated from the $\Delta H_c°$ values, enthalpies of formation of liquid water, gaseous carbon dioxide, and crystalline metal oxides[51] at T = 298.15 K and p = 101.325 kPa. The entropies of formation $\Delta S_f°$ were calculated from the entropies $S°(T)$ of the acetylenides studied (see Table 5), and the $S°(0)$ value was neglected. The Gibbs functions $\Delta G_f°$ for acetylenide formation from simple substances at 298.15 K and standard pressure were calculated by the $\Delta H_f°$ and $\Delta S_f°$ values at 298.15 K.

All values presented in Table 7 are referred to the combustion and formation of the acetylenides studied. As an example, let us consider the processes of combustion and formation of copper hexylacetylenide

$$\mathrm{C_8H_{13}Cu\ (cr.) + 11.75\ O_2\ (g.) =}$$
$$\mathrm{= 8\ CO_2\ (g.) + 6.5\ H_2O\ (liq.) + CuO\ (cr.),}$$

$$\mathrm{8\ C\ (cr.,\ gr.) + 6.5\ H_2\ (g.) + Cu\ (cr.) = C_8H_{13}Cu\ (cr.),}$$

where the physical state of reactants are indicated in parentheses: cr. is crystalline, g. is gaseous, liq. is liquid and gr. is graphite.

The logarithms of thermodynamic equilibrium constants of acetylenide formation from simple substances were calculated from $\Delta G_f°$ using the equation

$$\log K_f° = -\Delta G_f°/[2.303R \cdot 298.15\ (\mathrm{K})], \qquad (14)$$

where R is the universal gas constant.

* * *

In this work, we considered for the first time all published to date thermodynamic characteristics of copper, silver, gold, and mercury acetylenides: temperature plots of the heat capacity $C_p° = f(T)$, enthalpy

$H°(T) - H°(0)$, entropy $S°(T)$, and Gibbs function $G°(T) - H°(0)$ for the region from 0 to 340 K; standard values of enthalpies of combustion $\Delta H_c°$ and formation $\Delta H_f°$, entropy $\Delta S_f°$, Gibbs function $\Delta G_f°$ of formation at $T = 298.15$ K and standard pressure.

A linear dependence of the heat capacity of copper, silver, and gold phenylacetylenides on the mass of the corresponding metal atom at $T > 150$ K was observed. The difference in the contributions of the Ag and Au atoms to the heat capacity of these acetylenides and the contribution of the Cu atom at $T = 298.15$ K were estimated. Under the assumption of similar differences for other acetylenides, we determined the heat capacity values for silver and gold acetylenides with the same composition as the studied copper acetylenides. Using the data on the temperature plots of the acetylenides and the fractal version of Debye´s theory of heat capacity, we found the fractal dimensionalities D for each acetylenide studied. For the studied acetylenides, $1 \leq D \leq 2$, *i.e.*, they have the linear ($D = 1$), laminated ($D = 2$) or laminated-chain ($1 < D < 2$) structure. The heat capacity of these structures is described by the corresponding Tarasov´s functions of heat capacity. Based on the selection of the corresponding functions for the acetylenides considered and taking into account the experimental plots of their heat capacities, we estimated the corresponding interaction parameters of chains and layers. They vary from 0.3 for copper phenylacetylenide to 0.9 for mercury phenylacetylenide. Thus, analysis of the temperature plots of the heat capacities on the basis of the theory of heat capacity of solids gave a concept on the heterodynamic character of the acetylenides studied.

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