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Thermodynamic Properties of Tetraphenyltetrahydroxycyclotetrasiloxane, Octaphenyltetrahydroxytricyclooctasiloxane, Octaphenylpentacyclosilsesquioxane, and Polyphenylsilsesquioxane in the Range 0–300 K

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Abstract — The temperature dependences of the heat capacities of crystalline tetraphenyltetrahydroxycyclotetrasiloxane, octaphenyltetrahydroxytricyclooctasiloxane, and octaphenylpentacyclosilsesquioxane and of glassy polyphenylsilsesquioxane were measured in the range 6–300 K with an adiabatic vacuum calorimeter, with an accuracy of ~0.3%. From these data, the thermodynamic functions $C_p^0(T)$, $H^0(T) - H^0(0)$, $S^0(T) - S^0(0)$, and $G^0(T) - H^0(0)$ of these substances were calculated for the range 0–300 K. The standard entropies of their formation from elements at 298.15 K, $\Delta_f S^0$, and the entropies of mutual transformations of these substances in the range 0–298.15 K were calculated.

Hydrolysis of phenyltrichlorosilane followed by polymerization of hydrolysis products yields, along with the ladder polymer, polyphenylsilsesquioxane of molecular weight from 2×10^5 to 10^6, also low-molecular-weight products: tetraphenyltetrahydroxycyclotetrasiloxane **I**, octaphenyltetrahydroxytricyclooctasiloxane **II**, and octaphenylpentacyclosilsesquioxane **III**; polymerization of **III** also yields polyphenylsilsesquioxanes **IV** [1–3]. Formation of ladder polyorganosilsesquioxanes from cage cyclic organosilsesquioxanes is a rare example of transformation of polycyclic structures into a ladder macromolecular chain [4]. It was shown that the forming polyphenylsilsesquioxane consists of rigid double polymeric bonds with the *cis*-syndiotactic structure [5]; it is the first synthesized polymer structurally similar to such double-chain natural polymers as polypeptides and nucleic acids [1]. It shows promise as a heat-resistant insulating material [6, 7].

It is very interesting to study the thermodynamic properties of octaphenylpentacyclosilsesquioxane, a cubic octamer of unique structure, and to determine the thermodynamic characteristics of mutual transformations of **I**–**IV**.

The temperature dependence of the heat capacity of **I**–**IV** in the range from 68 to 300 K was studied calorimetrically in [8, 9]. Today it is feasible to study the temperature dependences of the heat capacities of these compounds at considerably lower temperatures (down to 5–10 K), which is necessary for correctly performing thermodynamic calculations. Our goal was a calorimetric study of $C_p^0 = f(T)$ for **I**–**IV** in the range 6–90 K and calculation from these data and the data from [8, 9] of the thermodynamic functions $C_p^0(T)$, $H^0(T) - H^0(0)$, $S^0(T) - S^0(0)$, and $G^0(T) - H^0(0)$ for the range 0–300 K, of the standard entropies of formation of **I**–**IV** from the elements, $\Delta_f S^0$, at 298.15 K, and of the entropies of mutual transformations of **I**–**IV** in the range 0–298.15 K (see scheme).

Heat capacity. The figure shows the temperature dependences of the heat capacity C_p^0 of **I**–**IV**, namely, the experimental C_p^0 values and the averaging curves $C_p^0 = f(T)$ for the range 6–300 K. The heat capacities in the range 0–6 K were estimated by extrapolation of the experimental C_p^0 values using the Debye heat capacity function (1):

$$C_p^0 = nD(\theta_D). \quad (1)$$

Here D is the Debye heat capacity function, and n and θ_D are specially selected parameters having the following values:

Comp. no.	n	θ_D, K
I	5	74.44
II	10	53.85
III	15	72.24
IV	8	70.25

With these values of n and θ_D, Eq. (1) describes the experimental C_p^0 values of **I**–**IV** in the range 6–

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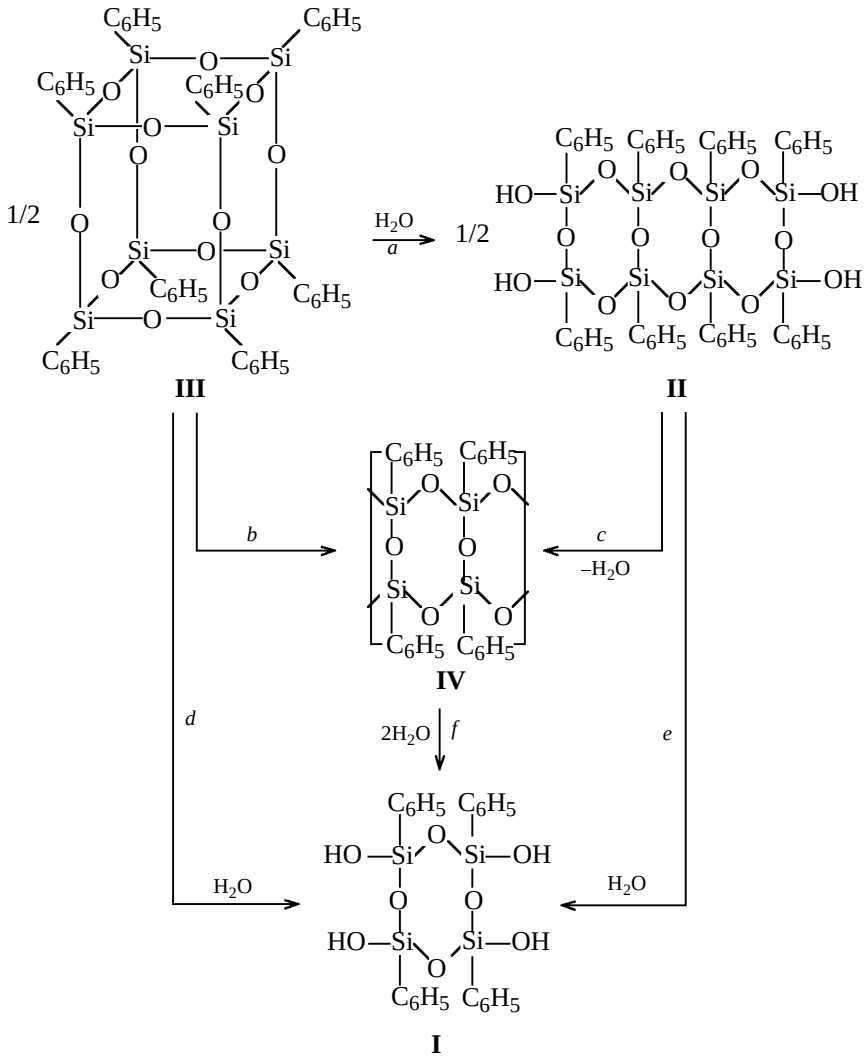


12 K with a ±1.5% accuracy. We assumed that, at $T <$ 6 K, it reproduces the C_p^0 values with approximately the same accuracy. In the examined temperature range, compounds **I**–**III** occur in the crystalline state, and compound **IV**, in the glassy state. As seen from the figure, the temperature dependences of the heat capacities of **I**–**IV** have no irregularities: C_p^0 smoothly grows with temperature.

Of particular interest is the temperature dependence of the heat capacity of **IV**, a polymer of unusual structure. From the experimental data on the heat capacity of **IV**, we estimated the fractal dimensionality D, the key parameter in the fractal version of the Debye heat capacity theory [10, 11]. The D value was determined from the plot of $\ln C_v$ vs. $\ln T$. At $T < 50-60$ K, we assumed that $C_p^0 \div C_v$. Then, Eq. (2) given in [10] [N is the number of atoms in the molecule; k, Boltzmann constant; $\Gamma(D + 1)$, γ function; $\xi(D + 1)$, Riemann ξ function; and θ_{max}, characteristic temperature] can be written as follows:

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

$$C_v = AT^D. \quad (3)$$

Here, $A = [3D(D + 1)kN\xi(D + 1)\zeta(D + 1)]/\theta_{max}$. Then, the D values can be readily determined from the $\ln C_v$–$\ln T$ curves as the slopes of their linear portions. As a result, we obtained the following D and θ_{max} values for various temperature ranges:

Range of T, K	D	θ_{max}, K	δ, %
10–25	1.9	120.6	1.02
20–30	1.4	195.6	0.15
30–50	1.1	281.3	0.16
40–60	1.1	311.2	0.13
50–70	1.0	375.7	0.11

Here, δ is error with which Eq. (3) reproduces the experimental C_p^0 values for **IV** with the quantities D and θ_{max} determined for this compound in the indicated temperature ranges. Note that, according to [12],

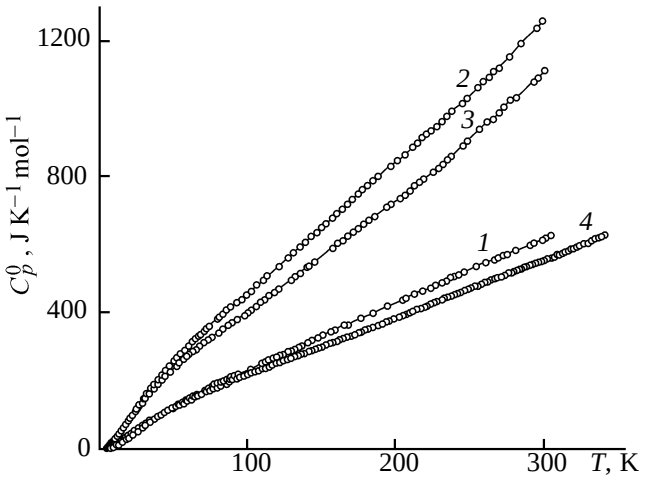
D = 1 corresponds to compounds of the chain structure; D = 2, to those of the layered structure; and D = 3, to those of the three-dimensional structure. Fractional values of D suggest the presence of mixed structures: layered–chain, three-dimensional–layered, etc. We found that, for **IV**, D increases from 1.4 to 1.9 as T is decreased from 30 to 10 K. Apparently, with T decreasing further, D will tend to 3, because the Debye T^3 law is valid for bodies of any heterodynamic structure at very low temperatures. With increasing temperature, the contribution of intermolecular interactions decreases, and the specific features of the heterodynamic structure start to be manifested. In particular, for **IV**, as T is increased from 30 to 60 K, D becomes close to unity; apparently, at higher temperatures it will remain on this level. This means that compound **IV** has a linear (chain) structure, which is consistent with the existing views [5].

It was also found that, in the range 38–60 K, the parameter C_p^0 of **IV** is well described by the Tarasov two-parameter heat capacity function [13, 14] for interacting chains:

$$C_{1,3} = D_1(\theta_1/T) - \theta_3/\theta_1[D_1(\theta_3/T) - D_3(\theta_3/T)]. \quad (4)$$

Here D_1 and D_3 are the Tarasov and Debye heat capacity functions [13–15]; θ_1 and θ_3 are the corresponding characteristic temperatures characterizing the intra- (θ_1) and interchain (θ_3) interactions; the θ_3/θ_1 ratio is the so-called interchain interaction parameter varying from zero to unity: $\theta_3/\theta_1 = 0$ corresponds to hypothetical chain polymers with no interchain interactions, and $\theta_3/\theta_1 = 1$, to polymers in which the energies of the interchain and intrachain interactions are virtually equal. For **IV**, the θ_1 and θ_3 values obtained by fitting the C_p^0 data in the range 38–60 K are 324.78 and 64.96 K, respectively. The ratio $\theta_3/\theta_1 = 0.2$ suggests noticeable interchain interaction. With these values of θ_1 and θ_3, Eq. (4) reproduces with experimental heat capacities of **IV** in the range 38–60 K with an accuracy of ±1.5%.

Thermodynamic functions. The enthalpies $H^0(T) - H^0(0)$, entropies $S^0(T) - S^0(0)$, and Gibbs functions $G^0(T) - H^0(0)$ of crystalline compounds **I**–**III** and glassy compound **IV**, calculated from our data for the range 0–300 K, are listed in Table 1. The enthalpies and entropies were calculated by numerical integration of the curves $C_p^0 = f(T)$ and $C_p^0 = f(\ln T)$, and the Gibbs functions, from the enthalpies and entropies at the corresponding temperatures. The calculation procedure was similar to that described in [16]. The $S^0(0)$ value for crystalline compounds **I**–**III** is, apparently, zero; for glassy compound **IV**, $S^0(0) \neq 0$. According to [17], for glassy substances the $S^0(0)$ values amount to ~10% of the entropies at 298.15 K of the same substances in the glassy state. Thus, according to Table 1, for **IV** $S^0(0)$ can be estimated at ~60 J K^{-1} mol^{-1}. We believe that the error of the calculated values of the functions is 1–2% for T < 30 K, 0.5% for 30–80 K, and 0.3% for 80–300 K.



Temperature dependences of the heat capacities of (*1*) tetraphenyltetrahydroxycyclotetrasiloxane, (*2*) octaphenyltetrahydroxytricyclooctasiloxane, (*3*) octaphenylpentacyclosilsesquioxane, and (*4*) polyphenylsilsesquioxane.

Entropies of formation. From the absolute entropies of the compounds, we calculated the standard entropies of their formation from the elements at 298.15 K. The results are given below.

Comp. no.	$-\Delta_f S^0$, J K^{-1} mol^{-1}
I	1960 ± 3.4
II	3425 ± 6.8
III	3115 ± 6.7
IV	1469 ± 3.5

These values refer to the following processes at 298.15 K.

$$24C(gr) + 12H_2(g) + 4Si(cr) + 4O_2(g)$$
$$\longrightarrow C_{24}H_{24}Si_4O_8(cr) \text{ for compound } \mathbf{I},$$
$$48C(gr) + 22H_2(g) + 8Si(cr) + 7O_2(g)$$
$$\longrightarrow C_{48}H_{44}Si_8O_{14}(cr) \text{ for compound } \mathbf{II},$$
$$48C(gr) + 20H_2(g) + 8Si(cr) + 6O_2(g)$$
$$\longrightarrow C_{48}H_{40}Si_8O_{12}(cr) \text{ for compound } \mathbf{III},$$
$$24C(gr) + 10H_2(g) + 4Si(cr) + 3O_2(g)$$
$$\longrightarrow -(C_{24}H_{20}Si_4O_6)-(gl) \text{ for compound } \mathbf{IV}.$$

Table 1. Thermodynamic functions of **I**–**IV** (p 101.325 kPa)

T, K	C_p^0, J K^{-1} mol^{-1}	$H^0(T) - H^0(0)$, kJ mol^{-1}	$S^0(T) - S^0(0)$,[a] J K^{-1} mol^{-1}	$-[G^0(T) - H^0(0)]$, kJ mol^{-1}
Crystalline tetraphenyltetrahydroxycyclotetrasiloxane **I** ($C_{24}H_{24}Si_4O_8$, M 552·791)				
5	0.9809	0.0012	0.3272	0.0004
10	6.736	0.0185	2.492	0.0064
15	18.43	0.0794	7.262	0.0296
20	32.97	0.2072	14.52	0.0833
25	48.87	0.4114	23.56	0.1776
30	65.46	0.6971	33.93	0.3208
35	81.74	1.065	45.25	0.5186
40	97.10	1.513	57.19	0.7748
45	111.4	2.034	69.46	1.091
50	124.7	2.625	81.89	1.469
60	149.5	3.998	106.9	2.413
80	195.4	7.452	156.2	5.046
100	236.9	11.77	204.3	8.653
150	337.5	26.09	319.0	21.76
200	438.1	45.52	430.1	40.50
250	537.3	69.49	536.7	64.69
298.15	626.5	97.56	639.2	93.01
300	629.8	98.72	643.0	94.19
Crystalline octaphenyltetrahydroxytricyclooctasiloxane **II** ($C_{48}H_{44}Si_8O_{14}$, M 1069·551)				
5	5.101	0.0064	1.721	0.0022
10	26.76	0.0834	11.55	0.0321
15	56.28	0.2885	27.77	0.1280
20	88.62	0.6506	48.39	0.3172
25	120.7	1.174	71.60	0.6160
30	152.0	1.856	96.38	1.036
35	182.1	2.692	122.1	1.582
40	210.2	3.674	148.3	2.258
45	236.3	4.790	174.6	3.065
50	260.7	6.033	200.7	4.003
60	306.4	8.871	252.3	6.269
80	388.2	15.84	352.0	12.32
100	463.3	24.37	446.8	20.32
150	663.3	52.52	672.4	48.34
200	860.4	90.67	890.5	87.44
250	1058	138.5	1103	137.3
298.15	1273	194.6	1308	195.3
300	1281	196.9	1316	197.8
Crystalline octaphenylpentacyclosilsesquioxane **III** ($C_{48}H_{40}Si_8O_{12}$, M 1033·522)				
5	2.500	0.0040	1.074	0.0013
10	22.05	0.0600	8.018	0.0202
15	49.65	0.2374	22.06	0.0935
20	80.87	0.5620	40.51	0.2483
25	112.8	1.048	62.06	0.5039
30	140.3	1.681	85.09	0.8714
35	167.7	2.451	108.8	1.356
40	193.6	3.356	132.9	1.960
45	216.6	4.383	157.1	2.685
50	238.0	5.520	181.0	3.530

Table 1. (Contd.)

T, K	C_p^0, J K^{-1} mol^{-1}	$H^0(T) - H^0(0)$, kJ mol^{-1}	$S^0(T) - S^0(0)$,[a] J K^{-1} mol^{-1}	$-[G^0(T) - H^0(0)]$, kJ mol^{-1}
Crystalline octaphenylpentacyclosilsesquioxane **III** ($C_{48}H_{40}Si_8O_{12}$, M 1033.522)				
60	277.8	8.107	228.1	5.578
80	345.3	14.35	317.4	11.04
100	407.5	21.88	401.1	18.24
150	577.4	46.44	598.0	43.25
200	742.2	79.56	787.4	77.92
250	928.8	121.1	972.0	121.9
298.15	1129	170.5	1152	173.0
300	1138	172.6	1159	175.2
Glassy polyphenylsilsesquioxane **IV** [–($C_{24}H_{20}Si_4O_6$)–, M 516.761]				
5	1.866	0.0023	0.6229	0.0008
10	12.64	0.0348	4.691	0.0121
15	26.70	0.1335	12.50	0.0540
20	42.04	0.3043	22.23	0.1403
25	57.01	0.5526	33.24	0.2786
30	71.79	0.8746	44.95	0.4738
35	85.68	1.269	57.07	0.7288
40	98.34	1.729	69.35	1.045
45	110.3	2.251	81.63	1.422
50	121.8	2.831	93.85	1.861
60	143.1	4.157	118.0	2.920
80	182.7	7.416	164.6	5.749
100	221.3	11.47	209.7	9.494
150	306.4	24.68	315.6	22.66
200	391.8	42.11	415.3	40.95
250	481.9	63.96	512.4	64.15
298.15	564.7	89.17	604.4	91.05
300	567.8	90.22	607.9	92.17
340	641.8	114.4	683.4	118.0

[a] For **I**–**III**, $S^0(0) = 0$; for **IV**, $S^0(0) \neq 0$.

In parentheses are the modifications and states of aggregation: gr, graphite; cr, crystalline; gl, glassy; and g, gaseous. When calculating $\Delta_f S^0$ for **I**–**IV**, we used data from [18] on the entropies of carbon (in the form of graphite), hydrogen (gaseous), oxygen (gaseous), and silicon (crystalline).

Entropies of mutual transformations. From the absolute entropies of **I**–**IV** given in Table 1 and the published value for water [19], we calculated the entropies of mutual transformations of these compounds (reactions *a*–*f*) in the range 0–298.15 K. Of particular interest was the transformation of the low-molecular-weight compounds into the polymer. The results are given below.

T, K	Physical state of reactants and products	ΔS^0, J K^{-1} mol^{-1}
a. $C_{48}H_{40}Si_8O_{12}$ (**III**) + $2H_2O$ ⟶ $C_{48}H_{44}Si_8O_{14}$ (**II**)		
100	cr, cr; cr	13
200	cr, cr; cr	40.8
298.15	cr, l; cr	16
b. 1/2$C_{48}H_{40}Si_8O_{12}$ (**III**) ⟶ –($C_{24}H_{20}Si_4O_6$)– (**IV**)		
100	cr; gl	69.6
200	cr; gl	82.0
298.15	cr; gl	88.8

T, K	Physical state of reactants and products	ΔS^0, J K^{-1} mol^{-1}
c. $1/2C_{48}H_{44}Si_8O_{14}$ (**II**) $\longrightarrow$ –$(C_{24}H_{20}Si_4O_6)$– (**IV**) + H_2O		
100	cr; gl, cr	63.1
200	cr; gl, cr	61.6
298.15	cr; gl, l	80.8
d. $1/2C_{48}H_{40}Si_8O_{12}$ (**III**) + $2H_2O$ $\longrightarrow$ $C_{24}H_{24}Si_4O_8$ (**I**)		
100	cr, cr; cr	–29
200	cr, cr; cr	–25.9
298.15	cr, l; cr	–76.7
e. $1/2C_{48}H_{44}Si_8O_{14}$ (**II**) + H_2O $\longrightarrow$ $C_{24}H_{24}Si_4O_8$ (**I**)		
100	cr, cr; cr	–35.5
200	cr, cr; cr	–46.3
298.15	cr, l; cr	–84.8
f. –$(C_{24}H_{20}Si_4O_6)$– (**IV**) + $2H_2O$ $\longrightarrow$ $C_{24}H_{24}Si_4O_8$ (**I**)		
100	gl, cr; cr	–98.6
200	gl, cr; cr	–108
298.15	gl, l; cr	–166

The entropies of the processes were calculated as the differences between the sums of the entropies of the reaction products and reactants; for the polymer, we took $S^0(0) = 60.4$ J K^{-1} mol^{-1}. For reactions *d*–*f*, $\Delta S^0 < 0$, and for reactions *a*–*c*, $\Delta S^0 > 0$. The absolute values of ΔS^0 for processes *a*–*c* are low. It is interesting that the transformation of cubic octamer **III** in the crystalline form into amorphous cyclolinear polymer **IV** (reaction *b*) is accompanied by the growth of the entropy. This is apparently due to the higher ordering of the structural elements in **III** as compared to **IV**. In all the cases, ΔS^0 appreciably depends on temperature.

EXPERIMENTAL

Samples of **I**–**IV** were prepared at the Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, by the procedures described in [20–22]. The weight-average molecular weight of **IV** was 8.5×10^5. The analytical data for **I**–**IV** were consistent with the composition within 0.5 wt %.

In the range 6–90 K, C_p^0 was measured with a fully automated adiabatic vacuum calorimeter designed and fabricated at the Termis Private Company (Mendeleevo, Moscow oblast). The calorimeter design and the experimental procedure are described in detail in [23]. In the range 70–300 K, the heat capacity was measured with an adiabatic vacuum calorimeter; its design and the experimental procedure were similar to those described in [24]. The reliability of the calorimeters was checked by measuring the heat capacity of reference substances: synthetic corundum and benzoic acid (K-2 grade), prepared at the metrological institutions of the State Committee for Standards of the Russian Federation. The results showed that the accuracy of measuring C_p^0 at helium temperatures was within 2%. At 40 K, the accuracy was 0.5%, and above 40 K, ~0.2–0.3%. Note that the experimental data on C_p^0 of **I**–**IV** obtained on different devices coincided within the measurement error.

The sample weights (kg) in the calorimetric experiments were as follows: **I**, 0.5805×10^{-3}; **II**, 0.6527×10^{-3}; **III**, 0.5094×10^{-3}; and **IV**, 0.4839×10^{-3}. All the experimental heat capacities of **I**–**IV**, obtained in successive measurement series, are given in Table 2. The heat capacities of the samples in the range 6–300 K amounted to 30–60% of the total heat capacity of the calorimetric ampule with the sample. The experimental C_p^0 values were averaged by power and semilog polynomials so that the rms deviation of the exprimental values from the smoothed curve $C_p^0 = f(T)$ be within the error of measuring the heat capacity.

Table 2. Experimental values of the heat capacity of **I**–**IV**, J K^{-1} mol^{-1}, *p* 101.325 kPa

T, K	C_p^0	*T*, K	C_p^0	*T*, K	C_p^0	*T*, K	C_p^0	*T*, K	C_p^0	*T*, K	C_p^0
Tetraphenyltetrahydroxycyclotetrasiloxane **I**											
Series 1											
6.18	1.964	9.83	6.473	12.41	11.79	16.45	22.54	21.42	37.41	36.12	85.11
6.47	2.389	10.22	7.106	13.10	13.54	17.16	24.41	23.82	45.18	38.61	92.76
7.02	3.003	10.60	7.849	13.79	15.28	17.82	26.53	26.26	52.96	41.11	99.95
7.34	3.350	11.00	8.611	14.49	17.08	18.49	28.43	28.71	60.83	43.60	107.3
7.67	3.646	11.48	9.610	15.16	18.92	19.15	30.42	31.17	69.51	46.10	114.9
9.06	5.295	11.87	10.48	15.83	20.62	19.81	32.33	33.64	77.80	48.60	121.4

Table 2. (Contd.)

T, K	C_p^0	T, K	C_p^0	T, K	C_p^0	T, K	C_p^0	T, K	C_p^0	T, K	C_p^0
Tetraphenyltetrahydroxycyclotetrasiloxane **I** Series 1											
51.11	127.9	56.12	139.6	61.13	152.8	66.13	163.9	73.63	182.1	78.65	192.7
53.62	133.1	58.62	145.9	63.60	158.5	71.14	174.8	76.14	187.4	81.16	197.8
Tetraphenyltetrahydroxycyclotetrasiloxane **I** Series 2											
80.43	197.6	92.42	221.2	107.12	250.3	119.32	274.8	136.31	307.1	164.21	369.1
82.57	200.6	93.48	222.3	108.90	255.4	121.75	279.2	140.00	315.0	167.22	372.0
85.04	205.5	94.87	226.2	109.56	255.6	124.18	283.8	143.07	323.1	175.75	390.1
87.50	210.4	97.32	230.8	111.64	260.5	126.61	289.2	146.50	330.0	183.57	404.0
87.78	211.6	99.78	236.0	112.00	260.8	129.04	293.2	150.23	339.7		
89.96	215.9	102.23	241.1	114.28	265.8	131.47	297.6	155.50	351.0		
90.57	217.5	104.67	245.7	116.88	270.3	133.89	302.3	158.12	355.5		
Tetraphenyltetrahydroxycyclotetrasiloxane **I** Series 3											
193.80	426.0	222.66	482.0	238.95	515.5	265.33	566.5	288.89	608.8		
203.30	443.5	225.59	489.9	241.90	519.7	267.99	571.1	291.75	616.3		
206.07	450.6	230.51	496.3	244.78	526.3	271.14	579.1	297.46	623.0		
211.67	462.8	233.48	503.0	253.29	545.6	273.90	583.7	300.13	629.3		
217.22	472.0	236.29	512.1	259.99	557.7	279.10	593.0	302.90	637.2		
Octaphenylpentacyclosilsesquioxane **II** Series 1											
6.39	11.25	9.63	24.79	14.07	50.32	21.78	99.50	46.94	246.6	69.49	344.1
6.63	11.85	10.02	27.06	14.76	54.66	24.24	116.2	49.46	259.6	70.77	352.3
6.95	12.77	10.41	28.79	15.45	58.99	26.76	131.9	51.98	271.3	72.15	358.4
7.26	13.88	10.79	30.89	16.13	63.31	29.28	147.5	54.51	282.6	73.81	364.0
7.57	15.34	11.19	33.25	16.80	68.05	31.80	163.9	57.03	291.9	78.85	384.1
7.88	16.71	11.58	35.23	17.47	71.96	34.33	178.8	59.56	303.8	80.20	388.4
8.18	18.06	12.06	38.33	18.15	76.63	36.85	192.0	64.60	326.3		
8.85	20.88	12.56	41.26	18.81	81.28	39.38	205.7	62.09	315.8		
8.48	19.41	12.95	43.67	19.48	85.22	41.90	218.7	67.12	338.2		
9.25	22.74	13.38	46.52	20.14	89.54	44.42	232.9	68.21	340.3		
Octaphenylpentacyclosilsesquioxane **II** Series 2											
82.82	400.2	95.15	443.1	109.13	499.6	129.25	582.5	145.04	642.7	158.88	699.6
85.33	411.5	98.51	458.6	112.58	514.5	134.02	599.6	148.38	656.1	160.21	702.3
87.86	421.4	101.93	469.0	120.02	542.0	137.79	612.5	151.66	669.0	162.38	710.0
91.64	433.9	105.59	485.0	126.15	567.8	141.48	630.9	155.26	683.7		
Octaphenylpentacyclosilsesquioxane **II** Series 3											
165.75	726.3	182.96	796.6	210.22	896.2	225.54	956.5	246.28	1040	267.18	1130
168.99	740.5	186.40	811.3	213.01	908.8	228.87	971.5	253.21	1070	274.50	1164
172.87	756.9	194.70	838.8	215.92	922.9	232.35	987.1	257.01	1092	282.06	1202
176.29	770.3	199.60	856.1	218.68	935.1	235.66	1001	260.43	1102	293.11	1247
179.59	782.4	204.51	874.4	222.14	946.4	242.85	1027	263.65	1120	296.95	1268
Octaphenylpentacyclosilsesquioxane **III** Series 1											
5.38	3.438	6.65	7.461	9.33	18.65	12.93	37.83	18.12	69.27	25.92	118.3
5.63	4.087	7.42	10.53	10.45	24.23	14.25	42.76	19.56	78.12	23.52	103.9
6.05	5.301	8.32	14.11	11.58	30.29	16.73	60.51	20.94	86.95	24.64	110.5

Table 2. (Contd.)

T, K	C_p^0	T, K	C_p^0	T, K	C_p^0	T, K	C_p^0	T, K	C_p^0	T, K	C_p^0
Octaphenylpentacyclosilsesquioxane **III** Series 1											
27.47	127.5	31.58	149.2	36.62	176.6	41.96	203.1	47.48	227.8	54.09	255.5
29.36	136.9	34.03	162.8	39.23	189.9	44.70	214.9	52.02	245.9	56.28	263.5
Octaphenylpentacyclosilsesquioxane **III** Series 2											
57.79	269.0	60.35	280.0	64.95	294.9	69.63	310.9	76.18	330.0	82.86	355.2
58.60	274.5	62.61	289.0	67.28	303.4	72.96	321.4	79.40	336.0	82.86	355.2
Octaphenylpentacyclosilsesquioxane **III** Series 3											
70.05	315.0	107.38	432.3	140.32	543.1	180.46	680.5	217.47	803.3	259.63	969.9
72.85	323.1	110.48	441.4	143.45	554.0	184.00	691.2	224.25	825.1	263.54	979.5
86.15	365.4	113.75	454.4	155.92	596.6	192.18	715.9	227.50	835.5	267.41	998.3
89.22	375.1	116.86	464.2	159.38	609.6	195.62	727.6	230.58	846.8	271.28	1016
92.11	382.3	119.81	475.3	162.76	617.6	200.90	744.3	233.23	861.1	274.83	1035
97.12	397.0	127.89	501.7	166.33	633.8	204.48	753.4	236.37	870.1	278.84	1044
99.34	404.1	131.19	513.8	169.99	643.9	207.92	765.3	243.56	902.0	290.51	1092
101.70	411.5	134.17	521.4	173.49	655.6	211.23	782.0	246.60	917.0	293.90	1102
104.60	420.9	138.70	540.8	176.86	668.0	214.42	793.3	254.93	950.0	298.02	1125
Polyphenylsilsesquioxane **IV** Series 1											
6.16	3.351	7.02	5.124	7.76	6.759	8.20	7.654	8.66	8.805	9.13	10.15
6.44	3.967	7.33	5.782								
Polyphenylsilsesquioxane **IV** Series 2											
7.69	6.452	8.94	9.807	10.31	13.59	11.74	17.63	13.91	23.68	16.15	30.09
8.05	7.304	9.37	10.78	10.78	15.01	12.38	19.40	14.67	25.80	17.00	32.43
8.47	8.385	9.84	12.29	11.25	16.41	13.15	21.48	15.42	27.71		
Polyphenylsilsesquioxane **IV** Series 3											
17.53	34.22	21.82	47.67	34.37	84.40	46.98	115.4	59.58	141.9	72.18	168.0
18.05	36.17	24.30	55.09	36.88	90.46	49.50	121.2	62.11	148.1	74.71	172.7
18.76	37.96	26.82	62.36	39.41	96.50	52.02	126.1	64.63	153.2	77.24	177.2
19.45	40.35	29.34	69.59	41.94	102.7	54.54	131.4	67.14	156.8	79.77	182.0
20.14	42.15	31.86	77.33	44.46	109.0	57.07	136.2	69.67	161.4	82.29	186.9
Polyphenylsilsesquioxane **IV** Series 4											
85.59	194.9	116.78	250.9	147.85	302.5	178.63	355.0	209.02	406.8	238.79	463.0
87.84	199.9	119.18	254.9	150.23	307.2	180.99	358.7	211.33	411.1	241.05	465.6
90.26	204.3	121.57	258.7	152.62	310.4	183.34	362.5	213.65	415.3	243.29	469.0
92.68	207.5	123.98	262.5	155.00	315.4	185.69	367.3	215.96	419.9	245.55	474.0
95.10	212.1	126.38	267.2	157.37	317.8	188.04	372.1	218.27	423.4	247.81	478.5
97.51	216.7	128.77	271.6	159.74	322.8	190.39	376.0	220.57	427.9	250.06	483.2
99.92	221.1	131.16	275.1	162.10	326.3	192.73	379.1	222.87	432.0	252.30	487.5
102.33	225.5	133.55	277.9	164.46	329.9	195.07	382.8	225.16	438.1	254.54	489.0
104.74	229.8	135.93	283.3	166.83	334.6	197.40	387.3	227.46	441.1	256.76	493.1
107.16	233.8	138.32	286.2	169.19	339.0	199.71	391.4	229.75	447.1	258.99	499.0
109.57	237.9	140.70	290.4	171.55	343.0	202.04	395.2	232.03	450.6	261.20	501.1
111.97	241.9	143.09	294.6	173.91	346.7	204.37	398.5	234.31	455.4	263.41	506.7
114.38	246.2	145.47	298.3	176.27	350.3	206.70	403.1	236.52	458.3	265.60	511.1

Table 2. (Contd.)

T, K	C_p^0	T, K	C_p^0	T, K	C_p^0	T, K	C_p^0	T, K	C_p^0	T, K	C_p^0
Polyphenylsilsesquioxane **IV** Series 4											
267.81	513.9	279.32	532.5	293.80	557.9	307.46	581.2	320.79	605.5	333.02	629.8
268.87	512.7	281.40	537.2	295.82	560.2	309.40	583.4	322.64	608.7	334.79	633.1
270.00	516.6	283.50	541.1	297.84	562.7	311.33	585.0	324.48	611.1	336.54	633.8
270.81	516.8	285.58	542.8	299.84	568.2	313.24	591.0	326.31	616.1	338.22	638.2
272.95	520.0	287.65	548.2	301.56	570.2	315.15	593.9	328.12	616.6	339.94	641.9
275.08	526.0	289.71	551.1	303.54	572.4	317.04	598.4	329.92	622.0	341.65	642.8
277.21	528.1	291.76	553.9	305.50	575.7	318.92	601.8	331.25	624.0		

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