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Abstract

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HEAT CAPACITY OF CHAIN STRUCTURES AT LOW TEMPERATURES

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At present there is no consensus on the nature of the temperature dependence of the heat capacity of chain and layered structures at low temperatures. All theoretical works devoted to this question ($^{1-8}$) may be divided into two groups, depending on whether or not the rigidity of the chains and layers is taken into account. The most substantial disagreements concern that temperature region in which the interaction of chains (layers) may be neglected.

Tarasov (^{1,2}), Gurney (^{4}), Rosenzweig (^{5}), Krummhansl and Brooks (^{6}) do not take rigidity into account and, for noninteracting chains, obtain a linear law of dependence of heat capacity on temperature, and for noninteracting layers —a parabolic law, irrespective of whether the chain (layer) is considered as a continuum or its atomic structure is taken into account.

Lifshitz (^{3}), Kamatsu (^{7}), and Newell (^{8}), taking rigidity into account, obtain for a layer a linear law, and for chains (Lifshitz) a $T^{1/2}$ law under the same condition of absence of interaction.

The existing experimental data do not allow an unambiguous choice between the two indicated directions, although most of them agree rather well with the theory of Tarasov et al.

In order to further clarify the nature of the temperature dependence of the heat capacity of chain structures in the low-temperature region, we measured the heat capacities of polyethylene in the interval from 58 to 273° K and of polyvinyl alcohol in the interval from 58 to 245° K. Experimental data on the heat capacity of Teflon (^{9}) and their treatment, carried out by Tarasov (^{2}), made it possible to expect in the temperature region investigated by us a linear (or $T^{1/2}$) dependence of heat capacity on temperature.

Both polyethylene and polyvinyl alcohol are organic linear polymers with strong valence interaction of atoms along the chain and weaker intermolecular interaction between chains. The heat capacity of polyethylene—the simplest of all existing organic polymers—is of special interest, since at low temperatures it is completely determined by transverse and longitudinal vibrations of the chain itself. (CH vibrations at these temperatures cannot yet be excited.)

The adiabatic vacuum calorimeter used in the work, in the main, did not differ in any way from those repeatedly described in the literature.

The samples were placed in a glass cylinder filled with helium, into which a silver cross was inserted to accelerate heat exchange. The temperature was measured with a platinum thermometer calibrated by the low-temperature laboratory of VNIIM. The rate of temperature equalization was approximately 20–25 min per 1°. The samples studied were taken in the form of finely crushed pieces, not exceeding in volume ···

that fell out, 1 mm^3. The factory samples of polyethylene and polyvinyl alcohol at our disposal were technically pure. We did not carry out a special chemical analysis of the samples. The mass of the polyethylene studied was 19.2 g, and the mass of the polyvinyl alcohol was 18.6 g. The heat capacity of the empty calorimeter was measured beforehand over the whole temperature interval at intervals of 5–8°. There are indications in the literature that glasses containing Na_2SiO_3, as, for example, in the case of the glass "23" used by us, have a chain structure with weak interaction of the chains. This circumstance makes it possible to regard the heat capacity of the glass not only as an auxiliary quantity for calculating the heat capacity of the polymers studied, especially since we found no data in the literature on the heat capacity of glass "23" at low temperatures. The heat-capacity measurements in the temperature region below 200° K were carried out at intervals of 2.5–3°. The scatter of the experimental points did not exceed 1.5%.

Table 1 gives not the experimental values of the heat capacity, but values calculated from the smoothed experimental curve.

Table 1

T, °K	Polyethylene	Polyvinyl alcohol	Glass "23"	T, °K	Polyethylene	Polyvinyl alcohol	Glass "23"
	c_p, cal/deg·g	c_p, cal/deg·g	c_p, cal/deg·g		c_p, cal/deg·g	c_p, cal/deg·g	c_p, cal/deg·g
58	0.0957	0.0569	0.0450	165	0.2376	0.1756	0.1302
60	0.0999	0.0618	0.0466	170	0.2438	0.1805	0.1336
65	0.1102	0.0714	0.0506	175	0.2495	0.1864	0.1365
70	0.1185	0.0784	0.0557	180	0.2552	0.1907	0.1399
75	0.1263	0.0860	0.0601	185	0.2603	0.1950	0.1432
80	0.1340	0.0929	0.0647	190	0.2660	0.2004	0.1466
85	0.1408	0.0988	0.0687	195	0.2722	0.2047	0.1496
90	0.1480	0.1037	0.0734	200	0.2790	0.2095	0.1526
95	0.1553	0.1101	0.0775	205	0.2852	0.2154	0.1552
100	0.1615	0.1138	0.0818	210	0.2919	0.2192	0.1583
105	0.1682	0.1187	0.0862	215	0.2987	0.2240	0.1614
110	0.1739	0.1219	0.0906	220	0.3069	0.2294	0.1640

Figure 1

Figure 1: Figure 1

T, °K	Polyethylene	Polyvinyl alcohol	Glass "23"	T, °K	Polyethylene	Polyvinyl alcohol	Glass "23"
115	0.1801	0.1257	0.0952	225	0.3152	0.2363	0.1661
120	0.1858	0.1305	0.0986	230	0.3235	0.2406	0.1694
125	0.1920	0.1348	0.1027	235	0.3328	0.2455	0.1721
130	0.1972	0.1397	0.1067	240	0.3426	0.2492	0.1755
135	0.2024	0.1440	0.1101	245	0.3540	0.2562	0.1771
140	0.2081	0.1488	0.1141	250	0.3644		0.1798
145	0.2143	0.1552	0.1171	255	0.3763		0.1822
150	0.2210	0.1601	0.1204	260	0.3887		0.1845
155	0.2257	0.1649	0.1241	265	0.4016		0.1865
160	0.2319	0.1708	0.1271	270	0.4151		0.1885

The character of the temperature dependence is most easily judged from the slope of the curve $\lg C$ with respect to the axis $\lg T$. In accordance with what was said above, in the temperature region where the interaction of the chains may be neglected, the heat capacity may be represented as $C = AT^m$, where $m = 1$ or $m = 1/2$, $A = \text{const}$. On a logarithmic scale these dependences are represented by straight lines with slopes equal respectively to 1 and 1/2. The slope of the experimental curves gives the experimental value of m.

From Fig. 1 it is seen that for polyethylene, in the temperature interval 58-95° K, the value of m changes continuously from a value greater than unity to a value equal to 0.89. In the interval 95-185° K the value of m remains constant and equal to 0.89, while from 185° K and above m increases continuously, which is connected with the beginning devitrification of the polymer in this region. For polyvinyl alcohol, in the interval 58-120° K, an additional heat capacity is observed on the heat-capacity curve, which may be a consequence of excit—

of rotation of the OH group. Its magnitude is about 15% of the total heat capacity at $T = 80°$ K, obtained by a smooth extrapolation of the curve. From $T = 120°$ K to $T = 245°$ K, m has a constant value equal to 0.96. In the temperature interval investigated, no glass-transition region was found for polyvinyl alcohol. The experimental value of m for glass is also very close to unity, but deviates from it toward larger values. Since glass, in addition to Na_2SiO_3 chains, contains other components, we shall not include it in the general discussion.

Fig. 1. $\lg C$ as a function of $\lg T$ for polyethylene (a) and polyvinyl alcohol (b) at low temperatures. For comparison, straight lines with $m = 1$ and $m = 1/2$ are shown in the figure.

The experimental data obtained by us, as well as data of other authors on the heat capacity of rubber (^{10}) and Teflon (^{9}), plotted in logarithmic coordinates, give a value of m which, although smaller than unity, is very close to it. For different polymers the deviation from unity is different. Hence the following conclusion suggests itself: the heat-capacity formula proposed by Tarasov et al. agrees with experiment better than Lifshitz's formula; however, the deviation of the experimental values of m from unity indicates the necessity of taking into account the stiffness of real chains. It seems to us that a more exact theory of the temperature dependence of the heat capacity can be obtained by a reasonable unification of the two existing approaches. Attempts to construct such a theory were made by Stockmayer (^{11}).

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