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Abstract

Full Text

Physical Chemistry

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Heat Capacity of Linear Polymers at Low Temperatures

(Presented by Academician A. F. Ioffe, 1959)

The dependence of heat capacity on temperature was investigated for linear polymers in the region of hydrogen temperatures and above, where, according to the works (^{1,2}), the influence of interaction forces between chains should become apparent. For comparison with theory, it is essential to consider such linear polymers as have no side radicals capable of rotation. The polyethylene and trifluoroethylene investigated in this work are such polymers.

The adiabatic calorimeter used in the work has been described by us previously (^{3}). The platinum thermometer was made, following the type of Strelkov' s thermometer (^{4}), from spectrally pure platinum of grade IONKh-5 and was compared with a thermometer of the same grade for which the resistance-temperature table from 10.8° to 90° K was known. The samples available to us were technically pure. The weight of the polyethylene studied was 22.6 g, and that of the trifluoroethylene 18.9 g. The heat-capacity measurements were carried out every 0.5 deg.; the rate of temperature equalization in the samples was 8–10 min/deg. The heat capacity of the empty calorimeter was measured beforehand over the entire temperature interval.

The results obtained by us are given in Table 1. In Fig. 1 these results are presented on a logarithmic scale.

Polyethylene. The heat capacity of polyethylene was measured in the interval from 17° to 60° K (measurements in the higher-temperature region had been made by us earlier (^{5})). If the dependence of heat capacity on temperature is represented in the form $c = AT^m$, then, as is seen from the figure, m is greater than unity over the entire temperature interval investigated and varies from 2.15 to 1.1. According to the works (^{1,2,6}), the value $m > 1$ is due to the influence of interaction forces between chains. The results of the present work and of work (^{5}) show that for polyethylene the interaction is noticeable up to temperatures of the order of 90°–100° K. A considerable temperature interval is noteworthy within which the behavior of the heat capacity is already not Debye-like, but, nevertheless, interaction between chains cannot be neglected.

Trifluoroethylene. The heat capacity of trifluoroethylene was measured in the interval from 23 to 120° K. As can be determined from Fig. 1, m, from a value of 1.3 at 23°, changes to $m = 1$ at 30° K and then rapidly passes to values less than unity. Already in the vicinity of 35° K, $m = 0.65$–0.70. Above 40 K the steepness of the heat-capacity curve increases somewhat, so that already at 60° $m = 0.8$. The value $m = 0.8$ is retained up to 120° K. The strong narrowing of the temperature interval in which the influence of interaction forces is noticeable, in comparison with the corresponding interval for polyethylene, is evidently to a significant extent connected with the difference in the masses of the groups CF_2 and CFH and the group CH_2.

The temperature dependence of the heat capacity of trifluoroethylene obtained by us does not contradict the dependence predicted in ([1,2]), and this applies both to the region where the interaction between chains is appreciable and to the region where it may be neglected. The experimentally observed change in the slope of the curve in the vicinity of 60° K may be a consequence of the

Table 1

Temp., °K	c, cal/deg·g polyethylene	c, cal/deg·g trifluoroethylene	Temp., °K	c, cal/deg·g polyethylene	c, cal/deg·g trifluoroethylene	Temp., °K	c, cal/deg·g polyethylene	c, cal/deg·g trifluoroethylene
17	0.0128	–	39	0.0574	0.0437	61	–	0.0600
18	0.0140	–	40	0.0597	0.0444	62	–	0.0611
19	0.0150	–	41	0.0618	0.0451	63	–	0.0620
20	0.0173	–	42	0.0639	0.0458	64	–	0.0630
21	0.0193	–	43	0.0661	0.0465	65	–	0.0641
22	0.0214	–	44	0.0682	0.0472	66	–	0.0650
23	0.0235	0.0261	45	0.0703	0.0479	67	–	0.0660
24	0.0256	0.0276	46	0.0723	0.0486	68	–	0.0670
25	0.0278	0.0292	47	0.0744	0.0492	69	–	0.0680
26	0.0299	0.0307	48	0.0765	0.0499	70	–	0.0689
27	0.0320	0.0321	49	0.0785	0.0506	75	–	0.0734
28	0.0342	0.0334	50	0.0806	0.0513	80	–	0.0775
29	0.0363	0.0345	51	0.0826	0.0519	85	–	0.0816
30	0.0384	0.0358	52	0.0845	0.0525	90	–	0.0853
31	0.0407	0.0368	53	0.0865	0.0533	95	–	0.0891
32	0.0428	0.0379	54	0.0885	0.0540	100	–	0.0927
33	0.0448	0.0386	55	0.0905	0.0547	105	–	0.0966
34	0.0470	0.0396	56	0.0923	0.0555	110	–	0.1006
35	0.0491	0.0405	57	0.0941	0.0563	115	–	0.1044
36	0.0512	0.0413	58	0.0959	0.0570	120	–	0.1081
37	0.0533	0.0421	59	0.0978	0.0581			
38	0.0554	0.0430	60	0.0996	0.0591			

Fig. 1. Logarithmic dependence of c_p on T for polyethylene (a) and trifluoroethylene (b). The dashed curve is for $m = 1$

Figure 1: Fig. 1. Logarithmic dependence of c_p on T for polyethylene (a) and trifluoroethylene (b). The dashed curve is for $m = 1$

excitation of pendulum oscillations of the CF_2 and CFH groups, not taken into account in this work (the so-called rocking oscillations of the CX_2 groups, which may have low frequencies in the case considered, owing to the heavy fluorine atoms ([7])).

As was noted earlier ([5]), for most linear polymers in the range of not very low temperatures the temperature dependence of the heat capacity is close to linear, although it differs from it in the direction of smaller values of m. This fact agrees fairly well with the dependence proposed by Tarasov ([6]). However, it can hardly be assumed that the experimentally observed heat capacity of such heavy polymers as trifluoroethylene and Teflon ([8]), at temperatures of the order of 80-100° K and higher, is due only to the acoustic spectrum of their skeleton. At these temperatures it becomes necessary to take into account that fraction of the heat capacity which is associated with the deformational vibrations of the CF_2 and CFH groups. This should lead to an even greater to the discrepancy between the experiment and Tarasov' s formula. At present we do not have the possibility of separating, with sufficient accuracy, from the total heat capacity of trifluoroethylene the part associated with the vibrations mentioned above. Nevertheless, the values $m = 0.65—0.70$ obtained in this work for trifluoroethylene in the region of sufficiently low temperatures indicate the possibility of a significant deviation from the dependence proposed by Tarasov.

Fig. 1. Logarithmic dependence of c_p on T for polyethylene (a) and trifluoroethylene (b). The dashed curve is for $m = 1$.

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