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THERMAL EXPANSIVITY OF TEFLON UNDER HIGH PRESSURE

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UDC 536.413

Results of $(\partial T/\partial P)_S$ measurements are presented involving Teflon. The dependence of its thermal expansivity α on the pressure has been determined within the stability range for various modifications of this material ($P \leq 13$ kbar, $0 \leq T \leq 50°C$).

Polymer materials are nowadays widely used. In high-pressure technology, e.g., Teflon (polytetrafluoroethylene, fluoroplastic-4) has been widely accepted as a structural material. Naturally, it seems worthwhile to more thoroughly study the behavior of this material under extreme pressures and temperatures.

Several studies have dealt with the properties of Teflon under high pressure: its phase diagram was determined [1], its equations of state were derived [2-4], and the pressure dependence of its thermal conductivity as well as of its specific heat was determined [5, 6]. The trend of the V(T) relation, determined at various pressures, suggests that the thermal expansivity of the initial low-temperature Teflon modification (II) under pressure is negative [2]. In a later study [4] this apparent negative value of α has been explained by a slow II → III transition. The high-temperature modification (III) is characterized by a high density, the transition causing the volume of a specimen to decrease with rising temperature, which could indeed lead to incorrect readings. Estimates of α on the basis of the equation of state [3] have yielded positive values for all three modifications, but the change of α during the transition cannot be easily determined from the results of that study. The thermal expansivity of Teflon under pressure at room temperature was also measured directly [6]. It was found to be positive over the entire range of measurements ($P \leq 40$ kbar), but the poor accuracy ($\sim$10%) of these measurements made a determination of its change during the transition impossible.

In this study was measured the pressure dependence of the derivative $(\partial T/\partial P)_S$. With this derivative known, and also the specific heat $C_P(P)$ [or $K_S(P)$] known, it is possible to determine α (or γ) from the relation

$$(\partial T/\partial P)_S = \frac{TV}{C_P}\,\alpha = \frac{T}{K_S}\,\gamma,$$

where K_S is the adiabatic modulus of isotropic compression and γ is the Grüneisen parameter.

The method of measurements was based on recording the temperature jump in a specimen due to a sharp change of pressure in the chamber [7]. The measurements were made in a high-pressure apparatus of the cylinder-piston type, under hydrostatic conditions. The pressure jump ($\approx$100 bars) was measured with a Manganin probe and the corresponding temperature change was measured with a Chromel—Alumel thermocouple. The accuracy of a $\Delta T/\Delta P$ determination was of the order of 2%. The specimen of Teflon had been prepared in the form of a cylinder $\approx$10 mm high and $\approx$8 mm in diameter.

The graph in Fig. 1 depicts experimental values of the derivative $(\partial T/\partial P)_S$ for Teflon under pressures up to 13 kbar at three different temperatures (curves 1-3), based on measurements during forward and reverse cycles. This range covers the stability ranges for all
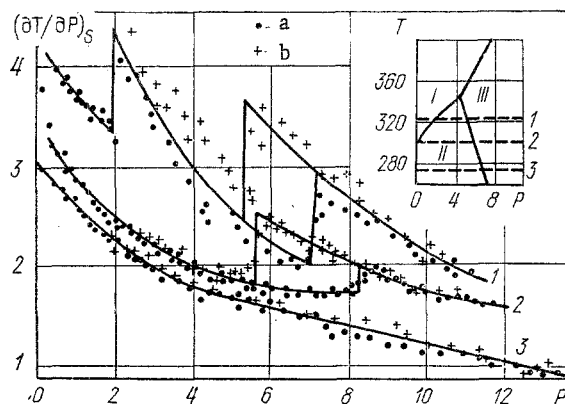
Fig. 1. Pressure dependence of the derivative $(\partial T/\partial P)_S$ (deg/kbar) for Teflon, measured at various temperatures: (a) readings obtained on a forward cycle; (b) readings obtained on a reverse cycle; P (kbar), T (°K).

three Teflon modifications (I-III). The thermal expansivity α of Teflon at room temperature was now calculated from these readings as well as the earlier-found pressure dependence of its specific heat [6] and volume [3]. These data are shown in Fig. 2. The specific heat and the volume are always positive and vary slowly with pressure. Therefore, the trend of the α variation is determined essentially by that of the derivative $(\partial T/\partial P)_S$. One can accordingly deduce what the trend of α will be at temperatures at 45 and 0°C, for which no data on the specific heat are available. Our results indicate that $(\partial T/\partial P)_S$ and thus also α are positive over the entire range of pressures and temperatures, i.e., for all three Teflon modifications, which confirms the results of other studies [3, 6]. The derivative $(\partial T/\partial P)_S$ decreases with rising pressure within the stability range of each modification. It increases with rising temperature for modifications II and III, these having been tested at various temperatures. During the phase transformations occurring in this case transition to the higher-density modification is accompanied by an increase of the derivative $(\partial T/\partial P)_S$ and correspondingly (with the change of C_P taken into account) of the thermal expansivity α. The jump of α during phase transition at room temperature is $\Delta\alpha/\alpha \sim 17\%$ on a forward cycle and $\Delta\alpha/\alpha \sim 21\%$ on a reverse cycle. Some difference between readings obtained on forward and reverse cycles, respectively, within the stability range for Teflon II (the values corresponding to a reverse cycle are somewhat higher than those corresponding to a forward cycle) can probably be attributed to the slow II → III transition.

Measurements within the range about 0°C have revealed no anomalies in the trend of the derivative $(\partial T/\partial P)_S$ which could be attributed to the phase transition, probably because the hysteresis of the II→III transition becomes larger at a lower temperature.

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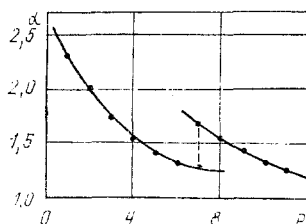
Fig. 2. Pressure dependence of the thermal expansivity of Teflon, α (°C$^{-1} \cdot 10^4$).

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EXPERIMENTAL INVESTIGATION OF LUMPY COHESIVE LOOSE

MATERIALS WITH THE OBJECT OF DETERMINING THE SIZE

OF THE OUTLET OPENING OF BUNKERS

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The article examines the determination of the shear characteristics of polydisperse loose materials containing both a cohesive fine fraction and large particles in connection with the problem of calculating the size of the bunker opening.

The physicomechanical characteristics of loose material for calculating the geometrical parameters of bunkers are at present determined in and outside the USSR by Jenicke's method [1, 2]. The method envisages determining the characteristics of loose material on a single-plane shear instrument with yokes of 100-mm diameter.

Regardless of the limited size of the instrument, the author of the method considers it suitable for materials with particles of any size. To determine the characteristics of such materials, it is recommended to test only the fine fraction, separated from the rest of the material by screening it, and the screen mesh may be chosen arbitrarily (e.g., with mesh size of 0.833 mm).

Such a recommendation is based on the assumption that the shear processes in polydisperse loose material occur only through the center of the smallest particles, and that the presence of an arbitrary number of large particles or lumps does not affect these processes at all. No matter what screen is used for separating the investigated fraction, the smallest particles are inevitably contained in it, and the results of shear tests do not change. However, this assumption was not confirmed by experiments specially carried out for testing them. It was found that with decreasing size a of the investigated fraction, the width of
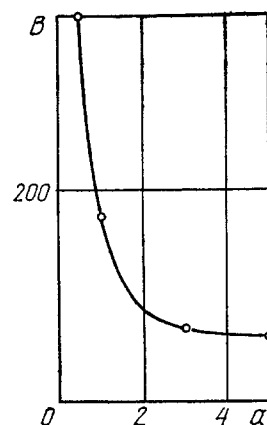

Fig. 1. Dependence of the outlet opening of the bunker on the size of the investigated fraction of loose material. a, mm; B, cm.