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HEAT OF TRANSFORMATION OF CHAINS IN AMORPHOUS SULPHUR

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Abstract

The heat Q of transformation of the chains in amorphous sulphur was measured calorimetrically. The mean value $\bar{Q}$ for samples remelted at T_f=443 K increases from 31.5 to 45.9 J g^{-1} in the measurement temperature range from 288 to 303 K.

For samples remelted in the T_f range from 443 to 573 K, the $\bar{Q}$ values are from 30.6 to 24.0 J g^{-1}.

The results are discussed on the basis of the theory of nucleation and growth of nuclei.

Keywords: amorphous sulphur, calorimetry, heat of transformation

Introduction

When liquid sulphur is quenched, its amorphous modification is formed. It contains long chains, S_n (n up to 12000), octaatomic rings S_8 and small quantities of other rings (S_6, S_7, S_9, etc.) [1]. The mass fraction of the chains increases with the temperature of the liquid sulphur, T_f, moreover, it rises discretely from 0.03 to 0.4 at T_f=432 K [2–5].

It T_f≥432 K, amorphous sulphur is obtained, in which, immediately after rapid heating from the cooling bath temperature (77 K) to room temperature, a rapid exothermic process takes place [5]. Its activation energy is 21 kJ mol^{-1} [5]. The rate of the process decreases with T_f [6].

In order to learn more about the nature of the transformation, it seemed worthwhile to measure its heat versus the temperature of the process and versus the temperature of the liquid sulphur.

Experimental

The experimental method has been described in [5, 6].

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Results

Samples remelted at T_f=443 K were investigated calorimetrically at 288, 293, 298 and 303 K.This yielded the graphical dependence of the temperature T_c of the calorimetric cell versus time t [5]. From curves $T_c=f(t)$, the total heat Q evolved by 1 g of sulphur was calculated from the formula

$$Q = \frac{K}{m}\left(T_{co} + \int_{o}^{\infty} T_c \mathrm{d}t\right) \tag{1}$$

where K=4.19 J K^{-1} is the thermal capacity of the cell with the sample [5], m is the mass of sulphur (in g), T_{co} is the temperature of the cell at time t=0 (corresponding to the first measured temperature T_c), and β=0.155 min^{-1} is the heating constant.

The Q values obtained are presented in Fig. 1, where Q is seen to increase strongly *vs.* the temperature of the process.

In the second part of the study, the heat Q was measured at 298 K for samples remelted at different temperatures T_f in the range from 443 to 573 K. The results indicate (Fig. 2) that elevation of T_f decreases not only the rate of the process [6], but also the transformation heat Q.

The opposite dependence of $Q=f(T_f)$ was obtained by a DTA method [4]. However, the DTA measurement was begun 2 min after defrosting of the sam-

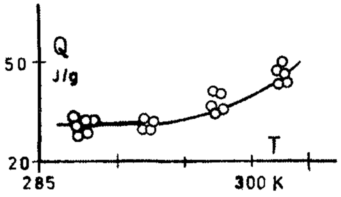

Fig. 1 Heat Q of transformation of chains in amorphous sulphur *vs.* temperature of the process (remelting temperature T_f=443 K)

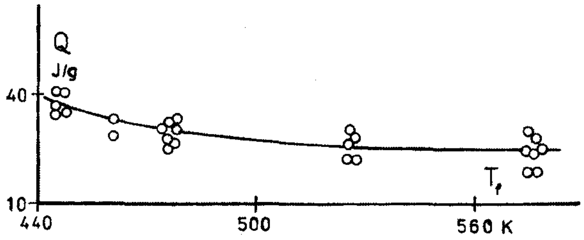

Fig. 2 Heat of transformation of chains in amorphous samples *vs.*temperature of liquid sulphur

ples. It is known that this time is too long and certain of the heat may not be registered, especially for samples remelted at lower temperatures T_f, when the transformation progresses quickly [6]. Moreover, the slowly progressing transformation in samples remelted at higher T_f is observed in the DTA method practically only at higher temperatures. This corresponds to an increase in the evolved heat (Fig. 1). Probably for these reasons, the dependence $Q=f(T_f)$ obtained by the DTA method is erroneous.

Discussion

The obtained results can be compared with those in [5, 6]. The studied transformation of the chains progresses in the stages of formation and growth of the nuclei. The nuclei are formed in the centres, i.e. in microregions in which the fragments of the chains are assembled more or less in parallel and their atoms are ordered adequately [4–6]. A similar order around the formed nucleus is probably necessary for its growth [6]. In reality, the above arrangements of the chains and of the atoms are more or less disturbed. Thus, in amorphous sulphur there are centres and regions that are differently suited for nucleation and growth of the nuclei. This modification also contains the small rings that make the local parallel arrangement of the chains impossible. In such disturbed regions, the transformation cannot progress completely to the end during the calorimetric measurement. Its degree depends on the temperature of the process. Elevation of the temperature of the process causes the number of nuclei formed to increase or the grains of the new phase to reach larger dimensions [5]. In both cases, the quantity of product formed and, consequently, the evolved heat Q increase (Fig. 1).

The transformation degree also depends on the temperature T_f of the liquid sulphur. The arrangement of the chains and their atoms becomes worse at higher remelting temperatures T_f. As a result, the number of nucleation centres, or of the regions suitable for the growth of the nuclei, is diminished. Thus, the number of nuclei formed, and also the number of grains and their dimensions decrease [6]. Consequently, the value of Q diminishes *vs.* the temperature T_f (Fig. 2).

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