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HEAT OF TRANSFORMATION OF CHAINS IN AMORPHOUS SULFUR DOPED WITH SELENIUM AND PHOSPHORUS

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Abstract

The heat of transformation (Q) of the chains in amorphous sulfur doped with selenium (0, 2, 4 and 6 at%Se) and phosphorous (0, 0.43, 0.86 and 1.28 at%P) was measured calorimetrically. All samples were remelted at temperature T_f=443 K. The admixtures decrease the Q: at the measurement temperature 298 K the mean value of $\overline{Q}$ is equal to 37.6, 20.4 and 9.1 J g^{-1} for the samples S, S+6 at%Se and S+1.28 at%P respectively.

The quantity of the evolved heat increases *vs*. the elevation of the measurement temperature. For the samples S+6 at%Se the value is equal 16.2 and 28.8 J g^{-1} at 288 to 303 K. For the samples S+1.28 at%P the value of $\overline{Q}$ increases from 9.1 to 25.0 J g^{-1} in the range of the measurement temperature from 293 to 308 K.

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

Keywords: amorphous sulfur, calorimetry, heat of transformation

Introduction

When liquid sulphur is quenched, its amorphous modification is formed. It contains chains S_n (n up to 12.000), 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 0.034 to 0.4 at T_f=432 K [2–5].

If $T_f \geq$432 K in the freshly obtained amorphous sample an exothermic process progresses quickly [6–11]. Probably, during this process an unstable modification containing the chains is formed [7, 8]. This modification changes into orthorhombic sulphur composed of ordered octaatomic rings S_8. The heat of the transformation for the amorphous 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 [9]. The elevation of the temperature T_f from 443 to 573 K decreases the values Q from 31.5 to 24.0 J g^{-1}.

The admixtures of Se [10] and of P [11] diminish the rate of the examined process. But their effect on the quantity of the product is unknown. In order to learn more

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about the nature of the transformation, it seemed worthwhile to measure its heat *vs*. the quantity of the admixtures and *vs*. the measurement temperature.

Experimental

The calorimeter, the measurement method, the preparation of the amorphous samples have been described earlier [6, 7].

Results

Amorphous sulphur doped with selenium

Samples doped with 2, 4 and 6 at%Se, remelted at T_f=443 K, were investigated calorimetrically at 298 K. This yielded the graphical dependence of the temperature T_c of the calorimetric cell *vs*. time *t* [7]. From curves $T_c=f(t)$, the total heat Q evolved by 1 g of the doped sulphur was calculated from the formula

$$Q=\frac{K}{m}\left(T_{c_0} +\beta\int_0^\infty T_c \mathrm{d}t \right) \tag{1}$$

where K=4.19 J K^{-1} is the thermal capacity of the cell with the sample, m is the mass of the doped 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 [7].

The values Q obtained are presented in Fig. 1, where Q for pure (0 at%Se) sulphur (data from [7]) are given too. The diagram illustrates that the admixtures of selenium decrease the heat of the examined transformation.

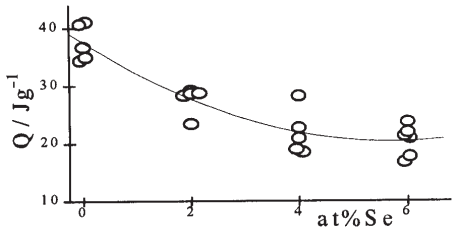

Fig. 1 Heat of transformation of chains in amorphous sulphur *vs*. quantity of admixtures of selenium at 298 K

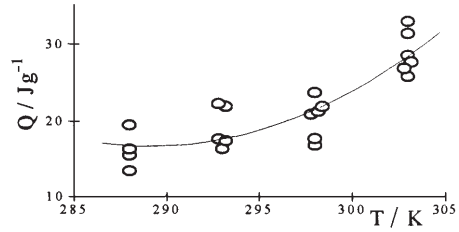

Fig. 2 Heat of the transformation of chains in amorphous samples S+6 at%Se *vs*. measurement temperature *T*

In the second part of the study the amorphous samples S+6 at%Se were examined at temperatures T=288, 293, 298 and 303 K. All samples were remelted at temperature T_f=443 K. The obtained results (Fig. 2) indicate that Q increases *vs*. the temperature T of the process.

Amorphous sulphur doped with phosphorous

Samples doped with 0.43, 0.86 and 1.28 at%P, remelted at T_f=443 K, were investigated calorimetrically at 298 K. The obtained values Q are presented in Fig. 3, where Q for pure (0 at%P) sulphur [7] are given too.

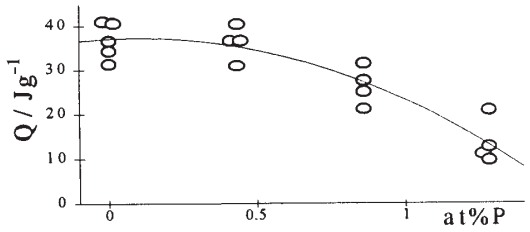

Fig. 3 Heat of transformation of chains in amorphous sulphur *vs*. quantity of phosphorous at 298 K

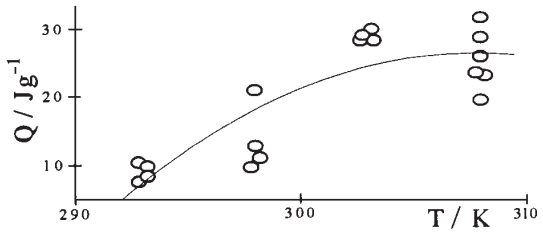

Fig. 4 Heat of transformation of chains in amorphous samples S+1.28 at%P *vs.* measurement temperature T

Similarly as in the case of S+Se-samples, the admixtures of phosphorous decrease Q.

The amorphous samples S+1.28 at%P were examined at temperatures T=293, 298, 303 and 308 K too. All samples were remelted at temperature T_f=443 K. The obtained results (Fig. 4) illustrate that the elevation of the process temperature increases Q.

Discussion

The obtained results indicate that the admixtures of selenium and phosphorous decrease Q evolved during the transformation of the chains occurring in the freshly formed amorphous samples. The elevation of the transformation temperature increases the value Q, what is in accordance with [9].

The results can probably be explained in such a way. The transformation of the chains progresses in the stages of the formation and of the growth of the nuclei. They are

formed during consecutive processes in the transformation centers, i.e., in the microregions where the chain fragments are arranged more or less parallelly and their atoms are ordered adequately [6–11]. Probably, a similar parallel configuration of the chains and adequate arrangement of their atoms are necessary for the growth of the formed nucleus [7–11]. During the melting of the mixture of sulphur and selenium the –S–Se–bonds are formed. Se atoms have different properties than S atoms (e.g., atomic radius, electronegativity). Thus, they additionally disturb the structure of the chains, what decreases the number of the transformation centers [10]. Consequently, the number of the grains of the product phase decreases. It is to expect too that the Se atoms disturb the configuration of the chains and the arrangement of their atoms in direct neighborhood of the formed nuclei, what diminishes the sizes of product grains. As result of the decrease of the number and of the sizes of the grains, the quantity of the product phase and consequently the evolved heat diminishes.

During the melting of the mixture of sulphur and phosphorus the –S–P(S–)(S–) bonds are formed and the chains become space-branched and its parallel packing is disturbed strongly [11]. It causes that the number and the sizes of formed grains of the product and, consequently, Q decreases.

Elevation of the temperature of the process causes the number of nuclei formed to increases or the grains of the new phase to reach larger dimensions [7–9].

Conclusions

The admixtures of selenium and of phosphorous decrease not only the rate of the transformation of the chains in amorphous sulphur [10, 11], but also the quantity of the product phase. These results are in accordance with supposition that for the run of the examined transformation the chains in amorphous sulphur should be more or less assembled in parallel and their atoms should be ordered adequately [6–11]. The elevation of the temperature, T_f, of the liquid sulphur [8], the atoms of the other elements and the branching [10, 11] strongly disturb the parallel packing of the chains and of their inner structure, what inhibits the process rate and decreases the quantity of the product.

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