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EFFECT OF TEMPERATURE OF LIQUID SULPHUR ON KINETICS OF TRANSFORMATION OF CHAINS IN ITS AMORPHOUS MODIFICATION

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Abstract

The rate of transformation of the chains in amorphous sulphur was examined by calorimetry at 298 K. The amorphous samples were remelted at the temperature T_f in the range from 458 to 573 K. Increase of T_f decreased the transformation rate. The results satisfy the equation $X = 1 - \exp[-(kt)^z]$ (X=transformation degree, t=time, and k and z=constants). A one-stage transformation was observed for samples remelted at $T_f \leq 473$ K. For $T_f \geq 523$ K, transformation in two stages was observed.

The effects of T_f on the kinetics of nucleation and the growth of the nuclei are discussed.

Keywords: crystallization in solid state

Introduction

Amorphous sulphur is formed by the quenching of liquid sulphur. This modification is composed of long chains S_n (n up to 12,000), octaatomic rings, S_8, and small quantity of other rings (S_6, S_7, S_9, etc.) [1]. The mass fraction of the chains increases with increasing temperature T_f of the liquid sulphur and it rises discontinuously from 0.03 to 0.4 at T_f=432 K [2–5]. In the case of $T_f \leq 443$ K, amorphous samples are obtained in which, immediately after rapid heating from the cooling bath temperature (77 K) to room temperature, an exothermic transformation of the chains proceeds quickly [6, 7]. This process probably involves the formation of small rings [6] or an unstable modification containing the chains [7]. The activation energy of this transformation is E=21 kJ mol^{-1} [7].

The kinetics of this process depends on the content of microregions in which the fragments of the adjacent chains are assembled in parallel and their atoms are arranged appropriately [6, 7]. Since a rise in T_f for the liquid sulphur decreases the arrangement of the chains and their atoms, it therefore brings about a lowering of the rate of transformation, as found by the DTA method [6]. How-

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ever, during the DTA measurement the transformation rate is accelerated continuously as a result of temperature rise, especially in the case of slowly transforming samples, and this makes it difficult to establish the real influence of T_f on the transformation. Accordingly, it was considered useful to carry out study at constant temperature in order to investigate the transformation kinetics in samples remelted at different temperatures T_f.

Experimental

The calorimeter, the measurement method and the preparation of the amorphous sample shave been described earlier [7].

Results

Amorphous sulphur samples remelted at T_f=458, 473, 523 and 573 K were examined at 298 K. The recorder sensivity and the paper speed were 0.0106, 0.00532, 0.000532 and 0.00532 K mm^{-1} and 50, 25, 10 and 10 mm min^{-1}, respectively. By the way of example, the measured temperatures T_c of the calorimetric cell *vs.* time t are presented in Fig. 1 for the samples remelted at 458 and 573 K. From these curves, the transformation degrees X *vs.* time t were calculated:

$$X = \frac{Q_t}{Q} \qquad (1)$$

where Q_t and Q=heats evolved by 1 g of sulphur in time t and $t=\infty$, respectively [7].

The curves $X=f(t)$ for the samples remelted at different T_f are presented in Fig. 2. The diagram obtained illustrates that a rise in T_f strongly decreases the rate of transformation of the chains in the amorphous modification.

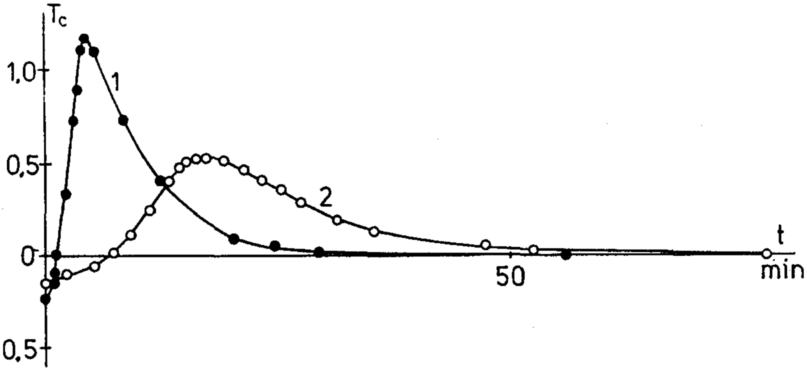

Fig. 1 Experimental curves for transformation of chains in amorphous samples remelted at 458 K (1) and 573 K (2)

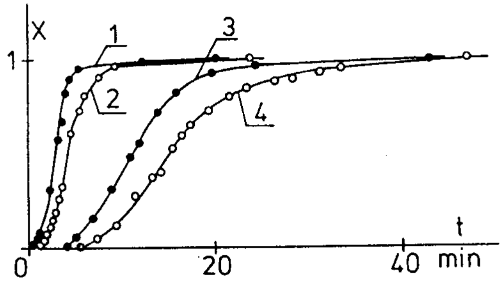

Fig. 2 Degree of transformation of chains, X, *vs.* time t for amorphous samples remelted at different T_f temperatures. 1 – 458 K, 2 – 473 K, 3 – 523 K, 4 – 573 K

The results were treated by the formula of Avrami and Erofeev [8, 9]:

$$X = 1 - \exp[-(kt)^z] \tag{2}$$

or in the logarithmic form:

$$\log[-\log(1-X)] = z\log k + z\log t - \log 2.303 \tag{3}$$

where k and z = constants, and log = common logarithms.

For the samples remelted at $T_f \leq 473$ K, function (3) is linear (Fig. 3), indicating that the results fit the above formula. For $T_f \geq 523$ K, dependence (3) is curvinilear. For a mathematical description of the results, it was assumed that

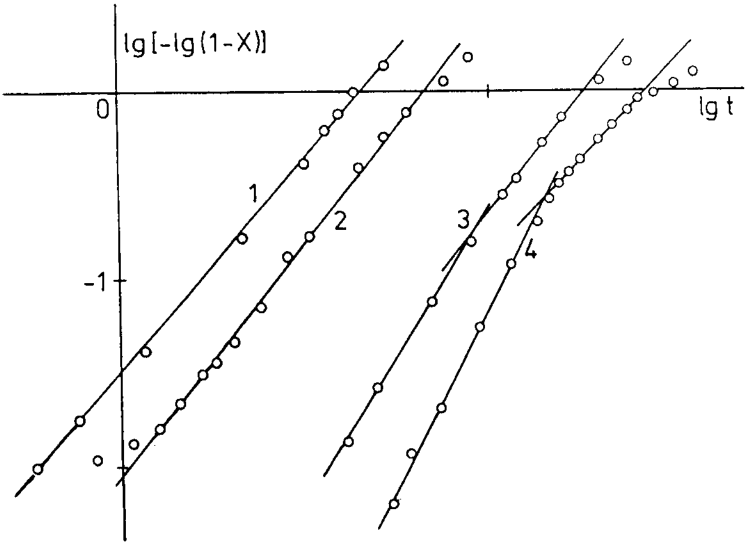

Fig. 3 Values lg[–lg(1 –X)] *vs.* lg$t$ for transformation of chains in amorphous samples remelted at different T_f temperatures. 1 – 458 K, 2 – 473 K, 3 – 523 K, 4 – 573 K

these curves arise from a combination of two straight lines, corresponding to two transformation stages, I and II. Their intersection point corresponds to X~0.4 (Fig. 3). Stage I of the process is probably identical with the transformation progressing in the samples remelted at $T_f \leq 473$ K. The nature of transformation stage II remains obscure.

From formula (3), the constants z and k were calculated. The values corresponding to stages I and II are given in Table 1, where the results for samples remelted at $T_f = 443$ K are also included. It may be seen from Table 1 that z_I increases with increasing T_f. The slope of the straight line $z_I = f(T_f)$ is equal to $b = 0.00516$ K^{-1}, with the standard deviation $S_b = 0.00175$ K^{-1}. It results from the Student table that, even at a significance level 0.01, b is not equal to zero. k_I decreases significantly with increasing T_f. z_I is approximately twice as large as z_{II}. The values of k_I and k_{II} are similar.

Discussion

The results indicate that the investigated transformation of the chains progresses in one or two stages (Fig. 3), depending on the temperature T_f of the liquid sulphur. The value of z_I corresponding to stage I increases with increasing T_f (Table 1).

It should be remembered that the stable nuclei that grow afterwards are formed at the beginning of the above-mentioned transformation [6, 7]. The nuclei are formed during consecutive reactions in the transformation centres, i.e. in the microregions where the chain fragments are arranged more or less in parallel and their atoms are ordered appropriately [6, 7]. z (formula (2)) is given by

$$z = i + \sum_{1}^{3} \chi_h \tag{4}$$

where the addends i and χ_h are described below.

The value of i depends on the number of slowly progressing processes of the nucleation [10]. The addend χ_h is the exponent in the equation

$$r_h = c_h(t - y)^{\chi_h} \tag{5}$$

where r_h and c_h = the dimension of the growing grain and its coefficient of linear growth in the definite space direction X, Y and Z, t = the duration of the transformation, and y = the moment of breaking of nucleus formation ($y<t$) [8–10].

The constant k (formula (2)) is given by

$$k = (\text{const.}\ L\ c_x\ c_y\ c_z\ k_1\ k_2\ k_3\ \ldots)^{1/z} \tag{6}$$

where L = the total number of centres, k_1, k_2, k_3 ... = the rate constants of the slowly progressing processes of nucleation, and c_x, c_y and c_z = growth coefficients from formula (5).

There are probably different degrees of internal arrangement of the centres. The less ordered the structure of the centre, the higher the values of i [7]. For a description of the process, the centres can be grouped in such a way that one i value corresponds to each group. Let these groups (1, 2, 3,... etc.) contain N_1, N_2, N_3,.. centres with the i values in the sequence $i_1<i_2<i_3<\ldots$. The observed increase in the function $z_I=f(T_f)$ is probably caused by the influence of T_f on the nucleation process. It seems that formation of small rings or an unstable modi-

Table 1 The constants z and k for the transformation of the chains in amorphous sulphur *vs.* T_f temperature

T_f	Stage I		Stage II	
	z_I	$k_I \cdot 10^3$	z_{II}	$k_{II} \cdot 10^3$
443 K	2.63	558		
	2.32	661		
	1.71	1240		
	2.82	631		
	2.90	758		
458 K	1.98	324		
	2.56	240		
473 K	2.82	72.4		
	3.16	100		
	3.51	112		
	2.62	63.1		
	2.42	132		
	2.49	199		
	2.94	175		
523 K	3.67	35.5	1.55	37.1
	3.30	35.5	2.27	31.6
	3.05	47.8	1.56	53.7
	2.40	41.6	1.46	39.8
	3.03	77.6	1.56	89.1
573 K	3.51	53.7	1.94	53.7
	3.60	47.9	2.30	48.9
	2.41	19.0	–	–
	3.71	64.5	1.92	63.0
	2.94	39.8	1.03	31.6
	2.86	63.0	1.35	21.9
	3.01	26.9	–	–

fication containing the chains occurs during stage I, as described previously [6, 7]. Initially, in stage I, the nuclei are formed in the best ordered groups of the centres, for which the values i_1, i_2, i_3, ... are within a narrow range. The experimentally detected i is a 'resultant' of these i_1, i_2, i_3, ... values. A rise in T_f intensifies the thermal vibrations of the atoms and of the chains in liquid sulphur, which is not favourable for local arrangements. Thus, the total number of centres $L=N_1+N_2+N_3+\ldots$ in the resulting amorphous modification diminishes. Moreover, the groups of centres with the best internal arrangement appear markedly fewer. For this reason, the contribution of these groups (for which the i values are relatively small) decreases during the course of stage I. At the same time, the fraction of groups with less ordered centres (for which the i values are larger) increases. This is probably the reason why the 'resultant' value of i_I and consequently z_I (formula (4)) increase with increasing T_f.

The occurrence of one or two stages may be explained by considering the influence of T_f on the nucleation and the nucleus growth. If the content of the appropriately arranged centres is very high, the transformation can proceed with their participation to the end. In that case, only stage I is detectable, as found for the samples remelted at $T_f \leq 473$ K (Fig. 3). If the content of the abovementioned centres is low and insufficient for the transformation to proceed to the end, the formation of the nuclei in these well-ordered centres terminates after some time. During the next time interval, i.e. during stage II, the growth of the nuclei formed earlier during stage I has the principal role. In that case, i_{II} is equal to zero. Since $i_I>0$, we have $z_{II}<z_I$ (formula (4)), which can explain the transformation course in two stages for samples remelted at $T_f \geq 523$ K.

During stage II, the nuclei can be formed in the poorly arranged centres too. However, this process probably does not have a significant influence on the course of stage II. For these centres, the i values are higher. In this case, one would expect $i_{II}>i_I$ and, consistently, $z_{II}>z_I$, which is not observed experimentally (Table 1).

A second interpretation of the occurrence of two stages is possible on the assumption that a parallel configuration of the chains and an appropriate arrangement of their atoms are necessary for growth of the nuclei. The better this arrangement around the nucleus and the more it spreads out (over a larger area), the faster the grains of the product grow and the larger the dimensions they attain, as determined by the coefficient χ_h in formula (5)[1]. The second explana-

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[1] According to formula (5), every grain of the new phase must sooner or later reach infinite dimensions. However, the exponential function $r_h=f(t)$ (formula (5)) for $0<\chi_h<1$ initially increases relatively rapidly, and later approaches infinity very slowly. Thus, initially the grain grows rapidly. This growth period is probably experimentally detectable. The later growth progresses very slowly and is no longer observable. The higher value of χ_h, the larger dimensions the grain reaches during the initial growth period. It was in this meaning that it was written above that the value of χ_h determines of the grain.

tion of the course of the transformation in one or two stages is as follows. At the beginning of the process, the nuclei are formed as described above. The number of nucleation centres with the correct internal arrangement is large and sufficient enough for the transformation to progress to the end, independently of T_f. The nucleation centres can differ somewhat in their internal arrangement. The values i_1, i_2, i_3, ... corresponding to these centres are contained in a narrow range. Their 'resultant' i is practically constant during the transformation. It increases with increasing T_f, as described above for stage I. However the growth of the nucleus depends on the arrangement in the immediate environment. If $T_f \leq 473$ K, the number of arranged regions is high and their dimensions are large. The grains of the new phase can grow rapidly and reach large dimensions. The transformation can progress rapidly to the end with participation of these regions, i.e. it progresses in one (stage I), for which the value of χ_{hI} is relatively high. $z_I = i + \sum_{1}^{3} \chi_{hJ}$. If $T_f \geq 523$ K, the number of large and appropriately arranged regions is small. Thus, after a relatively fast stage I with the participation of these well-ordered regions, the growth of the nuclei in the smaller and less arranged regions has the principal influence on the final period of the transformation, i.e. on stage II. The grains of the new phase attain smaller dimensions, for which the corresponding χ_{hII} values are less than χ_{hI}. Since the value of i is constant during the two stages, we have $z_{II} < z_I$ (Table 1).

It is difficult to decide which interpretation is correct. It seems, however, that the assumption of the necessity of an arrangement around the growing grain better explains the strong influence of T_f on the course of the process.

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