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POLYSULFIDES OF ARSENIC AND PHOSPHORUS

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In the sulfur—arsenic and sulfur—phosphorus systems, a number of stable compounds have been found, the highest of which are As_2S_3 and P_4S_{10} (1,2). As_2S_5 is formed under specific preparation conditions; upon sublimation it decomposes into As_2S_3 and sulfur and is not observed on phase diagrams. From consideration of these diagrams one may conclude that, in sulfur-rich regions, the indicated stable sulfides are present dissolved in an excess of sulfur. However, changes in a number of physical properties of sulfur melts containing arsenic and phosphorus do not occur monotonically with the amount of the introduced elements (3). Since sulfur at temperatures above 160° is a complex liquid consisting of various kinds of molecules in equilibrium with one another (4,5), such a change in physical properties is due either to the formation of new molecular forms or to a shift of the equilibrium among the preexisting ones. The latter, in turn, can evidently be caused only by the interaction of sulfur with the indicated elements. If interaction takes place, the question arises as to how it proceeds and into which molecular forms of sulfur arsenic and phosphorus are incorporated. Separation of the different kinds of molecules that are formed can be attempted by selective dissolution in carbon disulfide, analogously to the separation of the principal molecular forms of sulfur (4).

Table 1

As content in the initial alloy, %	Amount of sample transferred into solution, %	As content in the substance transferred into solution, %	Number of S atoms per 1 As atom in the insoluble part
2.31	93	1.10	~10
6.84	72	0.58	8
11.30	23	0.41	11
15.00	38	0.24	~8

To clarify the question, melts were prepared in sealed and evacuated thick-walled quartz ampoules. Chemically pure sulfur and specially prepared As_2S_3 and P_4S_{10} were taken as starting substances. Homogenization was carried out by shaking the ampoules. All ampoules were heated to a temperature of about 900°. The total duration of heating was six hours. After the ampoules had cooled, the resulting preparations were ground, and weighed portions were extracted with carbon disulfide in the apparatus used by Stock for extraction and recrystallization of phosphorus sulfides ([6]). The range of compositions up to a content of 7 at.% arsenic or phosphorus was investigated. Extraction was continued for 14 hours. Under such extraction, molecular forms with a relatively small number of atoms should pass into solution. The insoluble part should consist of polymeric products similar to the insoluble Sμ form. Tables 1 and 2 give the quantitative results of extraction and the analytically determined contents of arsenic and phosphorus.

To determine arsenic, weighed portions of the substances were treated with a mixture of sulfuric and nitric acids until complete decomposition and removal of nitric acid. Then $AsCl_3$ was distilled off by the Ladebourg method. In compositions with phos-

phorus, after decomposition in bromine-nitric acid and removal of bromine and nitric acid, phosphoric acid was determined by the Betger—Wagner method. In samples containing arsenic in the experiments after the second extraction, the insoluble residue was analyzed for arsenic by the modified Schullek—Villecz method. The weighed portion was decomposed with perhydrol and concentrated sulfuric acid, followed by reduction with sulfurous hydrazine, destruction of the excess of the latter by boiling, and subsequent titration with a 0.01 N solution of $KBrO_3$.

From the data given in Table 1 it is seen that in alloys with arsenic the soluble part of the samples decreases sharply when its content is increased above 4 at.%. Accordingly, the absolute amount of arsenic passing into solution also sharply decreases. It follows from this that arsenic is incorporated into long, linearly polymerized sulfur molecules and at the same time is bound by low-molecular forms. The latter is due to the interaction of the introduced stable sulfide with the S_8 rings and short biradicals forming the π-form of sulfur.

Table 2

Content of P in the initial alloy, %	Amount of sample passed into solution, %	Content of P in the substance passed into solution, %	Number of S atoms per 1 atom of P in the insoluble part
0.97	22.8	0.052	77
2.91	21.8	0.083	25
4.65	31.0	0.134	13
6.80	9.9	0.52	12

The short biradical molecules containing arsenic that arise in the melt are not capable of complete subsequent polymerization. This is due to their dispersion among the main mass of long linear forms, analogous to what occurs in liquid sulfur, in which long linear chains protect low-molecular forms. Upon their passage into the carbon disulfide solution during extraction, their biradical character is manifested in the formation of a product insoluble in carbon disulfide, which is the result of the cross-linking of individual molecules into highly polymerized products.

After complete evaporation of the carbon disulfide, a solid product is obtained. It was subjected to a secondary extraction, by means of which it was again possible to separate easily the soluble and insoluble parts. The first was almost pure sulfur, and the second was a sulfide whose composition corresponded to a content of one atom of arsenic per 25 atoms of sulfur.

After the first extraction, the arsenic content in the insoluble part for all the compositions studied was about nine atoms of sulfur per one atom of arsenic, despite the different arsenic contents in the initial alloys. Such behavior is due to the fact that arsenic atoms stabilize sulfur chains, but only in the case where its content in the chain is not less than this limiting value. Otherwise, under ordinary conditions the chains decompose and the content of the part of the sample soluble in carbon disulfide increases.

Similar experiments were carried out with sulfur—phosphorus samples, the results of which are given in Table 2. Here the soluble parts are much smaller than in the case of sulfur—arsenic samples. In addition, the number of sulfur atoms per one phosphorus atom in the insoluble part depends on the initial phosphorus content in the sample. At phosphorus contents up to 4 at.% this number is equal to 25, whereas at higher contents it decreases to 12. In contrast to the compositions with arsenic, in this case an increase is observed in the amount of phosphorus passing into solution as its content in the sample increases. In addition, the sulfur—phosphorus samples do not give an insoluble part upon secondary extraction with carbon disulfide of the product obtained after the first extraction that had passed into solution. All these data indicate a different structure and composition of the phosphorus sulfides formed, as compared with the arsenic sulfides. A certain increase in the solubility of phosphorus with an increase in its content in the initial-

···in the melt can be explained by the formation of P_4S_{10} molecules, which have appreciable solubility in carbon disulfide.

In order to determine the short-range order in the polysulfides formed, X-ray diffraction studies were carried out. Data for samples not subjected to extraction are given in the work of G. S. Zhdanov and one of us (7). Here we present results obtained by the method of radial distributions for the insoluble portions of sulfur-arsenic samples after the first and second extractions.

Fig. 1

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

In Fig. 1 are shown the experimental intensity curves of X-ray scattering, corrected for the polarization factor and incoherent scattering. The lower curve refers to the just-obtained insoluble portion of the sample after the first extraction; the next curve refers to the same sample, but recorded one day after preparation; and, finally, the upper curve refers to the insoluble portion of the sample after the second extraction. In Fig. 2 are presented the atomic-density distributions obtained from the intensity curves of Fig. 1 on the "Strela" machine at the Computing Center of Moscow University.

Fig. 2

For the freshly prepared sample after the first extraction (curve *II*), the maximum corresponding to the sulfur-sulfur interatomic distance is located near 2.18 Å, whereas for the unextracted melt with the corresponding arsenic content this maximum is at a distance of 2.30 Å. The observed decrease can be explained by the fact that, after washing out molecules with low molecular weights from the sample, macrovoids remain in it, and the chains of the insoluble portion tend to fill these voids. A looser packing is realized, which leads to an increase in the distance between the chains, causing a weakening of the intermolecular interaction and an enhancement of the intramolecular interaction, as well as a shortening of the sulfur-sulfur interatomic distance.

A similar maximum in the insoluble part of the sample after the second extraction (curve *I*) has a clearly asymmetric shape, which is the result of the superposition of two maxima corresponding to the interatomic distance in pure sulfur, 2.07 Å, and to the sulfur–arsenic interatomic distance, 2.30 Å. These phenomena are evidently associated with the processes of polymerization of biradical molecules and the packing of the aggregates formed.

The part of the sample that remained undissolved as a result of the first extraction is structurally unstable. Within a day the atomic-density curve changes its form (curve *III*), mainly because of the broadening of the maximum at 2.18 Å, although its area does not change or changes only very slightly. These changes most probably occur in connection with partial breakdown of the chain structure and the formation of ring sulfur.

Similar studies were not carried out for the extracted sulfur–phosphorus samples, since in these cases the soluble part of the samples is much smaller and there is no possibility of detecting any significant structural changes in comparison with samples not subjected to extraction.

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CITED LITERATURE

[1] *Gmelins Handbuch*, System No. 17, 1952, p. 415.
[2] J. van Wazer, *Phosphorus and its Compounds*, 1, N. Y., 1958, p. 289.
[3] J. Schenk, *Physica*, **23**, 325 (1957); J. van Wazer, *Phosphorus and its Compounds*, 1, N. Y., 1958, p. 301.
[4] P. Schenk, *Zs. anorg. u. allgem. Chem.*, **280**, 1 (1955).
[5] G. Gee, *J. Polymer Sci.*, **16**, 459 (1955).
[6] A. Stock, *Ber.*, **43**, 150 (1910).
[7] G. S. Zhdanov, A. I. Soklakov, *Crystallography*, in 2 (1962).

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