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# Chemistry

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**Abstract**

**Full Text**

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## Phase Diagram of Sulfur at High Pressure

*(Presented by Academician V. S. Sobolev, 22 III 1965)*

Recently, the question of melting of substances at high pressures has been attracting close attention from researchers. The shape of the melting curve makes it possible to judge not only the thermodynamic properties of a substance, but also the presence of phase transitions. An anomalous form of the melting curve, having a maximum (<sup>1-4</sup>) and not agreeing with Simon's equation (<sup>5</sup>), is as a rule associated with the emergence of a new phase.

Sulfur is an element that has several modifications at atmospheric pressure; moreover, it passes into a metallic state at ultrahigh pressure (<sup>6</sup>) and therefore represents a rather interesting object for investigation.

**Fig. 1.** Phase diagram of sulfur at high pressure. *a* —our data, *b* —data of Syuss et al., *v* —Tammann's data.

The present work continues our studies on the melting of sulfur under pressure. Investigations of this type have been carried out in various pressure ranges (<sup>7-9</sup>). The present work was carried out in a ram-type cubic multiplier (<sup>10</sup>) according to the previously described method (<sup>11</sup>). The apparatus was calibrated against known phase transitions in Bi and Tl. To these transitions were assigned the values determined by Kennedy and LaMori (<sup>12</sup>). According to our estimate, the accuracy of pressure measurement was up to 25 000 kg/cm<sup>2</sup>  $-\pm 1000$  kg/cm<sup>2</sup>, and above this  $-\pm 1500$  kg/cm<sup>2</sup>. For temperature measurement a chromel-alumel thermocouple was used, in whose readings no pressure correction was introduced. The work was carried out with sulfur containing no more than 0.001% impurities.

Figure 1 presents the phase diagram of sulfur, on which are plotted Tammann's data up to 3000 kg/cm<sup>2</sup> and the results of our work up to 11 000 kg/cm<sup>2</sup> under hydrostatic pressure. In addition, it also contains experimental values of melting temperatures under pressure determined by Syuss and co-workers (<sup>8</sup>) in the region of 20–60 kbar, and the data of the present work from 13 000

to 37 000 kg/cm<sup>2</sup>. The latter were obtained using pyrophyllite as the pressure-transmitting medium. In the work of Syuss <sup>(8)</sup> the results of Tammann and the roughly approximate data of Rose and Monte <sup>(9)</sup> are also given. On the basis of these data and their own results, in work <sup>(8)</sup> the conclusion is drawn that a new phase of sulfur exists and that there is a triple point in the region of 10–20 kbar. The shape of the melting curve of sulfur, determined in the present work, also indicates this. The melting curve of sulfur has a maximum in the region of 16 000 kg/cm<sup>2</sup> and 310°, and a triple point in the region of 19 000 kg/cm<sup>2</sup> and 290°. One of the confirmations of the presence of a new phase of sulfur is also the irregularity we observed on the compressibility curve of sulfur at

22,000–23,000 kg/cm<sup>2</sup> and room temperature. The experiment to determine the phase transition in sulfur was carried out as follows. Several cubic centimeters of sulfur were compressed in a multiplier. The displacement of the lower press plate was determined as a function of pressure. In the indicated pressure range, the compressibility curve showed a kink, indicating a sharp decrease in the compressibility of sulfur.

On the basis of the data obtained, it is very difficult to draw a conclusion about the nature of this phase transition. X-ray diffraction studies under pressure may provide the necessary clarity in resolving this question.

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*Note: Figure translations are in progress. See original paper for figures.*

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