THE MELTING CURVE OF SULFUR UP TO 11 000 KG/CM^2

I. E. Paukov and E. Yu. Tonkov

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There has been a noticeable growth of interest in the melting curves of substances under pressure. Simon's well-known equation [1], which predicts a continuous increase in melting point with increasing pressure, fits the experimental data for the majority of substances. However, recent work [2–4] has shown that Simon's equation is unsuitable for rubidium, cesium, and tellurium.

Some results are given below of a test of the applicability of Simon's equation to sulfur. Detailed investigations on sulfur have been carried out by Tammann [5] and Röse and Mügge [6]. Tammann investigated the sulfur melting curve only up to 3150 kg/cm^2, while Röse went as far as 19 300 kg/cm^2 and obtained different results. We note that the method used by Röse and Mügge casts doubt on the reliability of their results.

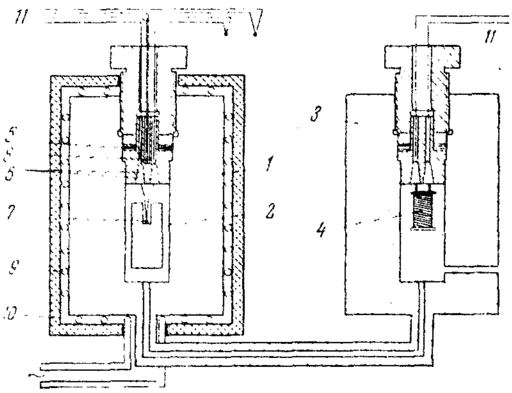

Fig. 1

The tests were carried out in high pressure equipment usable up to 12 000 kg/cm^2 at temperatures up to several hundred degrees. The apparatus consisted of two high-pressure pumps, a pressure booster, a high-pressure valve, and a chamber with a working volume greater than 50 cc. The pressure-transmitting medium was glycerine containing 10% water. A diagram of the high-pressure chamber is shown in Fig. 1. The chamber itself 1 was a high-pressure vessel made from 45KhMNFA steel. Pressure was transmitted from the pumps and pressure booster to working space 2 and chamber 3, which contained manganin manometer 4. The outlet hole from the working chamber was covered by a mushroom seal 5 with two conical electrical bushings 6 with mica insulation. The ampul temperature was measured with copper-constantan thermocouple 7. A second copper-constantan thermocouple 8 in the mushroom seal, with connections to galvanometer 11, was used as a control. The chamber was heated by nichrome spiral 9 and thermal isolation was obtained via asbestos covering 10. Figure 2 shows the ampul and the means of achieving a hermetic seal. Ampul 1, in which the sulfur was placed, was made of teflon, while the cover 2 was duralumin. Spring 3, pressing against cover 2, was tightened in cap 4 by screw 5.

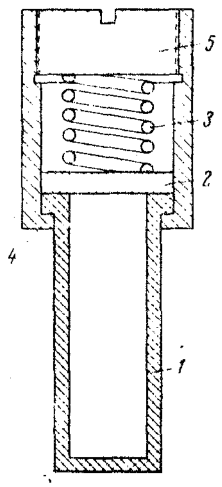

Fig. 2

It should be mentioned that ampuls of different construction were also used in this investigation, in particular, a completely hermetic lead ampul. Although some of the sulfur reacted with the ampul walls, the experimental results were completely satisfactory.

The manganin manometer, resistance ~106 ohms, was calibrated against a standard piston manometer (MOP-10 000) up to 10 000 kg/cm^2. The calibration accuracy was ±25 kg/cm^2. For pressure measurements above 10 000 kg/cm^2 the manometer calibration was extrapolated. The sensitivity of the measuring system was 1 kg/cm^2.

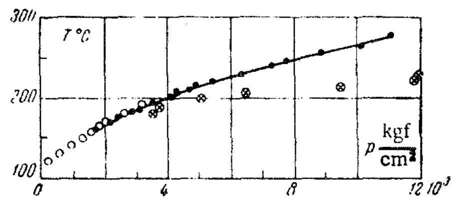

Fig. 3

The copper-constantan thermocouples were calibrated to 220° C with an accuracy of 0.1° [7]. The thermocouple calibration curves were extrapolated to 280° C; this may cause an error not greater than 0.3° at 280° C. Readings obtained with the two thermocouples did not differ by more than 0.1°. It should be noted that the majority of the experiments were carried out using only thermocouple 8 (Fig. 1).

The melting point of sulfur under pressure was measured in the following way. The pressure was raised to a predetermined value and heating commenced. When the chamber temperature was 7°–10° below the melting point at that pressure, a constant heating rate of ~0.2°–0.3° per minute was imposed. Subsequently, thermocouple and manometer readings were taken every two minutes. The onset of melting was indicated by an increase in the rate of pressure increase.

This method was used in several experiments to determine the melting temperature of tin at pressures from 2500 to 8000 kg/cm^2; satisfactory agreement with literature values [8,9] was obtained.

p	T, °C	p	T, °C	p	T, °C
1740	159.5	4740	212.4	2000	165.0
1830	161.0	4880	215.5	3000	184.7
2220	169.6	5460	220.7	4000	201.8
2480	176.2	6370	228.5	5000	215.3
2960	182.7	7320	240.4	6000	226.6
3150	186.0	7870	246.5	7000	237.2
3580	193.8	8910	256.8	8000	247.5
4140	202.2	10160	267.1	9000	257.3
4270	207.2	11120	278.3	10000	267.1
				11000	276.8

Two grades of sulfur were used: "extra pure," 99.999% purity, and "pure" stick sulfur, 99.6% purity. However, the experimental results were practically the same with both forms.

The experiments covered the pressure range from 1700 to 11 000 kg/cm^2; the results are given in the table and in Fig. 3 (filled circles). The results obtained by Tammann (open circles) and Röse and Mügge (crossed circles) are also shown in Fig. 3. To the right of the double lines in the table are given values of the melting point taken from the smooth curve in Fig. 3. The curve obeys Simon's equation up to 11 000 kg/cm^2, with constants a = 650 kg/cm^2, b = −3090, and c = 2.93.

The deviation of the experimental points from the smooth curve averages not more than ±0.9°. As a check, Debye crystallograms were taken of the original sulfur and of sulfur melted and recrystallized under pressure. They were identical.

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