

to exhibit x-ray characteristics identical to those reported in the literature¹⁶ for so-called plastic sulfur. It seems probable, therefore, that all data taken after the first temperature cycle were actually indicative of melting of plastic sulfur instead of rhombic. These points are shown by the open circles in Fig. 1 and it is seen that they correspond closely to the rhombic melting data. Within the limits of experimental error there appears to be no difference in the melting-point curves of rhombic and plastic sulfur. Since the data presented here extrapolate to the atmospheric-pressure melting point and since the transformation points of the rhombic and plastic forms agree within experimental error, it is felt that the data given do represent melting rather than just a rhombic to plastic transition, as such. (Owing to the scatter, the data of Fig. 1 are well represented by a straight line; the solid line shown has a slope of 15°C/kbar.

In order to arrive at the exact nature of the transformation of the rhombic sulfur to the plastic variety, further studies were made. It was found that at ambient conditions the plastic sulfur (formed by melting the rhombic under pressure) spontaneously reverted to the rhombic structure over a period of a few days. Samples of sulfur subjected to pressure and temperature conditions just short of those required to melt them (as indicated by the currently reported data) remained in the rhombic phase. Samples subjected to various temperatures exceeding the melting point, at the pressure in question, were all transformed to the plastic form. Without exception, all samples subjected to pressure and temperature conditions exceeding those required for melting were found to exist in the plastic form when returned to ambient conditions. Various reasonable rates of temperature change used in crossing the melting curve seemed to have no effect on the transformation to the plastic form.

It is interesting to note that Bridgman¹⁷ observed

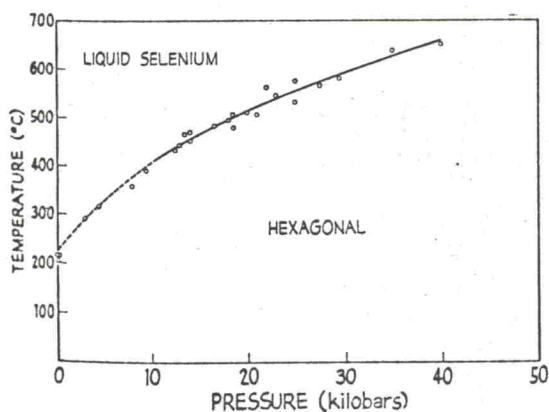


Fig. 2. Melting curve of selenium. The dashed portion of the curve is taken from Ref. 4.

¹⁶ N. S. Gingrich, *J. Chem. Phys.* 8, 29 (1940); and C. W. Tompson and N. S. Gingrich, *ibid.* 31, 1598 (1959).
¹⁷ P. W. Bridgman, *Phys. Rev.* 48, 825 (1935).

that combined shear and hydrostatic pressure initiated this same conversion of sulfur to the "amorphous, sticky variety," whereas hydrostatic pressure alone failed to do so. This further supports the conclusion that the data presented are indicative of melting and the transition to the plastic form is a secondary effect related to the recrystallization process. Pressure inhibition of the atmospheric pressure, 160°C liquid "change point" may explain the formation of plastic sulfur upon melting and cooling under pressure, since the formation process is apparently related to the recrystallization of the phase of liquid sulfur existing above the atmospheric "change point."^{17a}

Since the thermal conductivity of all forms of sulfur is comparatively very low,¹³ the magnitudes of the discontinuities (indicative of melting) in the temperature dependence of ΔT upon melting of the plastic sulfur were very small, as one would expect, since the thermal conductivity¹³ is about a factor of 3 smaller for plastic than for rhombic sulfur. The DTCA signals for sulfur were sometimes completely masked by recorder "ac pick-up" from the heater and transient effects in the signal during the approach to temperature equilibrium. These problems became so acute that we were unable to obtain reliable data on sulfur above 45 kbar.

B. Selenium

Selenium, like sulfur, exists in several allotropic forms, the most stable room-temperature crystal structure being hexagonal with the atoms arranged in spiral chains.¹⁸ A glassy, amorphous form of selenium can be produced by cooling the liquid. This form has no well-defined freezing point and shows a glassy consistency which is retained at room temperature.

The experimental data on the melting of selenium are shown in Fig. 2. The dashed line represents the data of Babb⁴ to 10 kbar and the agreement with our data is quite good. The solid line is what is considered the best fit to the experimental points.

The DTCA signals obtained upon melting of selenium were quite strong, though not as well defined as those for tellurium. However, the signals indicative of freezing were very small and often not seen at all. Also, the magnitude of the signals decreased with increasing pressure and were at times masked by the experimental difficulties discussed in the section on sulfur. We were unable to obtain reliable data above 40 kbar.

In order to establish whether the failure to obtain

^{17a} Note added in proof. By application of the theory of equilibrium polymerization, A. Eisenberg [*J. Chem. Phys.* 39, 1852 (1963)] has shown that the transition temperature associated with this "change point" decreases with increasing pressure, becoming equal to the melting temperature at about 0.8 kbar. Thus above 0.8 kbar liquid sulfur is the high-viscosity form which crystallizes in the plastic modification upon cooling. Presuming this theoretical result to be valid, the connection between the formation of plastic sulfur and the recrystallization process appears established.

¹⁸ A. von Hippel, *J. Chem. Phys.* 16, 372 (1948).