Supercooled Sulfur and its Viscosity

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It is not generally known that liquid sulfur, even though not highly purified, may be supercooled far below its melting point. Maximum supercooling may be brought about by allowing liquid sulfur, purified as directed in an earlier article,[1] to cool slowly, i. e., at the rate of about 0.5° per minute, at the same time taking care to reduce to a minimum all of the usual factors that tend to promote crystallization. The supercooled liquid may be kept indefinitely at 100° but its longevity decreases as the temperature is lowered. In the neighborhood of 50° it is possible only occasionally to maintain the liquid state in bulk (5 cc. or less) for about twenty minutes. When the temperature falls below about 50°, solidification always results.

The rate of cooling and the purity of the sulfur are not critical factors in obtaining extensive supercooling. For example, partially purified sulfur[1] may be supercooled readily to as low as 70° by thoroughly heating 25 g. at a temperature of 140° and above in a tube (20 × 3 cm.) completely immersed in an air-bath and cooling at room temperature by removing and suspending the tube at an angle of about 20° to the horizontal.

Liquid sulfur in the form of droplets (3 mm. or less in diameter) may be supercooled to room temperature. On standing at this temperature the larger drops crystallize within one or two weeks, while the smaller ones may persist in the supercooled state for years. These drops are indistinguishable from drops of sulfur in the true liquid state except that they appear to be of such high viscosity as to be solid. On contact the clear transparent droplets become opaque with solidification spreading rapidly from the point of indentation. In Fig. 1 are shown drops of supercooled sulfur at room temperature and a drop (A) which has crystallized spontaneously. When heated to above 120° the clear drops show no visible transition changes to the true liquid state. It would appear that this form of sulfur may be classed with such undercooled liquids of high viscosity as glass, certain alloys, waxes, etc. Supercooling of sulfur is comparable to that shown by its nearest homolog—selenium.
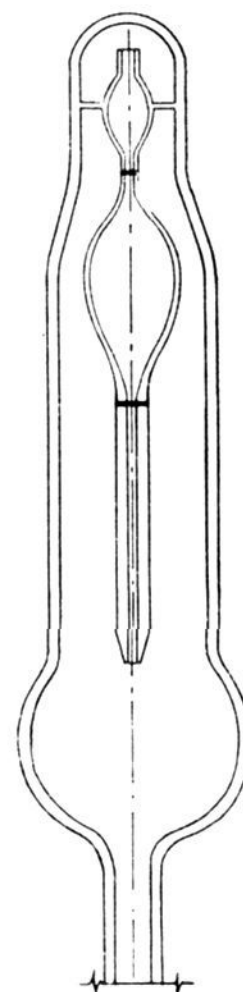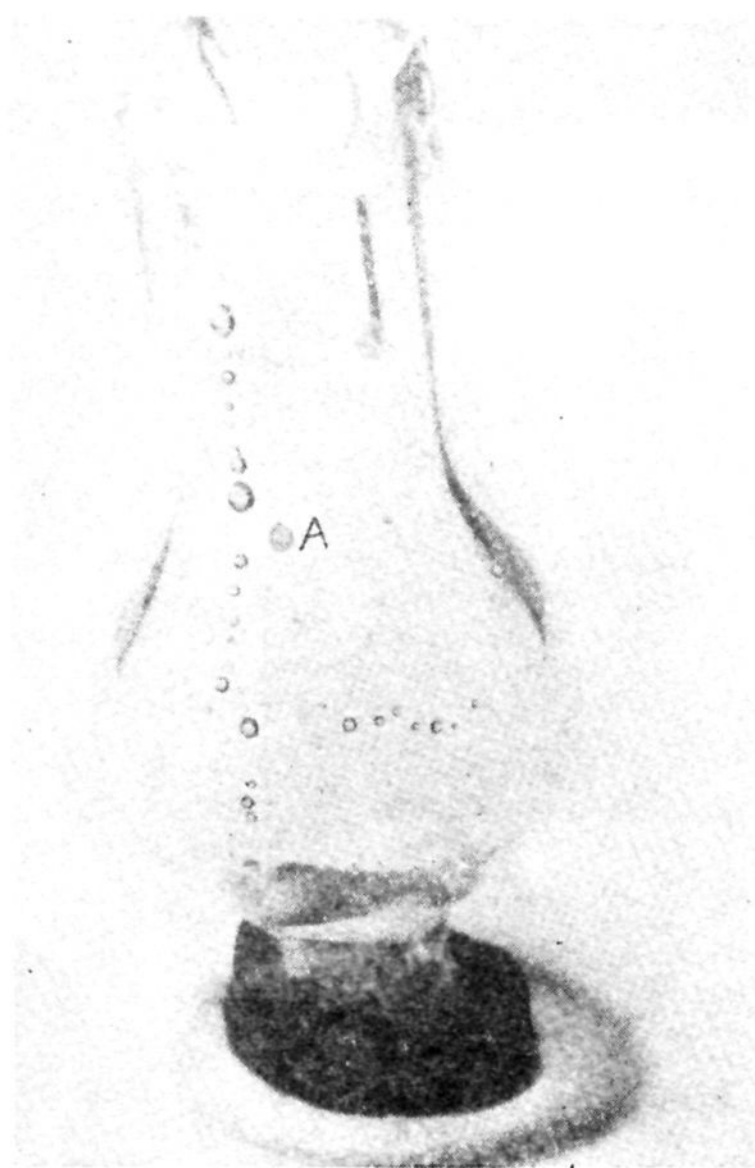

Fig. 1.—Supercooled drops of sulfur on the inner surface of a glass tube at room temperature. "A" drop which crystallized spontaneously.

Fig. 2.—Viscometer used to determine viscosity of supercooled sulfur.

The Viscosity of Supercooled Sulfur

Farr and Macleod[2] determined the "time of flow" of sulfur at various temperatures down to 80° but did not convert these values to C. G. S. units. In view of the anomalous viscosity[3] of sulfur above 160°, and its possible importance for fundamental study in chain formation, it was believed worth while to determine viscosity of sulfur in the supercooled region and thus complete the viscosity–temperature curve for the known liquid range, namely, about 50 to 444°.

(1) R. F. Bacon and R. Fanelli, Ind. Eng. Chem., 34, 1043 (1942).

(2) C. C. Farr and D. B. Macleod, Proc. Roy. Soc. (London), 118A, 584 (1928).

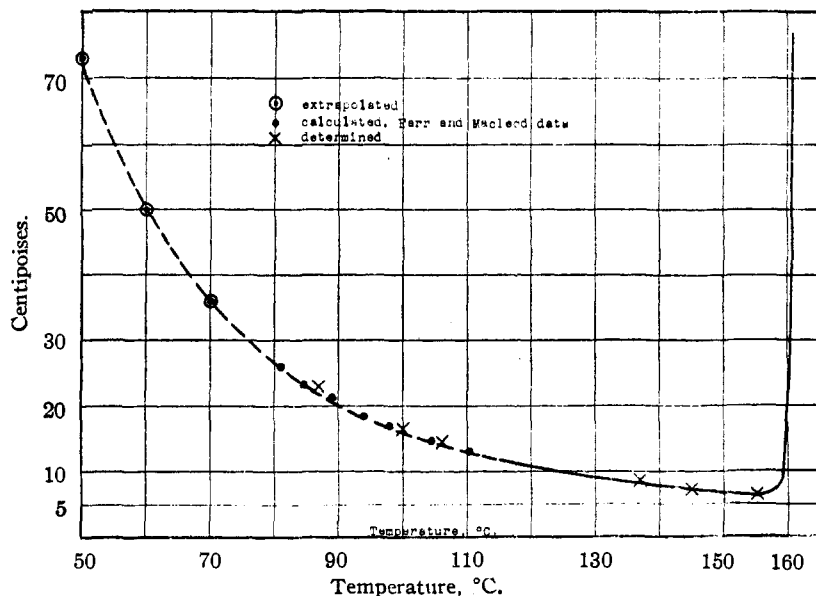(3) R. F. Bacon and R. Fanelli, THIS JOURNAL, 65, 639 (1943).

Fig. 3.—Viscosity of supercooled sulfur: ⊙, extrapolated; ● calculated from Farr and Macleod data; ×, determined.

Experimental Methods

A special viscometer shown in Fig. 2 was used. After charging with purified sulfur[1] the viscometer was sealed at its open end and mounted in a cradle set in an air-bath.[3] The cradle could be rotated through 360°. The temperature was given by an iron–constantan couple fastened to the narrow end of the viscometer. The viscometer was rotated from the filled position through 180° and the time of emptying the larger bulb noted. The viscometer was calibrated with a water–glycerol mixture of known viscosity. The densities of sulfur in the supercooled region are not known but the necessary values may be obtained by extrapolation of the known values[4] between 115 and 160°, all of which fall on a straight line.

The data obtained are shown in Table I and are plotted × as in Fig. 3. The continuous curve above 115° has been determined by two different methods and independent investigators.[3,5] The determined values above 115° fall sharply on this curve, thus proving the validity of the method employed. Farr and Macleod's "times of flow" were converted into C. G. S. units using sulfur as the reference liquid. These data are shown as ● on the curve and are based on the known viscosity and density of sulfur at 120.4°: namely 11.0 centipoises and 1.805, respectively,

at which temperature Farr and Macleod's "time of flow" is given as 47.6 seconds. Attempts to determine the viscosity below 80° were unsuccessful, but by plotting all the supercooled values on log/log paper (Fig. 4), extrapolated values for temperatures between 50° and 80° may be obtained. These are shown as ⊙ in Fig. 3.
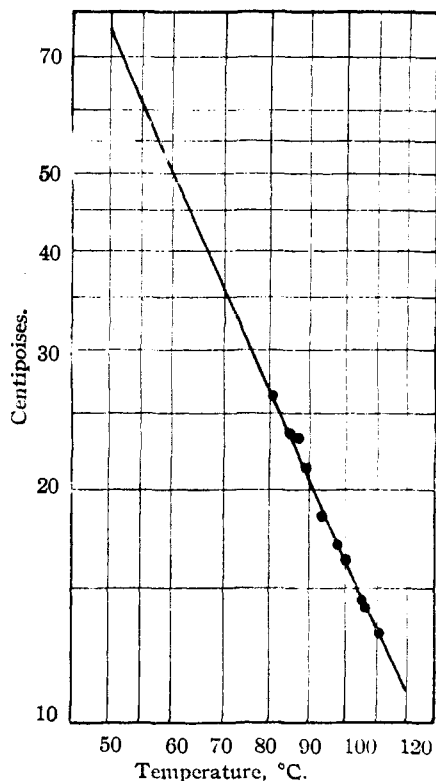

Fig. 4.—Viscosity of sulfur between 50 and 120°.

TABLE I

VISCOSITY OF SULFUR BETWEEN 50 AND 155° IN CENTIPOISES

Temp., °C.	Visc., c. p.	Method	Temp., °C.	Visc., c. p.	Method
50	73	Extrap.	97.9	17.1	Calcd.
60	50	Extrap.	100	16.3	Detd.
70	36	Extrap.	104.5	14.7	Calcd.
80.8	26.2	Calcd.	106	14.4	Detd.
84.7	23.6	Calcd.	110.3	13.2	Calcd.
87	23.3	Detd.	130	8.9	Detd.
88.8	21.4	Calcd.	145	7.4	Detd.
93.8	18.4	Calcd.	155	6.7	Detd.

(4) A. M. Kellas, J. Chem. Soc., 113, 903 (1918).

(5) C. C. Farr and D. B. Macleod, Proc. Roy. Soc. (London), 97A, 80 (1920).
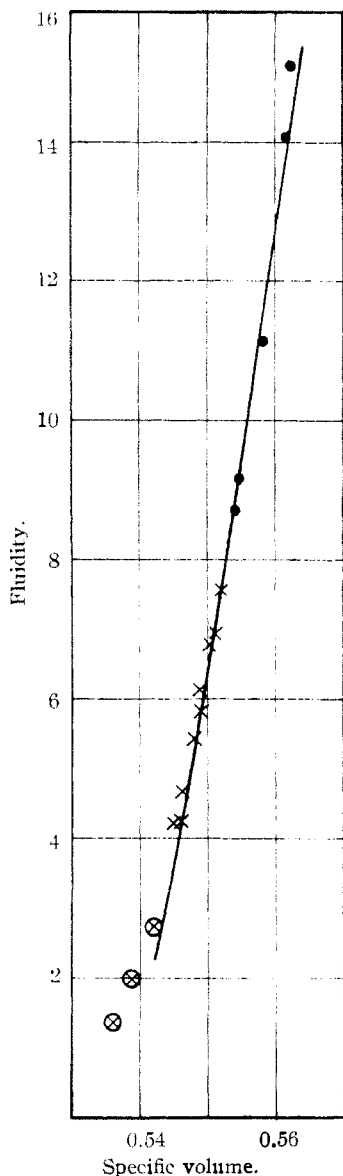
Fig. 5.—Relationship between fluidity and specific volume
of sulfur from 50–120°

Discussion

The viscosity of a liquid depends not only upon its molecular complexity but also upon the molecular structure. The uniform decrease in the viscosity and the density of sulfur with increase in temperature to about 160° indicates that the liquid is made up of relatively simple molecules. Warren and Burwell[6] by X-ray analysis show that the sulfur molecule in the orthorhombic and monoclinic forms is an eight-membered puckered ring and that just above the melting point S_8 molecules predominate. Ewell and Eyring[7] by calculation from viscosity data confirm the presence of S_8 molecules in the liquid up to about 160°.

According to Batschinski[8] the empirical relationship $v = w + c/\eta$ where v is the specific volume, η the viscosity and w, c are constants, holds for a number of non-associated liquids. The expression indicates a linear relationship between the fluidity $1/\eta$ and the specific volume. The relationship between the fluidity and the specific volume of sulfur is shown in Fig. 5. The determined data for temperatures above and below 115° are shown by ● and ✕, respectively, the extrapolated data below 80° by ⊗. A straight line passing through nearly all of these values tends to confirm the presence of simple non-associated molecules in the entire liquid range shown in Fig. 3. For a discussion of the properties of liquid sulfur above 160°, see Powell and Eyring.[3,9]

Summary

Liquid sulfur may be supercooled in bulk to about 50° and in droplets to room temperature.

Viscosity values of supercooled sulfur are given down to 50°.

The nature of the supercooled liquid is essentially the same as that between 115 to about 160°.

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(6) B. E. Warren and J. T. Burwell, J. Chem. Phys., 3, 6 (1935).
(7) R. H. Ewell and H. Eyring, ibid., 5, 726 (1937).
(8) A. J. Batschinski, Z. physik. Chem., 84, 643 (1913).
(9) R. E. Powell and H. Eyring, THIS JOURNAL, 65, 643 (1943).