[CONTRIBUTION FROM THE TEXAS GULF SULPHUR COMPANY, INC.]

The Surface Tension of Sulfur

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The history of the many attempts to determine the surface tension of sulfur is replete with frustration and contradiction. Eminent investigators[1] in the field of capillarity abandoned their trials because of the difficulties encountered.

Fig. 1A.—Surface tension of sulfur below 160°: ● this work; ◉ Kellas' data for tubes <0.5 mm. diameter.

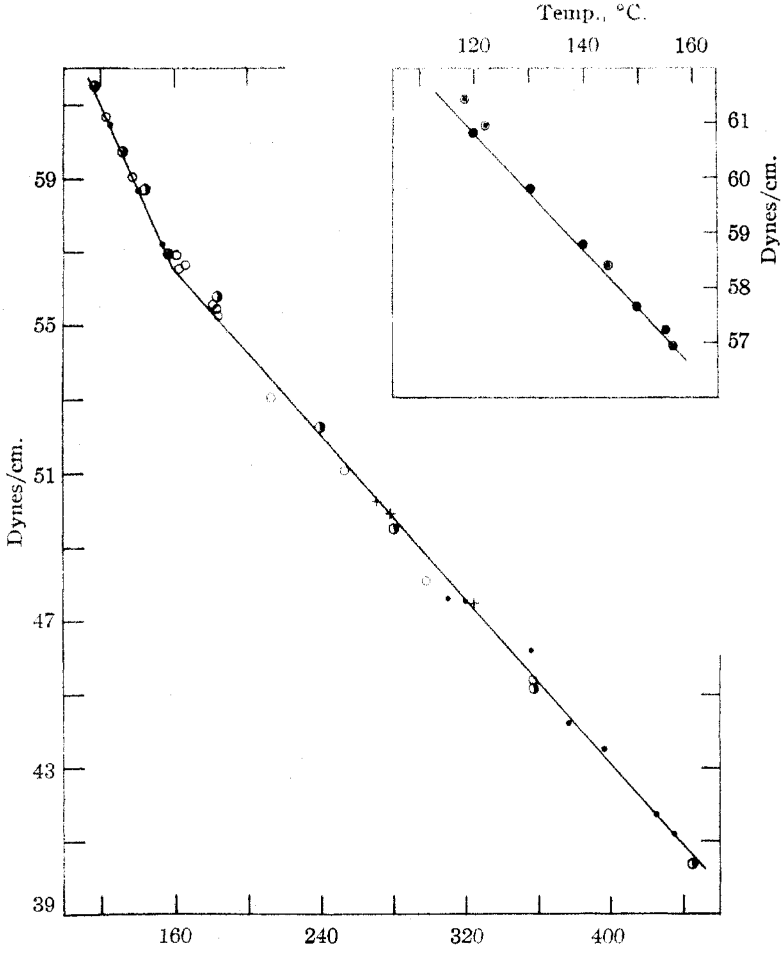

Fig. 1.—Surface tension of sulfur by the maximum bubble pressure method: ●, rising temperature; ×, falling temperature; ◑, Kellas' capillary rise values multiplied by 1.035; ○, values given by sulfur saturated with hydrogen sulfide.

Pisati[2] found that sulfur appeared to behave in a normal manner in that the surface tension fell with rise in temperature while Capelle[3] reported that it increased. Rudge[4] indicated that the capillary rise appeared to be constant in the temperature range below 160°. Reported surface tension values by the capillary rise method vary from 11.6 to 61.2 dynes per cm. at 120°. Zickendraht[5] employed the maximum bubble pressure method, for measuring the surface tension of sulfur. His values are erratic and discordant. They rise with increasing temperature to a maximum of 118 dynes per cm. at 250° and then fall sharply.

The first attempt to clarify the problem was made by Kellas.[6] With great difficulty he was able to show that sulfur, properly prepared, gave consistent values by the capillary rise method from 118.9 to 444.6° in spite of its high viscosity. He also showed that impure sulfur gave a varying contact angle and that only when the sulfur was properly treated did its contact angle approach zero. His values, however, appeared to be dependent upon the bore of the capillary tube. In general, the wider the bore the lower were the surface tension values. The extreme values differed by about 5.5 dynes per cm. at 130°. Three tubes with bores less than 0.5 mm. gave the highest and essentially the same values. Kellas was not sure of the degree of purity of the sulfur he prepared.

In view of these facts and the increasing uses of sulfur in some of which surface tension may be an important factor, it was believed worthwhile to redetermine the surface tension values using Sugden's[7] double capillary modification of the maximum bubble pressure method. This method is independent of such factors as contact angle and the presence of minute impurities which give so much trouble in the capillary rise method.

Experimental

The all-glass apparatus and the method of calculation employed have been described in detail by Sugden. The instrument was modified to take a calibrated long stem thermometer so that the mercury bulb dipped below the liquid surface in the reservoir tube whose inside diameter

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[1] Ramsay and Shields, *J. Chem. Soc., Trans.*, **63**, 1089 (1893); Ramsay and Aston, *ibid.*, **65**, 167 (1894).

[2] G. Pisati, *Gazz. chim. ital.*, **7**, 357 (1877).

[3] G. Capelle, *Bull. soc. chim.*, [IV] **3**, 764 (1908).

[4] W. A. D. Rudge, *Proc. Camb. Phil. Soc.*, **16**, 59 (1910).

[5] H. Zickendraht, *Ann. Physik*, **21**, 141 (1906).

[6] A. M. Kellas, *J. Chem. Soc.*, **113**, 903 (1918).

[7] S. Sugden, *ibid.*, **121**, 858 (1922); **125**, 27 (1924).

was about 4 cm. Supplemental details and the procedure followed appear elsewhere.[8,9]

The instrument was calibrated against purified benzene (28.88 dynes/cm. at 20°), chloroform[8] (26.54 dynes/cm. at 25°), and water (27.14 dynes/cm. at 20°). With each liquid the average deviation of a single observation from the mean of at least ten determinations was less than $^1/_{1000}$. The constants for the instrument given by these liquids were, respectively, 0.006861, 0.006860 and 0.006822. The mean of these was employed in the calculations.

In the experiments employing gases the procedure was to completely saturate the liquid sulfur and just before a determination substitute nitrogen for bubble formation. After the determination the nitrogen was replaced by the gas and the temperature raised to the next value, etc.

Surface Tension in the Mobile Range—Below 159°.—This is the temperature range in which the mining of sulfur (Frasch process) and most applications of liquid sulfur are carried out. Seven series of experiments were made, each with determinations at three or four different temperatures using purified sulfur[10] and samples of pure sulfur melted under a pressure of about 1 mm. and then kept under this pressure at various temperatures below 160° for one hour. At the end of this period, the temperature was reduced to 120° before making the determinations with rising temperature. In the seventh series the pure sulfur was kept at the boiling point in air for several minutes then cooled down to 120° prior to determining the surface tension. The data of each series were plotted separately and from each curve values at 120, 130, 140 and 150° were taken and averaged. The average deviation of a single observation from the mean for each of the above temperatures fell between one and two parts per thousand. The averaged values are given in Table I and plotted as ● in Fig. 1A. Also plotted are Kellas' values given by capillaries with bores less than 0.5 mm.

TABLE I

SURFACE TENSION OF SULFUR BELOW 159°

t, °C.	γ, dynes/cm.
120	60.83
130	59.77
140	58.73
150	57.67

TABLE II

SURFACE TENSION OF SULFUR ABOVE 159°

t, °C.	γ, dynes/cm.
124.9	60.46
139.6	58.64
153.8	57.26
270	50.2
278	49.9
310	47.6
320	47.5
324	47.5
356	46.2
377	44.2
396	43.5
424	41.7
435	41.2

Surface Tension in the Viscous Range—above 159°.—Normally the results given by the maximum bubble pressure method are independent of the bubble rate but in the case of viscous sulfur widely scattered values were obtained with varying bubble rates. Above 275°, however, the determinations appeared to be independent of the rate of bubble formation. The values given in Table II are shown in Fig. 1 for the range 120 to 440°. Rising temperature data are shown by ● while falling temperature values are plotted ×.

The Effect of the Sulfur Viscosity Modifiers.—It has been shown that hydrogen sulfide and the halogens[9,11] (except fluorine),[12] have a tremendous effect above 160° on the sulfur viscosity even when present in minute amounts. These substances, it is believed, function by reacting with the long sulfur chains to form short segments thereby reducing the viscosity. It was of interest to determine whether this change would be reflected in the surface tension values of the treated sulfur.

The Effect of Hydrogen Sulfide.—The solubility of this gas in liquid sulfur increases with rising temperature, passes through a broad maximum and at 375° falls off to its lowest value at the sulfur boiling point.[13] The data clearly indicate that chemical reaction takes place between the hydrogen sulfide and its solvent. The surface tension values given by this system are plotted as open circles in Fig. 1. The data are essentially the same as given by pure sulfur. Between 200 and 300°, the range of maximum solubility, the values tend slightly downward.

The Effect of Chlorine and Bromine.—A mixture containing 2% by weight of chlorine added to the pure sulfur in the form of sulfur chloride gave the values plotted ⊗ in Fig. 2. They practically all fall on the broken curve given by pure sulfur.

Elemental bromine was added to pure sulfur to give a 2% by weight mixture. Values given by this mixture are shown ○ in Fig. 2 and, like chlorine, are essentially the same as given by pure sulfur.

The Effect of Iodine.—Of the additives which reduce the sulfur viscosity, iodine alone lowers the surface tension of sulfur above 160°. The data given by a 3.5% iodine solution in pure sulfur are plotted ● in Fig. 2. The extensive lowering of the surface tension with rising temperature is surprising, considering that it is least effective among the halogens in reducing the sulfur viscosity and also in view of the general belief that it does not combine directly with sulfur. The experiment was repeated employing a smaller concentration of iodine with essentially the same total lowering. The volatility of the sulfur halides and the halogens in the high temperature range is such that the actual concentrations are lower than indicated.

The Effect of Sulfur Dioxide, Ammonia, Oxygen and Water.—All of these substances except water are regarded as catalysts for the internal sulfur equilibrium. These were employed only in the temperature range below 160°. In the case of sulfur dioxide and ammonia, the sulfur was saturated by bubbling the gases through the liquid overnight. The effect of oxygen was simply determined by employing it for bubble formation. Sulfur treated with these gases showed little change in surface tension. The maximum variation was but a few tenths of a dyne per cm. The addition of a few drops of water to the pure sulfur at 123° followed by vigorous agitation produced no change in the surface tension value.

Sulfur samples containing oils as mined gave increasing values with rising temperature, for example, sulfur with 0.028% oil gave 48 and 49 dynes per cm. at 120 and 155°, respectively. Thus it is evident that the low and increasing surface tension values with rise in temperature reported by several investigators[3,5] were probably due to the use of impure sulfur.

Discussion

The results given by the maximum bubble pressure method using pure sulfur are about two dynes per cm. higher than those shown by Kellas' curve for the capillary rise method. The sharp break in the surface tension–temperature curve occurs at the same point as found by Kellas, namely, 160°. At this temperature most of the physical properties of sulfur show a sharp discontinuity indicating a definite change in molecular complexity at this sole transition temperature for the liquid phase. Using Eötvös' law and his surface tension values, Kellas found the molecular complexity below 160° to be S_6 and above in the

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[8] R. Fanelli, THIS JOURNAL, **70**, 1792 (1948).

[9] R. F. Bacon and R. Fanelli, *ibid.*, **65**, 639 (1943).

[10] R. F. Bacon and R. Fanelli, *Ind. Eng. Chem.*, **34**, 1043 (1942).

[11] R. Fanelli, *ibid.*, **38**, 39 (1946).

[12] R. Fanelli, THIS JOURNAL, **70**, 1965 (1948).

[13] R. Fanelli, *Ind. Eng. Chem.*, **41**, 2031 (1949).

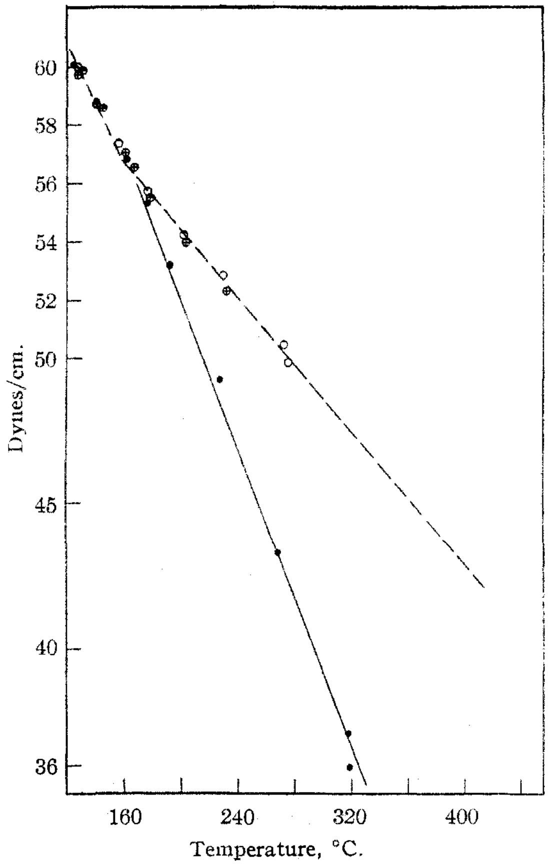

Fig. 2.—Effect of the halogens on the surface tension of sulfur: — — —, pure sulfur; ⊗, 2% chlorine; ○, 2% bromine; ●, 3.5% iodine.

viscous range it varied between S_{14} and S_{29}. At temperatures not too far from 160°, *i. e.*, 156–184°, the sulfur molecule approximated S_{29}. For longer temperature ranges it was S_{18} and consequently the change from the mobile to the viscous state was represented by $3S_6 \rightleftarrows (S_6)_3$. Kellas apparently followed the same capillary rise method used by Ramsay and Shields. It is now generally recognized that the method as employed gave low values by about 3.5%. Kellas' values used for his curve multiplied by 1.035 are plotted in Fig. 1. The corrected data fall very close to the curve showing the values given by the maximum bubble pressure method.

The new surface tension values give S_7 as the apparent molecular complexity between 120 and 160° and in the viscous range, S_{17} for the interval 160–190°, and for 160–270°, S_{23} for 270–324° and S_{19} for 160–435°. The differential coefficients found for these temperature intervals were, respectively, 0.95, 0.54, 0.52, 0.44 and 0.50. In calculating the multiplication factor for S_2 the Eötvös constant was taken as 2.2. These data admit of various interpretations with respect to the polymerization reaction as set forth by Kellas. However, it is now generally believed that there is no Eötvös constant for all liquids, consequently the above values for the molecular magnitude are of limited and doubtful significance. Indeed Adam[14] indicates that our present knowledge relative to the kinetic theory of liquids makes it futile to employ surface tension data to determine molecular complexity. Kellas' work has been widely accepted as experimental evidence for the existence of the S_6 molecule. In reality, there are few worthy data to support the presence of the S_6 molecule in any of the sulfur phases.

Summary

The surface tension of sulfur purified by a special method has been determined by the maximum bubble pressure method using Sugden's form of double capillary unit. The values are about two dynes per cm. higher than those given by Kellas' curve obtained by the capillary rise method.

The effect of the additives, H_2S, Cl_2, Br_2, I_2, SO_2, NH_3, O_2 and H_2O on the surface tension of pure sulfur has been determined. Of these iodine alone lowers the surface tension appreciably.

The molecular complexity of liquid sulfur proposed by Kellas is discussed.

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[14] N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd ed., Oxford University Press, p. 160.