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Nucleation in Liquid Sulfur Droplets

Shuichi HAMADA, Yoshihiro NAKAZAWA and Toshiaki SHIRAI

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

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The freezing behavior of supercooled liquid sulfur droplets were studied by means of a microscopic method. The number fraction of the solidified droplets in the experiments of continuous cooling on well-purified sulfur was only about 15% over the temperature range from 120°C to −70°C at the cooling rate of 0.20°C/min, and no abruptly discontinuous nucleation was found in these supercooling temperatures. The number fractions of the solidified droplets were found to be related to their volumes below −20°C. The nucleations in the well-purified liquid surfur droplets were confirmed to be a homogeneous process under these conditions. The specific nucleation rates per unit of volume were estimated to be 0.450, 1.13, and 1.16 cm^{-3}sec^{-1} at the specified temperatures of −20, −40, and −50°C respectively. The dependences of $(\ln I + \Delta F_A/kT)$ on $1/(\Delta T)^2 T$ obeyed the theory of Turnbull and Fisher. The interfacial free energy of sulfur at the liquid-crystal surface was estimated to be 12.1 erg/cm^2; this value was considered to be an appropriate one according to the Zadumkin consideration.

At an initial step of transformation, a nucleation passes through a homogeneous or a heterogeneous process in an unstable phase. In the homogeneous nucleation process, the nuclei grow in number nearly in proportion to the time; therefore, the nucleation rates can be estimated. On the other hand, it is well known that instantaneous crystallizations are observed at low degrees of supercooling or supersaturation in the presence of small amounts of chemical or physical heterogeneities. These instantaneous crystallizations are recognized to be based on the heterogeneous nucleation process. In the heterogeneous nucleation process, the number of nuclei is governed by the amounts of the chemical or the physical heterogeneities; therefore, the rates of crystallization are mainly decided by the growth rates of the nuclei.

Gibbs[1)] has introduced a theoretical approach to the homogeneous nucleation in supercooled liquids and in supersaturated, one-component vapors. Frenkel,[2)] Volmer,[3)] and Becker and Döring[4)] developed further the theories of the homogeneous nucleation. Turnbull and Fisher[5)] proposed absolute values for the rates of homogeneous nucleation in condensed systems on the basis of the Becker and Döring theory. The first experimental measurements on the nucleation rates were carried out by Vonnegut[6)] using the dilatometric technique on a system of supercooled liquid metal droplets. An advantage of the technique using tiny droplets is that the homogeneous nucleation breaking up of heterogeneous nucleating centers is observable. Moreover, experiments concerned with the kinetics of the homogeneous nucleation of many metals, inorganic and organic compounds, and polymers have been reported by Pound[7)] and Turnbull.[8,9)] The nucleation phenomena in the supercooled liquid sulfur droplets have been reported by Ford *et al.*[10)] and by Gorskii.[11)] Gorskii has reported a measurable nucleation rate in the supercooled liquid sulfur droplets at a temperature of 50°C, but Ford *et al.* found a very small fraction of solidified droplets even at temperatures as low as −45°C in the aerosol states.

In this work, the rates of the nucleation of the supercooled liquid sulfur droplets were studied by means of the microscopic method.

Experimental

Materials. A guaranteed-grade sulfur was obtained from the Kanto Chemical Company. The sulfur was

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1) J. W. Gibbs, *Trans. Conn. Acad.*, **3**, 108 (1876).

2) J. Frenkel, "Kinetics Theory of Liquids," Oxford University Press, New York, N. Y. (1946).

3) M. Volmer, *Z. Elektrochem.*, **35**, 505 (1929).

4) R. Becker and W. Döring, *Ann. Physik*, **24**, 719 (1935).

5) D. Turnbull and J. C. Fisher, *J. Chem. Phys.*, **17**, 71 (1949).

6) B. Vonnegut, *J. Colloid Sci.*, **3**, 563 (1948).

7) G. Pound and V. K. La Mer, *J. Amer. Chem. Soc.*, **74**, 2323 (1952).

8) D. Turnbull, *J. Chem. Phys.*, **20**, 411 (1952).

9) R. L. Cormia, F. P. Price and D. Turnbull, *J. Chem. Phys.*, **37**, 1333 (1962).

10) G. Ford and V. K. La Mer, *J. Amer. Chem. Soc.*, **72**, 1959 (1950).

11) F. K. Gorskii, *J. Expl. Theor. Phys.*, **18**, 45 (1948).

recrystallized six or seven times with freshly-distilled carbon disulfide and then dried *in vacuo*. The carbon disulfide had been shaken with mercury before the distillation in order to remove hydrogen sulfide. The tests of the purification of the recrystallized sulfur were carried out using the following method of continuous cooling.

Procedure. The sample of liquid sulfur droplets was prepared in the following manner; the fine powder of the purified sulfur was dispersed on a clean microscopic cover-glass, and then it was melted in an electric heating block at 120°C for 15 min. The sample was slowly cooled from 120°C to 55°C in the heating block; then it was transferred into a cooling apparatus designed in our laboratory maintained at 55°C. The sample was placed on an aluminum block in contact with a cascade-type semiconductor thermo-module. The temperatures were controlled with an accuracy of ±0.1°C using the thermistor controller. The changes in the sample were microphotographed continuously through the quartz window. The droplets were photographed at specified intervals with the camera mounted on an Olympus reflecting microscope, Model STS, with an object-lens with a long working distance (10×, about 3.8 cm). The temperatures over the range from 120°C to −50°C were measured with a standard thermometer, and those lower than −50°C, with a chromel-alumel thermocouple which was calibrated using materials of known melting points. The errors in the temperature measurements were within the range of ±0.1°C.

The specimens were observed by means of continuous-cooling experiments over the temperature range from 55°C to −70°C for over-all liquid droplets, and by means of isothermal cooling experiments at −20, −40, and −50°C for several droplets classified as to diameter.

In both the experiments, only the nucleation rate is approximately observable, as the growth rate is generally greater than that of nucleation on tiny droplets. Therefore, the number fractions of solidified droplets with respect to the overall droplets or the classified droplets were employed in discussing the nucleation rates.

Results

The droplets were directly observed. Fortunately, the transmittances of the crystalline and the liquid sulfur are sufficiently different for the two kinds of droplets to be easily distinguishable even without the use of polarized light, as is shown in Phot. 1.

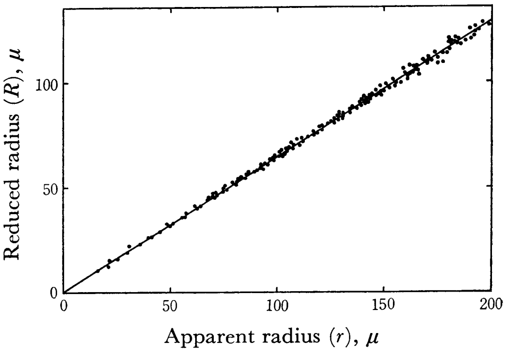
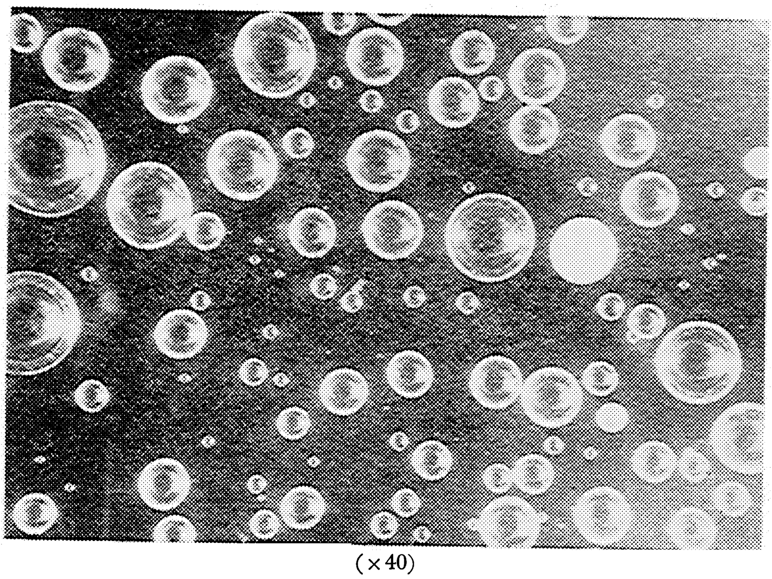


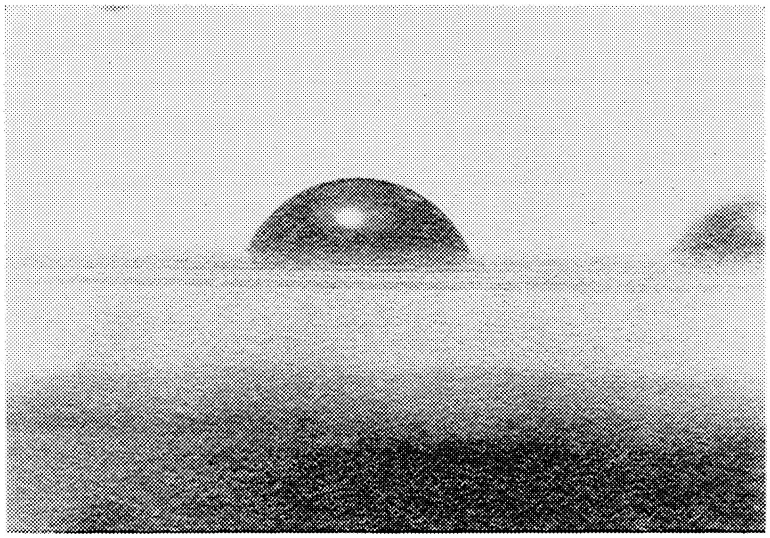
Fig. 1. Plot of reduced radius against apparent radius.

The liquid sulfur droplets on the microscopic cover-glass were regarded as approximately spherical segments, as is shown in Phot. 2. The volumes and the reduced radii of the individual droplets were calculated from the apparent radii and heights. Figure 1 shows the relationship between the apparent radii, r, and the reduced radii, R, of the sphere the volumes of which were the same as in the sulfur droplets. The R is related to the r as in the following equation; $R=0.645r$. The droplets were classified at intervals of 25μ in the apparent diameter, D.



(×40)

Phot. 1. Photograph of liquid sulfur droplets.



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Phot. 2. Side view of liquid sulfur droplet.

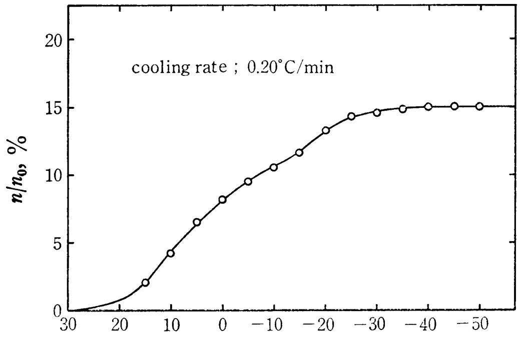

Fig. 2. Plot of number fraction of solidified droplets against temperature.

The Variation in the Number Fraction of the Solidified Droplets by the Continuous Cooling. The results of the continuous-cooling experiment over the size range from 10 μ to 400 μ in the apparent diameter are shown in Fig. 2. The specimen was continuously cooled at the rate of 0.20°C/min. This curve shows the number fractions, n/n_0, of the solidified droplets as a function of the temperatures from 30°C to −60°C. It is shown that the sulfur droplets scarcely crystallized at all at 30°C; moreover, only about 15% of the total droplets solidified even at −60°C —*i. e.*, the temperature of supercooling was 173°C. The crystallization in the whole droplets was not observed under the experimental conditions, while the critical supercooling at which an abruptly discontinuous crystallization occurred was observed to be 55°C in the liquid polyethylene droplets,[9] for example. On the contrary, imperfectly-purified liquid sulfur droplets crystallized entirely at the temperatures from 50°C to 30°C.

The Relationship between the Number Fractions of the Unsolidified Droplets and Radii. The samples were each kept at temperatures from 15°C to −50°C for 2 hr, and the number fractions of the unsolidified droplets were estimated with respect to their radii.

Turnbull[9] expressed the number fraction of the solidified droplets at the specified temperatures as follows:

$$1 - n/n_0 = \sum_{R=0}^{\infty} N_R^0 \exp(-k_R t)$$

where R is the radius of the droplets; $N_R{}^0$, the number fraction of the droplets with the radius of R; k_R, the specific nucleation rate of the droplets with the radius of R, and t, the cooling time. If the nucleation takes place throughout the volume of the droplets, *i. e.*, through the homogeneous nucleation process:

$$k_R = v_R I$$

where v_R is the volume of a droplet with the radius of R, and I, the nucleation rate per unit of volume at the specified temperature.

Concerning each droplet's range, the following expression is approximately applicable:

$$1 - (n/n_0)_R = \exp(-k_R t)$$

where $(n/n_0)_R$ is the number fraction of the solidified droplets in the narrow range of droplets with the radius of R. From the expression, the following equation is obtained if the temperature and the cooling time are specified:

$$\log(2 - \log N_{u,R}) = 3 \log R + C$$

where $N_{u,R}$ is the percentage of unsolidified droplets connected with the narrow-range droplets with the radius of R, and C, the constant.

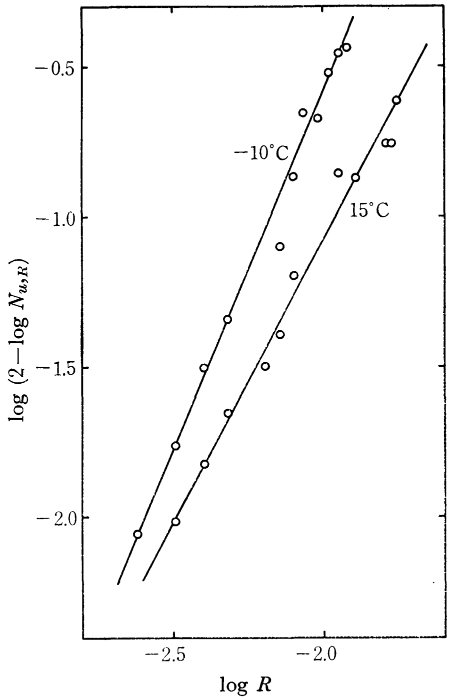

Fig. 3. Relationship between radius and number fraction of unsolidified dropets at 15 and −10°C.

If the nucleation in the sulfur droplets takes place through the homogeneous process, the log (2−log $N_{u,R}$) relation should vary linearly against the log R with the slope of 3 at specified temperatures and cooling times. Figures 3 and 4 show the relationships at 15 and −10°C, and at −20 and −40°C, respectively. At the temperatures of 15 and −10°C, the slopes were roughly estimated to be 2, but those at −20 and −40°C were nearly equal to 3. The slopes of the relationships between log (2−log $N_{u,R}$) and log R at several temperatures are summarized in Table 1.

Table 1. The slopes of the linear relationships between log (2−log $N_{u,R}$) and log R

Temp., °C	Slope	Temp., °C	Slope
15	1.88	−15	2.30
10	2.13	−20	3.00
5	1.94	−40	3.00
−10	2.39	−50	3.00

The slopes were estimated to be approximately 2 above −15°C, while they were close to 3 below −20°C, as is shown in Figs. 3 and 4 and in Table 1 respectively. The nucleations in the sulfur droplets under the conditions below −20°C were confirmed to be homogeneous, while those above −15°C were confirmed to be heterogeneous.

The Nucleation Rates in the Droplets through the Homogeneous Process. The dependences of the cooling times on the isothermal solidification were observed at the temperatures of −20, −40, and −50°C; the temperatures of supercooling were 133, 153, and 163°C respectively.

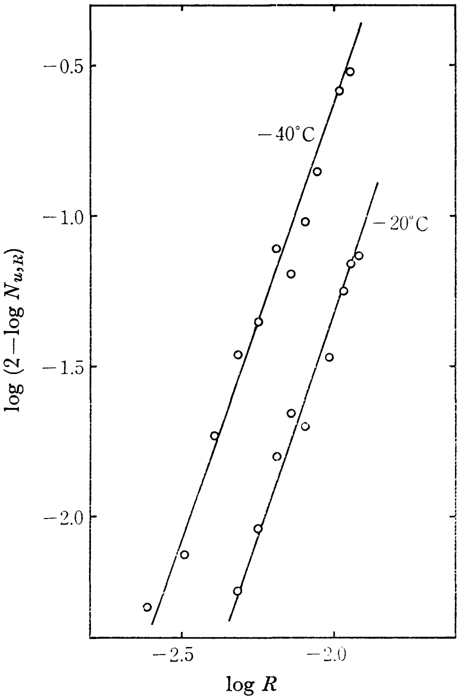

Fig. 4. Relationship between radius and number fraction of unsolidified droplets at −20 and −40°C.

According to Turnbull's theory, the nucleation rate, k_R, of the droplets with the radius of R is expressed as follows:

$$\ln (n_{u,0}/n_u)_R = k_R t$$

where $(n_{u,0}/n_u)_R$ is the reciprocal of the number fraction of the unsolidified droplets with the radius of R, and t, the cooling time. The results of the experiment at −40°C are shown in Fig. 5. The values of $(n_{u,0}/n_u)_R$ were estimated by eliminating the number of droplets solidified above −15°C, based on the heterogeneous process. The elementary theory would predict that the homogeneous nucleation was a first-order reaction after several times. The figure shows the linear variations in the ln $(n_{u,0}/n_u)_R$ relation to the cooling times, though the variations did not obey the linear relationship before 30 min or 1 hr.

The values of k_R for each of the droplets with the radius of R were estimated from the slopes of the linear relationships. The specific nucleation rates, I, per unit of volume at the specified temperatures were calculated from the k_R values and the volumes of the droplets, as the k_R was expressed as follows: $k_R = v_R I$. The specific nucleation rates, I, were all given as approximately the same value with respect

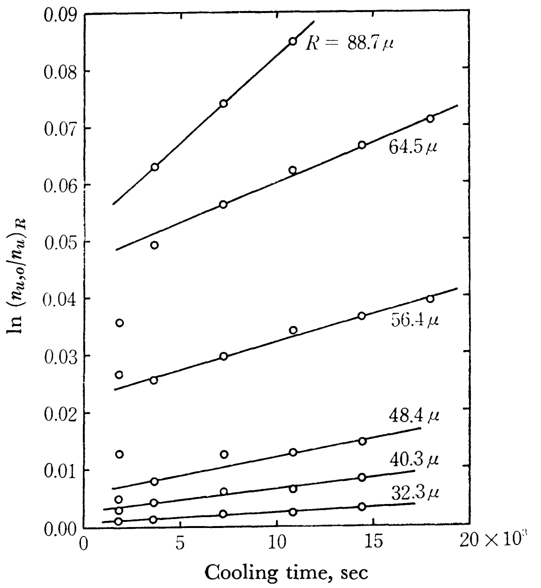

Fig. 5. Plot of $\ln (n_{u,o}/n_u)_R$ against cooling time at −40°C.

to the radii. Table 2 shows the values for k_R and I at −40°C.

TABLE 2. THE VALUES FOR k_R AND I AT −40°C

D, μ	R, μ	k, sec^{-1}	I, cm^{-3}sec^{-1}
100	32.3	1.59×10^{-7}	1.13
125	40.3	3.14	1.15
150	48.4	5.75	1.21
175	56.4	9.00	1.20
225	72.6	1.37×10^{-6}	1.09
250	80.6	2.40	1.05
275	88.7	3.06	1.05
		Average	1.13

The values for I were calculated to be 0.450, 1.13, and 1.16 cm^{-3} sec^{-1} at −20, −40, and −50°C respectively. These values were nearly equal to those for some molecular liquids, such as benzoic acid and white phosphorus.[12]

Discussion

The well-purified and imperfectly-purified sulfur droplets showed characteristic behavior in the crystallization phenomena in the experiments of continuous cooling. Gorskii[11] showed a measurable nucelation rate in the sulfur droplets, even at the temperature of 50°C. Presumably the sulfur used in his study contained second-phase impurities, which served to nucleate on the basis of the heterogeneous process, judging from the observations made in the continuous-cooling experiments. It is, therefore, meaningless to discuss the crystallization in Gorskii's temperature range in terms of the homogeneous nucleation processes. There then arises the question of whether the nucleation below 30°C is a heterogeneous or a homogeneous process. The probabilities of the crystallization in individual droplets depend on their sizes. Therefore, the homogeneity of nucleation can be examined from the derivative of Turnbull's theory. Under the conditions of the specified temperatures and the cooling times, the variations in $\log (2-\log N_{u,R})$ against $\log R$ should be linear, with a slope of 3 in the homogeneous process. As is shown in Figs. 3 and 4, the dependences of the number fraction of solidified droplets on the radii show a homogeneity in nucleation at temperatures below −20°C, though a heterogeneity remains at those above −15°C.

Turnbull and Fisher[5] proposed that the rate of the homogeneous nucleation in supercooled liquids was as follows:

$$I = (nkT/h)\exp(-\Delta F_A/kT)$$
$$\times \exp[-16\pi\sigma^3 T_0^2/3\lambda^2 k(\Delta T)^2 T]$$

where n is the number of atoms or molecules per unit of volume; ΔF_A, the free energy of activation for the short-range diffusion across an interface of liquid and crystal; σ, the interfacial free energy between the liquid and crystalline nuclei; λ, the latent heat of fusion per unit of volume; T_0, the melting point, and ΔT, the difference between the melting point and the nucleating temperature, T_0-T. This expression is derived by assuming the nuclei to be spherical and the entropy change to be independent of the temperature. Turnbull has applied his results to the freezing of supercooled liquid metals using the equation. These results agreed quantitatively with those obtained using the equation when the value of ΔF_A was assumed to be that of the activation energy for viscous flow.

The equation is transformed as follows, since the term of $\ln(nkT/h)$ is almost constant over the temperature range from −20°C to −50°C:

$$\ln I + \Delta F_A/kT = C - (16\pi\sigma^3 T_0^2/3\lambda^2 k)[1/(\Delta T)^2 T]$$

In this work, the value for ΔF_A was estimated to be 5.20 kcal/mol, a value which was obtained from the temperature dependences of the viscous flow in the λ-sulfur.[13] If the homogeneous nucleation is applicable to the liquid sulfur droplets, the variations in $(\ln I+\Delta F_A/kT)$ against $1/(\Delta T)^2 T$ should be linear. Figure 6 shows the relationship between $(\log I+\Delta_A F/2.303\,RT)$ and $1/(\Delta T)^2 T$. An excellent straight line was obtained. The value of the term of $16\pi\sigma^3 T_0^2/2.303\times3\lambda^2 k$ was estimated to be 1.66×10^7 from the slope of the linear relationship. Assum-

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12) D. G. Thomas and L. A. Staveley, *J. Chem. Soc.*, **1952**, 4569.

13) T. Matsushima, *Sci. Res. Inst., Tohoku Univ., Ser.*, **A11**, 474 (1959).

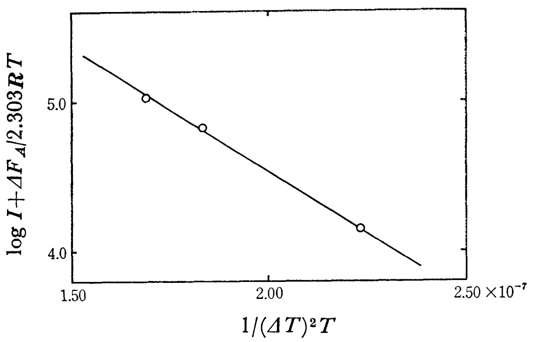

Fig. 6. Plot of (log $I+\Delta F_A/2.303RT$) against $1/(\Delta T)^2 T$.

ing the sulfur nuclei to be spherical, the σ was calculated to be 12.1 erg/cm^2 using the value of the melting point of α-sulfur, 386.0°K,[14] and that of the heat of fusion, λ, 9.13×10^8 erg/cm^3.[15]

Zadumkin[16] calculated the interfacial free energies of the melt-crystal for 36 elements involving the chalcogen elements to be 8—15% of the surface tension of their liquids at all the melting points except those of Ge, Si, and Sb. The interfacial free energy of sulfur at the liquid-crystal surface was estimated to be 20% of the surface tension of liquid sulfur at the melting point, 60.5 erg/cm^2. Since the interfacial free energy of selenium, which is an analogous element of sulfur, corresponds to 16% of the surface tension at its melting point,[17] the empirical value of that for sulfur may be considered to be an appropriate one.

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[14] B. Meyer, "Elemental Sulfur," Interscience Publishers, New York (1965), p. 87.

[15] "Handbook of the Physicochemical Properties of the Elements," ed. by G. V. Samsonov, Plenum, New York (1968), p. 250.

[16] S. N. Zadumkin, *Akad. Nauk Ukr., SSR*, **1**, 21 (1961).

[17] S. Hamada, unpublished.