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**Publication Date**

1966-02-01

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ELEMENTAL SULPHUR

Berkeley, California

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Ch7 book Inorganic Sulphur Chemistry  
Pergamon Press

UCRL-16700

UNIVERSITY OF CALIFORNIA  
Lawrence Radiation Laboratory  
Berkeley, California  
AEC Contract No. W-7405-eng-48

ELEMENTAL SULPHUR

Beat Meyer

February 1966

# ELEMENTAL SULPHUR

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## I. Introduction:

In a world which is dominated by plastics, and high strength and high temperature materials it is easy to forget that sulphur, in the form of sulphuric acid, is still the workhorse of the chemical industry: In the year 1965 the world production of elemental sulphur was estimated (1) to be 21 million long tons, with the United States contributing 8.3 million tons, Canada 1.8, Mexico 1.7, and France 1.5. It is estimated that 85% of this sulphur is used in the manufacture of sulphuric acid. About one-third of all sulphuric acid is used for the manufacture of fertilizers (2); considerable quantities go into the manufacture of petrochemicals, inorganic pigments, steel, alcohols, man-made fibres, detergents and in almost all branches of chemical industry.

Elemental sulphur is one of the classic chemicals, known and used since antiquity, purified in large quantities (for gunpowder) since the fifteenth century, and burnt in "lead-houses" into sulphuric acid in ton-quantities since about 1750. Even some of the newly studied applications, such as its use as cement, have been in the literature for over two thousand years; and it was already known around thirteen hundred that sulphur reacts easily with almost all metals, except gold (3).

The two major production and recovery processes for the element, the Frasch process (1902) and the Claus process (1894) were developed almost at the same time and made the volcanic sulphur of Sicily expendable. Today somewhat more than half of the world production comes from elemental deposits, about one third from smelter gases and most of the rest is recovered from pyrites.(4).

Sulphur has been studied by almost every scientist who was in need of a model substance for testing his theories or experimental techniques. Its physical and chemical properties make sulphur an ideal test material. It is readily available in elemental form, non-toxic, solid at STP, liquid just above the boiling point of water and can be boiled, in the absence of air, without appreciable reaction in quartz or even pyrex containers.

Considering these assets and in view of its history and its commercial importance it is hard to believe how little is known about the element. Various properties have been reported, but most have been contradicted. It was not even clear whether the element can appear in three or thirty allotropic forms. The reason for this lies in the behaviour of sulphur which is unusually complex for an element. During the last ten years, however, many important facts and factors have been discovered or confirmed.

Several general reviews on elemental sulphur are available (3,5) but the comprehensive handbooks reflect the confusion in the field. Since most names have been used for different allotropes, and since there is not even one generally accepted name for one single allotrope (6) the nomenclature alone makes it impossible to draw any valuable conclusions. No immediate change in this situation can be expected. This is regrettable, since many valuable experiments or observations, published but buried in inaccessible form, have been distrusted and have had to be reinvented and repeated. It took almost sixty years before Biltz's assumption of  $S_5$  and  $S_7$  as vapour components (7) was seriously considered, and the existence of  $S_6$  as molecular constituent in rhombohedral crystals (8) was only reconfirmed 50 years after its stipulation.

A. Characteristic Problems:

Some specific problems which, if neglected, all lead to irreproducible

results have recently been reviewed (6):

(1) Sulphur reacts with many impurities and slowly changes its physical and chemical properties

(2) Sulphur is photosensitive

(3) The sulphur-sulphur bond character, distance and bond angle make possible the formation of many different rings and thousands of chain molecules, of which a large number have similar stability.

(4) The intermolecular interaction of sulphur molecules can, for each of the many allotropes, lead to a variety of similarly stable polymorphs.

Most systems studied before 1950 consisted of mixtures of different polymorphs, often different molecular species. Some properties of special systems have since been studied, and are reviewed in a recent survey (9).

#### B. Impurities:

Most Frasch and recovered Claus sulphurs are 99.99% pure or often better. During storage and shipping, however, many impurities are added. Some standard contamination in industrial sulphurs are listed in Table I.

The sulphur used in research work has in the past, unfortunately, been of very poor quality. Precipitated and sublimed sulphur, pharmaceutical grades, with chalk and other additives have been commonly used. Five to ten percent additives or contaminations are quite common in such grades. The first basic breakthrough in the work on sulphur was based on a purification method developed by Bacon and Fanelli (10), who boiled sulphur with magnesium oxide and obtained samples which gave reproducible viscosities in the liquid phase. Since then many methods have been developed. They all produce high purity samples, but it is still essential that researchers know the origin and treatment of their material. Murphy,



Clabough and Gilchrist (11) developed, for example, a process during which impurities are oxidized. The samples are then washed with water and dried. Such a sample was recently used for heat capacity measurements (12). Very precise results were obtained, and a very small, before unknown, transition was found at 101°C. Studies presently in progress did not lead to reproduction of this transition (13). It seems that the observation was caused by traces of water introduced during the above mentioned treatment.

Samples have often been prepared by recrystallization from solvents. In this way big crystals can be obtained (14), but solvent inclusions ( $\text{CS}_2$ ) have for many years led to new interpretation of the IR spectrum of pure sulphur (15).

A very elegant purification method was invented by von Wartenberg (16), who obtains a high purity sample by immersion of a red hot quartz heater into the liquid. In this way organic impurities decompose and escape as  $\text{CS}_2$ ,  $\text{SO}_2$ , and  $\text{CO}_2$ .

In recent years 99.9999% (6N) sulphur has become commercially available. The samples are usually obtained by a combination of methods, the most popular of which presently is zone melting (17). Analytical methods have been developed to handle the control of high purity samples (18).

### C. General Properties:

Reference books and the literature are full of general descriptions of sulphur. Almost all of these data are "overall", average values of more or less representative allotropic mixtures, which usually contain at least 3 forms: orthorhombic ( $\alpha$ ), monoclinic ( $\beta$ ), and polymeric sulphur. Very little is known about the properties of pure allotropic forms, and still less about the anisotropic behaviour of the crystalline

forms. Therefore it seems appropriate here not to list general properties. Reference to these can be found in many handbooks (3,5,19).

Several years ago chemical studies of allotropic reactivities were started (20). Reference to these results will be made under the individual allotropes.

D. Pedigree of Allotropes:

At STP only orthorhombic ( $\alpha$ ) sulphur is stable. It consists of cycloocta sulphur molecules. On heating orthorhombic ( $\alpha$ ) sulphur converts to monoclinic ( $\beta$ ) sulphur. Table II indicates all the equilibrium forms, and the thermally deduced metastable allotropes.

Table III lists polymorphs deduced from solutions containing only cycloocta sulphur.

Table IV indicates the allotropes in chemically precipitated sulphur. Exposure to light influences the products greatly.

The behaviour of sulphur under pressure has been repeatedly studied. Analytical reviews indicate that a metallic form has not yet been found (21). The fusion curves have been determined up to pressure of 40,000 kg/cm<sup>2</sup>. The results on very high pressure allotropes are still contradictory and will be discussed later.

## II. Sulphur Vapour

Sulphur vapourizes already at 100°C to an appreciable amount, and its vapour pressure reaches at 444.6°C one atmosphere. This makes the 100°C to 1000°C region the most interesting temperature region for experimental research.

Like the other phases, the vapour has a complex composition. Only the last six years brought a clearer understanding (22) and work is still underway to determine detailed properties. Original vapour pressure measurements indicated a molecular weight of about 6 (7). Later studies at higher temperature indicated that  $S_2$  was a predominant component, and still later it was recognized that the sulphur vapour constitutes a dissociating system (23). Detailed pressure measurements indicated that besides  $S_8$ ,  $S_6$  and  $S_2$  at least one other component had to be present. The resulting assumption was that  $S_2$ ,  $S_4$ ,  $S_6$  and  $S_8$  were the only important vapour constituents. The unfortunate belief still persists widely and probably will continue to appear in new textbooks for many years to come. The results of mass spectroscopy during the last six years, clearly demonstrated that sulphur vapour also can contain  $S_{10}$ ,  $S_9$ ,  $S_7$ ,  $S_5$ ,  $S_3$  and also atoms. The careful and ingenuous studies leading to the conclusive identification of vapour components with odd numbers of atoms also lead to the deduction of more reliable thermodynamic data. Table V shows the heat of formation and the entropy of formation for the major vapour constituents. The energy per bond in a molecule (assumed to be ring shaped) increases from  $S_2$  (51.5 kcal/mole) to  $S_3$  (55.5),  $S_4$  (57.5),  $S_5$  (60.5), and levels off at  $S_6$  (61.5),  $S_7$  (62),  $S_8$  (62.5),  $S_9$  (~ 62), and  $S_{10}$  (~62.5). The rings with six and more atoms have all about the same bond energy and

can form with little stress on the "free" S-S bond distance or bond angle. It seems, therefore, quite astonishing that  $S_8$  was earlier assumed to play such a dominant role (24).

The analysis of vapours with the help of mass spectroscopy is somewhat complicated by the processes in the ion source, where part of the vapour is not only ionized but also fractionized. The observed  $S_4^+$  peak, is therefore not only due to  $S_4$  in the tested vapour, but also due to fractionization of  $S_5$ ,  $S_6$ ,  $S_7$ ,  $S_8$ ,  $S_9$  and  $S_{10}$ . Recently negative sulphur ions were also observed (25). This indicates that ion part formation might occur.

At temperatures above  $2500^\circ\text{K}$  and a pressure below  $10^{-5}$  mm Hg atoms dominate: below this the very wide pressure and temperature region down to  $400^\circ\text{C}$  and a pressure of several mm Hg belong to the  $S_2$  molecule. The composition of saturated sulphur vapour above the liquid phase is shown in Fig. 1. At lower temperatures, however, the vapour equilibration was found to be very slow, and the vaporization from solids leads to metastable, unequilibrated systems in which the composition depends strongly on the solid. Above orthorhombic sulphur  $S_8$  is most abundant. However, above the rhombohedral sulphur, which exhibits almost a fifty times higher vapour pressure,  $S_6$  is more abundant. Polymeric sulphur, finally, leads to an unusually high concentration of  $S_7$  (26). If the recently reported (27) new dark green allotrope consists really of  $S_{10}$ , then undoubtedly  $S_{10}$  vapours can also be preferentially produced. In such metastable vapours, equilibrium can be obtained with the help of catalysts. All grades of alumina have been found especially active (26).

Vapour studies are complicated by the complex nature of the vapour, and the fact that of the individual components only  $S_8$ ,  $S_6$ ,  $S_2$  and the atom have been studied in reasonably pure form. It is clear that the chemistry of each

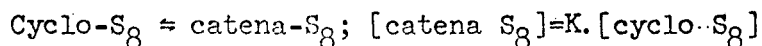
of these components is distinctively specific. The future undoubtedly holds many exciting discoveries on the synthetic applications of these molecules which can be made continuously and in very high yields. The usual sources for vapours of various compositions are Knudsen cells, containing  $S_{\alpha}$ ,  $S_{\rho}$  or  $S_{\mu}$ , to give  $S_8$ ,  $S_6$  or  $S_7$  respectively in high yield, and double furnaces for unsaturated vapour with higher  $S_6$ ,  $S_3$  and especially  $S_2$  concentrations. Unsaturated vapours can also be produced by the thermal decomposition of sulfides, such as HgS, CdS, FeS, etc., (22). An exceedingly clean and elegant electrolytic vapour source has recently been developed (28). From it precisely measured amounts of sulphur can be released from a Rickert-type cell. Atoms and  $S_2$  can be prepared by photolytic decomposition of sulphur-containing compounds such as  $CS_2$  and COS (29). The resulting sulphur radicals are initially partially produced in excited electronic states, the reaction of which very often is highly specific. Sulphur atoms have, as a matter of fact, been used to pioneer the chemistry of such excited radicals. Properties of the sulphur atom are described in Chapter I of this book.

The best known spectroscopic properties belong to  $S_2$  (30). Like  $O_2$ ,  $S_2$  has twelve electrons for which 18 electronic states have been observed. They form part of three systems, transitions between which are "forbidden" and so weak that they have not yet been observed. The relative position of these states correspond to those of  $O_2$ , but all states are closer together and the transitions occur at lower energies. The Schuman-Range bands, for example, which cause the atmospheric oxygen absorption of sunlight in the ultraviolet, appears in  $S_2$  in the visible and causes the deep blue color of hot sulphur vapour. The spectrum of  $S_4$  has been twice (31) observed, but not yet analyzed. For  $S_6$  and  $S_8$  only IR analysis has been reported (32).

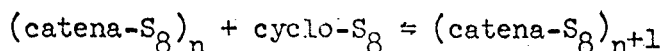
The magnetic properties of sulphur vapour have been studied over a broad temperature region (33), but like all other properties, only over-all data for the complex mixture is available, and the properties of the individual molecules are still unknown. This is also true for heat conduction, heat capacity, etc.

### III. Liquid Sulphur

The physical properties of liquid sulphur are so unusual that they are demonstrations familiar to every high school student: At the melting point sulphur forms a light yellow low viscosity liquid. On heating, the liquid darkens and the viscosity increases and goes through a maximum at 159°C. At this temperature sulphur gets so viscous that it cannot be poured from containers. Together with this viscosity, the specific heat, the density, the electric conductivity, the velocity of sound, and almost all physical properties show a discontinuity around 160°C (34). This is caused by the equilibrium polymerization of sulphur which is initiated by the ring scissions (35)



and propagated by the condensation reaction:



$$[(\text{catena-S}_8)_n] = K [\text{cyclo S}_8] + (K_3 [\text{cyclo-S}_8])^{n-1}$$

Quantitative descriptions for the processes have during recent years been deduced (36). The number-average degree of polymerization P can be expressed as

$$P = \frac{1}{1 - K_3 [\text{cyclo S}_8]}$$

and the total concentration of S<sub>8</sub> units in monomers and polymers is

$$[\text{S}_8] = [\text{cyclo-S}_8] + K [\text{cyclo S}_8] / (1 - K_3 [\text{cyclo S}_8])^2$$

The thermal constants for these two processes have been given as:

$$\begin{aligned} \Delta H^\circ &= 32.8 \text{ Kcal/mole}; \quad DS^\circ = 23 \text{ cal/deg. mole} \\ \Delta H_3^\circ &= 3.1 \text{ Kcal/mole}; \quad DS_3^\circ = 4.6 \text{ cal/deg. mole.} \end{aligned}$$

The above theory describes many properties of liquid sulphur below and above the viscosity maximum very well by assuming that, at the melting point, the liquid constants of free  $S_8$  units, which towards  $160^\circ\text{C}$  polymerize to a number-average degree of over  $10^5$   $S_8$  units. At still higher temperatures a steady depolymerization is assumed. Many properties indicate, however, that liquid sulphur is in reality still a much more complicated system than described above. The melting process is a good example of such behaviour: It is long known that sulphur has a "natural" and an "ideal" melting point. It seems that a new component forms in the liquid phase, which, as a solute, causes a self-solution of sulphur in cyclo- $S_8$ . The search for this component has after almost one hundred years of intermittent work recently been taken up again and molecular weight determinations of this " $S_\pi$ " and the cryoscopic data indicate that it might consist of catena- $S_8$ . This component  $S_\pi$  can be separated from cyclo- $S_8$  by dissolving it in  $\text{CS}_2$  at dry ice temperature, where orthorhombic sulphur is not very soluble (37). The assumption of up to 4% catena- $S_8$  in liquid sulphur is however complicated by the ESR evidence that only irrelevant amounts of free radicals exist below  $160^\circ\text{C}$ . However, short chains of up to eight atoms might stabilize the free electron through resonance and might, therefore, give a very broad ESR signal (38). Since preparation and isolation of such small molecules is experimentally feasible (27) it seems not timely to speculate about their properties. The melting phenomenon might be caused by another component besides cycloocta S: The gas phase studies indicate the presence of more than 10% of  $S_6$  and  $S_7$  each in the saturated vapour at  $120^\circ$  (22), and it seems reasonable to assume that both occur also in the liquid.

The mass spectroscopic data indicate that at the boiling point  $S_7$  (~ 40% of vapour) and  $S_6$  (~ 30%) are more abundant than  $S_8$  (20%) in the



saturated equilibrium vapour. Six percent  $S_5$ , 3%  $S_2$  and 1%  $S_4$  are also estimated to be present. The boiling liquid can then be assumed to be a very complex system, containing molecules with between two and many thousand atoms. If one remembers that the S-S band energy levels off at molecules with more than six atoms, one can assume that  $S_7$ ,  $S_8$ ,  $S_9$  and even  $S_{10}$  all might exist as comparably stable rings. The bond distance and band angles in "free" sulphur chains also indicate that such molecules can exist, and it even seems that at least one new molecules (26) besides  $S_8$  and  $S_6$  has been prepared in pure form.

Since UV light leads to S-S scission (39) it can be assumed that light influences the composition and therefore the properties of liquid sulphur. Traces of impurities also influence the polymerization propagation, and alter the characteristics of the liquid drastically. Figure 2 shows, for example, the viscosity of liquid sulphur as a function of  $H_2S$  impurities.

#### IV. Solid Allotropes

It is not easy to determine how many solid sulphur allotropes can exist, how many have been observed or how many have been described. An analysis (40) of many thousand publications on sulphur allotropes shows that at periodic intervals scientists have, for over one hundred and fifty years, changed back and forth between the belief that only two or three forms can really exist, and they believe sulphur can appear in many dozens of form.

##### A. Nomenclature

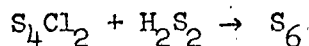
A clear mirror of this uncertainty is the nomenclature (41). The complete Greek alphabet, almost all colors and many trivial names were employed to designate allotropes, but nevertheless there is literally not one single allotrope for which one name has been generally accepted. The situation is reviewed in a recent article where criteria have been established for sensible naming of allotropes. We reproduce here a list of well-derived names and allotropes. (Table VI) Much confusion could be prevented if a clear distinction between molecular species (catena-S<sub>8</sub>; cyclo-S<sub>8</sub>, etc.) and intermolecular polymorphs (S<sub>α</sub>, S<sub>β</sub>, S<sub>γ</sub>) would be generally accepted. The latter always should be completely and unambiguously described with space group and/or trivial names to prevent misunderstandings between such forms as β and γ, which are both monoclinic. The most profound confusion stems, however, from incompletely characterized and analyzed mixtures which often, because of their great complexity, are reported as new allotropes. Such systems can usually not easily be reproduced and their description leads then often to endless controversy in the literature.

## B. Allotropes

The smaller and more important molecular species have been mentioned in the section on sulphur vapour. There we refer only to those which can be either prepared or stored at room temperature.

Sulphur atoms recombine at room temperature immediately. They can, however, be produced in solution through photolysis, or through nuclear reactions.  $S_2$  has been trapped at low temperature, and  $S_3$ , thiozone, undoubtedly can also be stored in inert solutions.  $S_4$  and  $S_5$  are so little known that their stability is difficult to judge.  $S_7$  and  $S_9$  are not yet described, but both probably are quite stable and might ultimately be isolated in pure form.

Cyclohexa Sulphur. Cyclohexa sulphur can be prepared after the methods of Aten or Engel (42) which have been widely used but not significantly improved. Concentrated hydrochloric acid is slowly stirred into a concentrated thiosulfate solution at 0° to 10°C. Cyclohexa sulphur and cycloocta sulphur are then extracted from the mother liquid with toluene or benzene. On evaporation or cooling of the extract cyclohexa sulphur crystallizes in dark yellow-red rhombohedral crystals with a yield of about 12%. The mechanism of the cyclohexa sulphur formation has been carefully studied.(43). The intermediate products are polythionate chains which undergo ring closure, and not, as commonly described in textbooks, free atoms or small molecules of elemental sulphur. Cyclo  $S_6$  can also be prepared by the specific reaction (27).



Cyclohexa sulphur is thermodynamically unstable, but as pure crystal or in pure solution it can be stored for extended periods of time, even at

60°C. However, in the presence of impurities, it decomposes within a few hours. Cyclohexa sulphur is chemically very reactive: with triphenyl phosphate it reacts about  $10^4$  times faster than cycloocta sulphur (43).

No physical properties have yet been reported, and only preliminary UV and IR spectra are available (26). The cyclohexa sulphur crystals have the space group  $R\bar{3} - C_3^2i$ . The lattice constants are (44,45)

$$\begin{aligned} a_o &= 10.818 \text{ \AA} & \text{bond length} &: 2.057 \pm 0.02 \text{ \AA} \\ c_o &= 4.280 \text{ \AA} & \text{bond angle} &: 102.2^\circ \pm 1.5^\circ \\ & & \text{torsion angle} &: 74.5 \pm 2.5^\circ \end{aligned}$$

The molecules are very efficiently packed. The crystal with a unit cell of 18 atoms, has a density of  $2.21 \text{ g/cm}^3$ ; the highest density of any known allotrope, including the thermodynamically stable orthorhombic ( $\alpha$ ) sulphur.

Cycloocta Sulphur. The crown shaped cycloocta sulphur molecule has been well studied and its spectra have been reported in solution, in the liquid, and in the two stable solid polymorphs orthorhombic and monoclinic ( $\beta$ ). The average parameters are (45)

$$\begin{aligned} \text{bond distance} &: 2.048 \pm 0.002 \\ \text{bond angle} &: 108^\circ 4^{1 \pm 3} \text{ } ^{\circ 1} \\ \text{torsion angle} &: \end{aligned}$$

Since cycloocta sulphur is the thermodynamically stable form, and the most frequently observed one, it was long believed that the bond parameters of cycloocta sulphur represented very closely the "ideal" values of the free S-S-S band. It has, however, since been shown that the free S-S-S band values are intermediate values, between cycloocta and cyclohexa sulphur.

Three polymorph of cyclo  $S_8$  have been crystallographically identified (45).

(a) Orthorhombic ( $\alpha$ ) sulphur.

This form is the STP thermodynamically stable form of sulphur. It is the well known form which can be found in volcanic areas and occurs in large crystals in nature. The crystals can easily be grown from solution but they then include appreciable amounts of solvent. The unit cell contains 128 atoms. The space group is  $Fddd-D_{2h}^{24}$  and the lattice constants are (45)

$$a_o = 10.467 \pm 0.001 \text{ \AA}$$

$$b_o = 12.870 \pm 0.001 \text{ \AA}$$

$$c_o = 24.493 \pm 0.003 \text{ \AA}$$

The density of orthorhombic sulphur is  $2.07 \text{ g/cm}^3$ . Most general and unspecified properties of sulphur refer to allotropic mixtures, rather than to the stable orthorhombic ( $\alpha$ ) form. The properties of the latter are astonishingly little known, and its mechanical properties, for example (51), have only very recently been studied. Even of the few studied properties such as the thermal conductivity only few will be of permanent value, since precise measurements will have to take into account the anisotropic behaviour. The anisotropic effects are partly quite large: The elastic constants (46) along the C axis are only one quarter that of the value along A and B. The velocity of sound along C is reported to be 150% of that of A and B (47) and the thermal conductivity (48) in the direction of C is 127% of A and B. Special attention has been recently paid to the electric and photoconductive properties of orthorhombic ( $\alpha$ ) sulphur, and it is likely that these properties, together with the x-ray data, are the best studied characteristics of  $S_{\alpha}$  (49). The results are, however, still

incomplete, and the resistivity,  $\rho$ , for example, cannot be given more precisely than  $4 \times 10^{20} \pm (10^3) \Omega \text{ cm}$  at  $75^\circ\text{C}$ .

(b) Monoclinic ( $\beta$ ) sulphur

If a sulphur melt crystallizes, monoclinic ( $\beta$ ) crystals form. Such crystals can be grown to very big specimens. Below  $95.4^\circ\text{C}$  the crystals transform slowly into the orthorhombic ( $\alpha$ ) form with a heat of transition of 96 cal/mole, but the quenched crystals can be maintained at room temperature up to a month. The density is  $1.96 \text{ g/cm}^3$ , the space group  $P 2_1/a - C_{2h}^5$  and the lattice constants are, at  $103^\circ\text{C}$ . (45),

$$a_o = 11.04 \text{ \AA} \quad \beta = 96.7^\circ$$

$$b_o = 10.98 \text{ \AA}$$

$$c_o = 10.92 \text{ \AA}$$

The structure of this stable high temperature form was unknown until very recently. Some doubt has been raised whether the molecular unit was  $S_8$ . However, preliminary results of a recent study (50) indicate that the structure is similar to that of orthorhombic ( $\alpha$ ), except for the presence of disordered sites, in which the molecules, at random, can assume a normal or an upside-down position.

Some mechanical properties (51) of  $S_\beta$  have recently been studied, and heat capacity, heat conductivity and some electric constants are available. The IR spectrum is also known.

(c) Monoclinic ( $\gamma$ ) Sulphur

The mother-of-pearl sulphur is well known. It reportedly occurs even in nature, but its stability is still disputed. It is often prepared from an undercooled melt or by slow crystallization in an alcoholic ammonium polysulfide solution which oxidizes in air at a temperature below  $15^\circ\text{C}$ .

The "sheared penny roll" crystal can be described in three different ways. Using the conventional setting, the space group is  $F2/c$  and the lattice constants are (45)

$$a_0 = 8.50 \text{ \AA}$$

$$b_0 = 13.16 \text{ \AA}$$

$$c_0 = 9.29 \text{ \AA}$$

$$\beta_0 = 124^\circ.49^1$$

The melting point is given as  $106.8^\circ\text{C}$ . Monoclinic ( $\gamma$ ) sulphur transforms into monoclinic ( $\beta$ ) and/or into orthorhombic ( $\alpha$ ) sulphur. These transformation processes have been carefully studied.(52).

(d) Transient or Insufficiently  
Identified Forms

A great number of the allotropes of cycloocta sulphur have been described (41), but their identification is either incomplete or doubtful:

(1) Under the microscope a "fourth allotrope of Muthman" can be obtained by quick quenching of molten sulphur. The transformation rates to  $\gamma$ ,  $\beta$  and  $\alpha$  sulphur have been measured, but very little else is known about this form (52).

(2) High pressure forms: Contrary to reports in the literature, sulphur seems not to become metallic, even under pressures up to 400 kbar. Recent reports indicate, however, that under high pressures, and at elevated temperatures, new allotropes can be produced (53). These allotropes reportedly can be quenched. According to one author, a cubic modification with a density of  $2.18 \text{ g/cm}^3$  and a unit cell of  $a_0 = 13.66 \text{ \AA}$  is produced. The triple point (54) cubic-liquid-orthorhombic is given as  $300^\circ\text{C}$  and 28 kbar. According to another report an optically active allotrope is produced above  $300^\circ\text{C}$  and 30 kbar.

The results of more work are needed before the high pressure characteristics of cycloocta sulphur can be understood (54). A special problem in analyzing high pressure work is that the sulphur, because of poor heat conductivity, can locally overheat and at least partially transform into other molecular units such as polymer chains. It is conceivable that elemental sulphur under high pressure might transform over such an intermediate plastic form into high density forms, such as rhombohedral sulphur, which have a higher density.

(3) From solutions, cycloocta sulphur crystallizes in a variety and in a mixture of forms (see Table III). Some selected crystal characteristics such as refractive index and density have been employed as criteria and proof of new allotropes, but it is usually not possible to evaluate these incompletely defined forms. The insufficiently defined forms are (3,5,6):

ξ - sulphur, forming reddish-brown crystals cocrystallizing with selenium (55); η - sulphur another isomorph of selenium with a half-life of 10 minutes (55); θ - sulphur which crystallizes with γ sulphur and forms ditetragonal bipyramids with a lifetime of less than one minute (56); ο - sulphur which coprecipitates with δ-sulphur and transforms within seconds into γ-sulphur (57); monoclinic spirals of ξ-sulphur; τ-sulphur which forms in only one of one thousand experiments if an oxylene solution of sulphur is boiled (58); monoclinic k-sulphur which has an unusually high refractive index, and many other forms (6) which are equally ill defined. It is, however, quite possible that some of these forms, or at least some of their components constitute truly new allotropes, the conclusive identification of which would be quite difficult.



Cyclodeca Sulphur. Recently an olive green solid has been prepared by a slow reaction of  $H_2 S_6 + S_4 Cl_2$  in dry ether in the dark (27). The molecular weight determination indicated that the reaction product was indeed  $S_{10}$ . This observation indicates that new sulphur molecules might be prepared by "directional" reactions, and it can be hoped that such work breaks the barriers of inorganic chemistry which through generations of textbooks led scientists to believe that only  $S_8$  could be made at STP.

Catena and Polycatena Sulphur. Radiation and heat lead to homolytic S-S bond scission which is followed by polymerization or ring formation. If a viscous sulphur melt ( $T > 160^\circ C$ ) is quenched in air, in ice water, in dry ice, or even in liquid nitrogen, high yields of a plastic material are obtained. The plastic solid can be purified by washing with  $CS_2$  and it can be stretched to long fibres. During the stretching two phases form. The phases can clearly be observed under the microscope (59) and electron microscope (60). This solid, with or without the orthorhombic ( $\alpha$ ) inclusions, and before or after stretching, has been widely studied and analyzed. For various portions of it the terms polymeric sulphur,  $\omega$ ,  $\psi$ ,  $\phi$ ,  $\mu$ , fibrous, plastic, elastic and many other names have been employed. A reproducible method for preparing long fibres has been recently described (59): Sulphur is heated for five minutes to  $300^\circ C$  (in a nitrogen atmosphere) and then poured into ice water in a thin stream. Long fibres form which are then stretched under ice water. The fibres obtained in this way are highly elastic and can be stretched 10-15 times their length over more than a dozen cycles. At  $23-25^\circ C$  the fibres can be still elongated up to eight times their original length, but stretching at  $45^\circ C$  and above leads to breakage. The stretched fibres

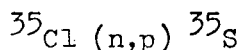
display a typical x-ray pattern, not unlike stretched rubber. Several research groups (59,61) are still investigating the geometry and the packing of this form which seems to consist of sulphur helices with about three and one-half atoms per turn. The carbon disulfide insoluble solid is commercially available in several forms as "super sublimation sulphur", "Crystex" or under other trade names. Since the insoluble forms slowly transform into orthorhombic ( $\alpha$ ) sulphur and, at STP, consist of mixtures which have ill defined, unreproducible, and time dependent properties, in the future more low temperature studies of the pure metastable solid should be undertaken.

Sulphur Solutions. Reactions with sulphur are usually performed in solution. Two kinds of solvents can be distinguished: neutral solvent in which sulphur shows only physical interaction, and reactive solutions in which sulphur, during the solvation process, interacts with the solvent under formation of new molecular species. Such chemical solvation occurs for example in  $\text{SO}_3$  (62), concentrated  $\text{H}_2\text{SO}_4$ , liquid ammonia (63) and  $\text{S}_2\text{Cl}_2$  and is usually accompanied by deep colours. It is not yet clear whether the green and blue sulphur colours in liquid alkali halogenides are caused by chemical effects or by the thermal conditions which favour small molecules and perhaps even  $\text{S}_2$ .

The classical solvents for sulphur are  $\text{CS}_2$  and non-polar solvents such as benzene, toluene, cyclohexane, etc. Such solutions have been studied for over a hundred years and show partly quite unusual properties. A recent review (64) discusses over twenty solvents and cites liquid-liquid mixtures with cycloocta sulphur (for example with naphthalene below  $150^\circ\text{C}$ ) and with polycatena sulphur (for example with triphenyl methane.) All sulphur solutions are highly light sensitive. It is long known that

most solutions become cloudy when exposed to light. The suspended "photosulphur" (65) dissolves again on storage in the dark.

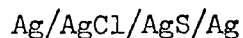
In recent years sulphur, and especially S<sub>2</sub> and sulphur atoms have been frequently produced in non-equilibrium solutions (66), both in the liquid and in the solid phase. Solid solutions can be prepared by condensing sulphur and solvent, for example, as molecular beams. They also can be prepared by irradiation of sulfides or sulphur containing molecules with  $\alpha$ ,  $\beta$ ,  $\gamma$  or UV radiation. A typical system is for example solid CO in which COS solution can be photolyzed to give atoms which then, depending on the temperature, diffuse in the solid until they react with other solute, or with each other (67). A most elegant synthesis of sulphur atoms employs nuclear reaction, for example



Such reactions lead to "hot" atoms which obey special chemical laws (68).

With methane, for example, both H<sub>2</sub>S and CH<sub>3</sub>S are obtained.

Finally, sulphur can be electrolytically released in solids, for example, in a Rickert-cell (28)



V. Conclusions

The explanation of the systems mentioned in the foregoing paragraph has only started and undoubtedly opens entirely new avenues for chemical synthesis. It seems generally that sulphur chemistry is undergoing a renaissance. Much of the new impetus has been the result of the success of work performed with newly developed experimental techniques. Such techniques, which were often a fall-out of space or nuclear research, are now becoming sufficiently sophisticated to take into account more of the related parameters which affect the behaviour of sulphur. It seems likely that the next ten years will bring a drastic increase of our knowledge of this element, which despite its tremendous industrial importance is still so poorly characterized.

This work was supported in part by the United States Atomic Energy Commission.

Table I. Common Impurities in Commercial Sulphur Forms  
(parts per million)

	Ash	Oy	H <sub>2</sub> S	HeSo <sub>4</sub>	NaCl	As	Se	Te
Commercial Crude Sulphur								
high grade	50	<100	>100	0	0	<0.25	<2	<2
low grade	3000	5000	10	500	0	1300	1600	1000
Crystex	1500	500	<	1000	<	<0.25	<2	<2
Precipitated sulphur	<10,000	<60,000	<10,000	<10,000	<10,000	<	<	<
Zone refined sulphur (99.9999%)	<10	<	<	<	<	<	<	<

Table II. Thermal Allotropic Transformations (T°K)

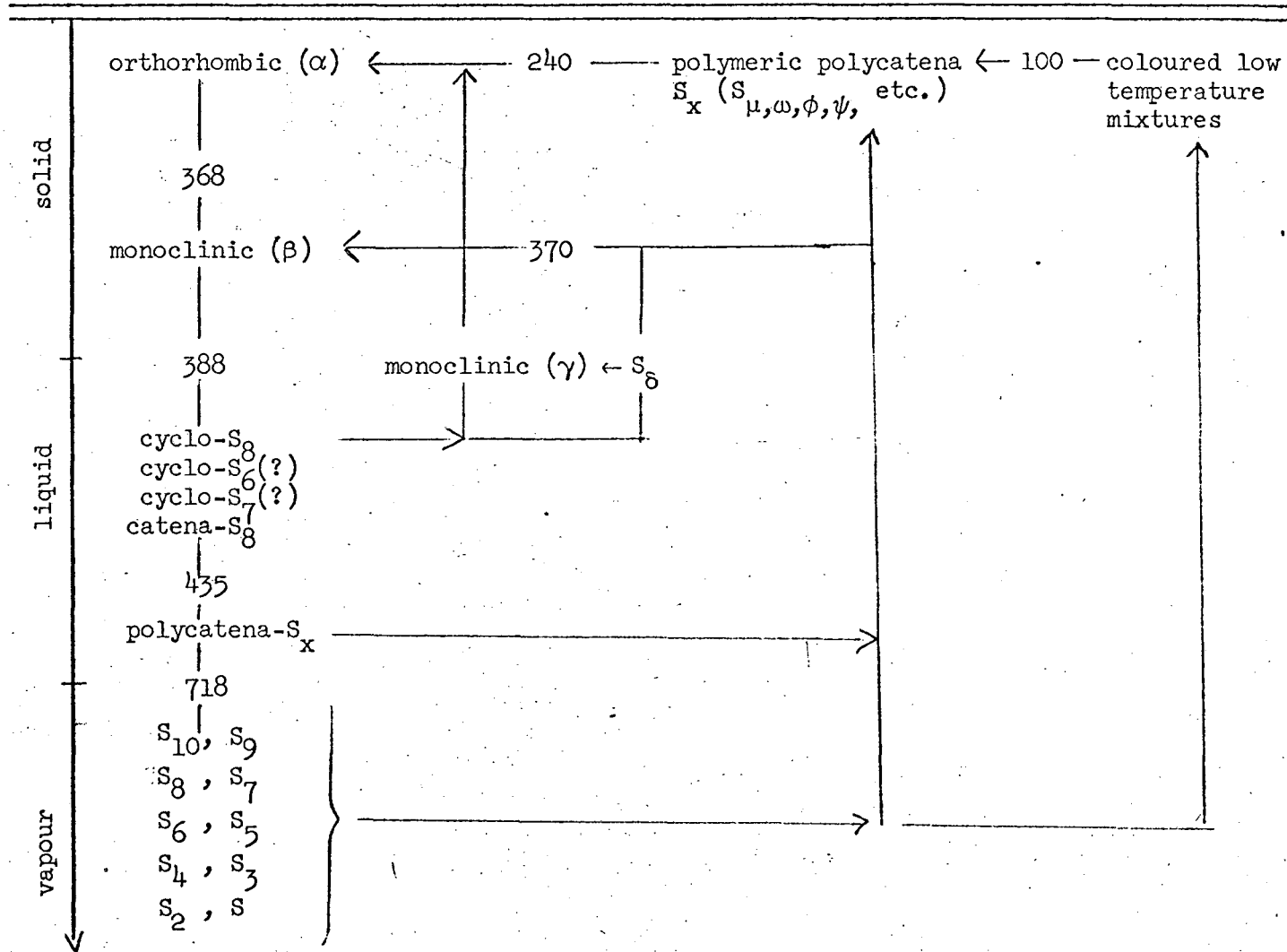




Table IV. Chemically Prepared Allotropes

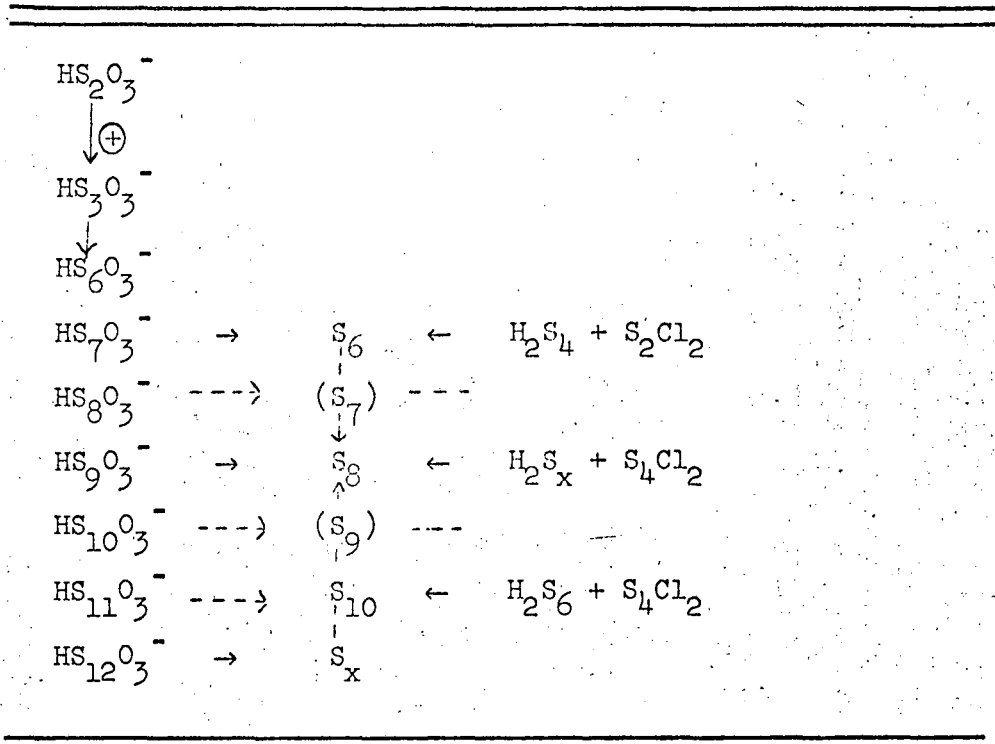




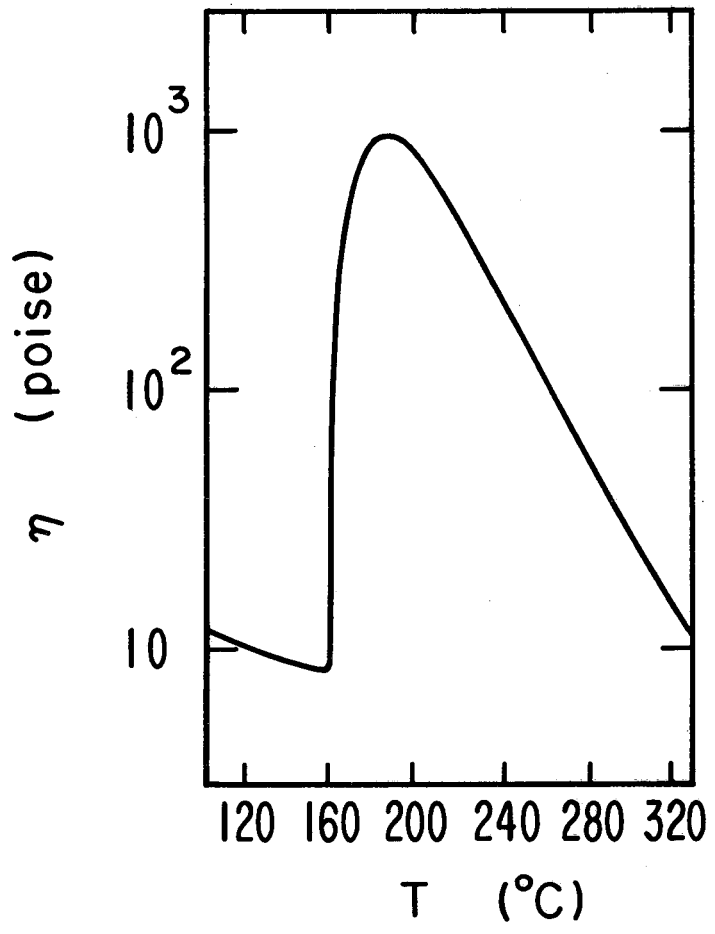
Table V. Thermodynamic Data

Transitions	Temp., °K.	$\Delta H$	$\Delta S$ , cal./deg. g-atom
$\alpha, \beta$	368.46±0.01	0.096 <sup>a</sup>	0.261±0.002
$\beta, ?$	374.2	0.000 <sup>f</sup>	0.0 <sup>f</sup>
$\alpha$ -Subl., $\lambda$	368.5	3.01 <sup>a</sup>	8.17
$\beta$ -Subl., $\lambda$	368.5	2.92 <sup>a</sup>	7.93
$\epsilon, \rho$	300	4.02 <sup>a</sup>	8.38
Fusion $\alpha$ , $\lambda$	383	0.507 <sup>a</sup>	
Fusion $\beta$ , $\lambda$	388.33	0.410 <sup>b</sup>	0.75
$\lambda$ , $\pi$	432	4.1 <sup>a, d</sup>	2.88
Polymer, $\lambda, \pi, \mu$	442.8	0.396 <sup>a, e</sup>	0.58
Vap. $\lambda, \lambda$	444.600 (°C)	2.5 <sup>a</sup>	3.5
7/8 $S_\lambda, S_7$	400	5.7 <sup>c</sup>	
3/4 $S_\lambda, S_6$	400	6.2 <sup>c</sup>	
5/8 $S_\lambda, S_5$	400	14.3 <sup>c</sup>	
1/2 $S_\lambda, S_4$	400	20.5 <sup>c</sup>	
3/8 $S_\lambda, S_3$	400	22.5 <sup>c</sup>	
1/4 $S_\lambda, S_2$	400	23.5 <sup>c</sup>	

<sup>a</sup>Units in kcal./g.-atom; 1 g.-atom of sulphur = 32.066 g. <sup>b</sup>Unit in 5 kcal./g.-atom. <sup>c</sup>Units in kcal./mole. <sup>d</sup> $K = (\pi)/(\lambda) = 1.137 \times 10^4 \exp(-16520/T)$ . <sup>e</sup> $K_3 = (\pi)/(\pi\lambda) = 10.43 \exp(-1596/T)$ ; <sup>f</sup>See ref. 13.

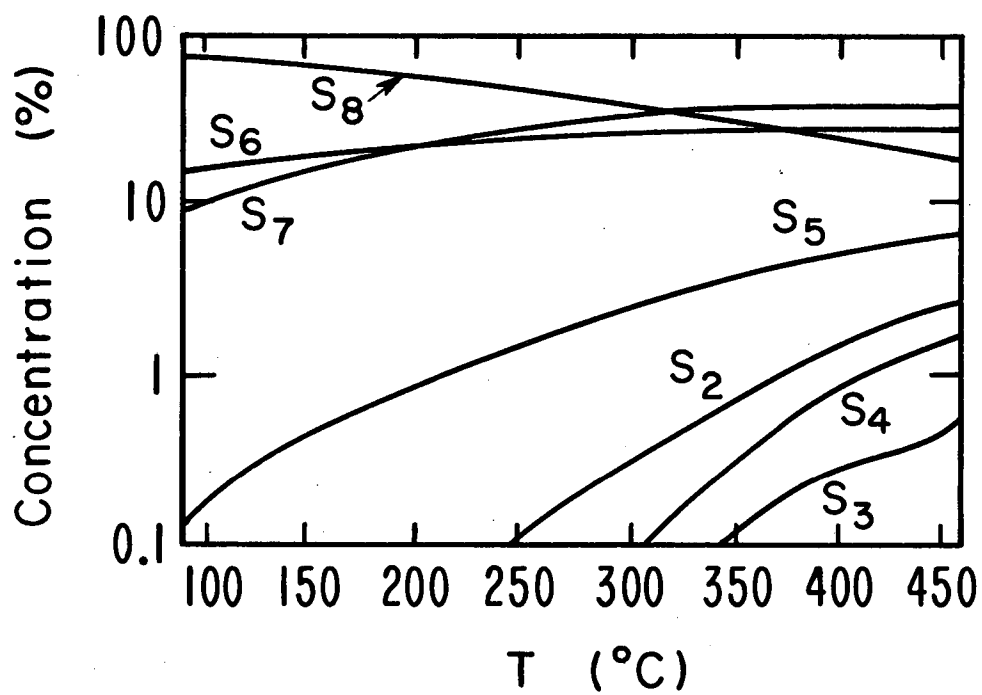
Table VI. Names of Well-defined Allotropes

Old and present names	Recommended name	Characteristics or remarks
Rhombohedral sulphur Aten sulphur Engel sulphur Trigonal sulphur $\epsilon$ -Sulphur $\rho$ -Sulphur	Rhombohedral ( $\rho$ ) sulphur	Crystalline cyclo-S <sub>6</sub> Space group $R\bar{3}$
Rhombic sulphur $\alpha$ -Sulphur Orthorhombic sulphur Muthmann's sulphur I	Orthorhombic ( $\alpha$ ) sulphur	Crystalline cyclo-S <sub>8</sub> Space group Fddd
Monoclinic sulphur Prismatic sulphur $\beta$ -sulphur Muthmann's sulphur II	Monoclinic ( $\beta$ ) sulphur	Crystalline cyclo-S <sub>8</sub> Space group $P2_1/c$
$\gamma$ -Sulphur Nacreous sulphur Mother-of-pearl sulphur Muthmann's sulphur III Gernez's sulphur	Monoclinic ( $\gamma$ ) sulphur	Crystalline cyclo-S <sub>8</sub> Space group $P2/n$
Fibrous sulphur $\psi$ -Sulphur	Fibrous sulphur	Crystalline catena-S <sub><math>\infty</math></sub> Space group not known
Plastic sulphur Elastic sulphur $\nu$ -Sulphur $\eta$ -Sulphur	Mixture	Probably cyclo-S <sub>8</sub> and catena-S <sub><math>\infty</math></sub>
Insoluble sulphur Das sulphur White sulphur Supersublimation sulphur $\omega$ -Sulphur	Insoluble ( $\omega$ ) sulphur, if crystallized. Polymeric sulphur, if below glass temperature.	Probably catena-S <sub><math>\infty</math></sub> , x-ray pattern reproducible



MUB-9498

Fig. 1. Composition of saturated sulphur vapour above the liquid phase.



MUB-9497

Fig. 2. Viscosity of liquid sulphur as a function of H<sub>2</sub>S impurities.

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