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**Berkeley, California**

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Berkeley, California

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Beat Meyer

March 7, 1964

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## I. INTRODUCTION

During the last hundred and fifty years a large amount of detailed information on elemental sulfur has been accumulated, and more than thirty allotropes have been described; however, many basic properties of sulfur are not yet known. Much of the data are so inconclusive or contradictory that it is difficult to establish the present status of our knowledge, and an inconsistent terminology hampers the coordination of observations. Three reasons for this situation are:

1. Many authors assume that sulfur, being an element, should have a simple behavior pattern. Based upon this assumption, the observations of experimental data are frequently interpreted with very few parameters. This approach is wrong and often yields contradictory observations. The solubility of plastic sulfur, for example, has been studied by different authors using the same method but reporting different results. It would be tempting in such a case to doubt the reliability of one author and to select one result as describing the situation correctly. The primary cause for the confusing situation mentioned above is, however, that both groups neglected to give an important parameter, namely, the age of the sample. It is generally observed that sulfur allotropes form or transform under the influence of minor disturbances such as sunlight, recrystallization and impurities, or even with time alone. The half life of many of these forms can be of the order of the time required for investigation, and the sample changes its composition under the hands of the investigator. It is hard or impossible to isolate one single allotrope in such a multicomponent system. Often a mixture is so complex that it can be mistaken for a new homogeneous form. The behavior of sulfur is complex and capricious and can only be reproduced under well-defined conditions.

2. Impurities are another source of confusion: the properties of sulfur depend critically upon contaminations (13, 20). Selenium (280), hydrocarbons (239), and many other impurities react with the element (even under mild conditions) and cause time-dependent observations. A satisfactory method (12, 13) for purifying sulfur was developed only in 1943. Earlier data were obtained with samples containing considerable amounts of other materials, and even in recent years the influence of contaminations has been frequently underestimated.

3. Elemental sulfur is used in chemistry, crystallography, physiology and so many other fields that there is often very little contact between different research groups. Therefore, the literature contains a considerable amount of observations that are uncorrelated to existing data; further, the same information has been frequently printed twice, but in different terminology. This situation could be improved if a survey of this field were available.

This review represents an attempt to survey the present knowledge (January 1964) about solid sulfur allotropes. Here, sulfur is considered solid at or below standard temperature even if it does not form a regular lattice. Wherever possible, a systematic relationship between formation, structure, and the origin of the different allotropes is indicated. Reference is occasionally made to old literature since the work of recent years has confirmed some observations which had long been considered incorrect.

## II. TERMINOLOGY AND NOMENCLATURE

The lack of coordination of knowledge about the different sulfur allotropes shows clearly in terminology and nomenclature. Many criteria have been applied to the labelling of sulfur; in consequence, a systematic nomenclature does not exist (106). There is, as a matter of fact, not even one allotrope for which one single name is commonly used. Often, a modification was first named after a particular property which the discoverer wanted to stress. Some allotropes were, for example, called purple, green, and black sulfur, and orthorhombic, prismatic and monoclinic sulfur. Unfortunately, most of the mentioned properties are shared by several allotropes and do not conclusively describe a modification; thus, a second definition was introduced or added, such as 4th monoclinic form, or monoclinic form of Gernez, etc. Another insufficient nomenclature refers to the origin or the preparation of a sample, as in precipitated sulfur, sublimated sulfur or Frasch sulfur. In an attempt to clearly label different allotropes, a Greek letter nomenclature was introduced, but in explaining new observations these letters were distributed very freely. As a result, Greek letters often do not designate equivalent particles, but sometimes stand for molecules (e. g.  $S_\lambda$ ), sometimes for modifications (e. g.  $S_a$ ), or even for complicated mixtures (e. g.  $S_\mu$ ) in liquid or solid phase. A further difficulty encountered in the literature is the frequent renaming of allotropes with new or previously used symbols. Such a case of accidental or purposeful name shifting is, for example,  $S_\mu$  for which here only a few synonyms are listed:  $S_\gamma$ ,  $S_x$ ,  $S_n$ ,  $S_\nu$ , etc.

Table 1 lists the names, synonyms and other data for some allotropes.



Table 1. Nomenclature of Sulfur Allotropes.

Name	Synonyms	Status of identification	Stability	Molecular species	Section
$\alpha$	1st modification 1st Muthmann modification orthorhombic	Conclusive	Only thermodynamically stable form at STP	Cyclo-octa-S	IV. B.3
$\beta$	2nd modification 2nd Muthmann mod. monoclinic (I) sulfur prismatic	Structure not known	Stable $\geq 95.6^\circ\text{C}$	Cyclo-octa-S	IV. B.3
$\gamma$	3rd Muthmann mod. 2nd monoclinic, Nacreus sulfur, Mother-of-Pearl sulfur, Gernez mod.	Incomplete	Metastable (?)	Cyclo-octa-S	IV. C.3. b
$\delta$	4th Muthmann mod. 3rd monoclinic $\gamma$ -monoclinic	Ambiguous	Unstable	Cyclo-octa-S	IV. C.3.e
$\epsilon$	Engel sulfur, Aten sulfur, Rhombohedral mod, Monoclinic Engel	Conclusive	Unstable	Cyclo-hexa-S	IV. C.5.b
$\zeta$	5th monoclinic	Ambiguous	Unstable	Cyclo-octa-S	IV. C. 2.c
$\eta$	4th monoclinic	Ambiguous	Unstable	Cyclo-octa-S	IV. C.2. f
$\chi$	Tetragonal	Ambiguous	Unstable	Cyclo-octa-S	IV. C.3. e
i	---	Inconclusive	Unstable	Cyclo-octa-S	IV. C.3.e
$\lambda$	Free or bound cyclo-octa-S	Conclusive	Stable	Cyclo-octa-S	IV. C.1.a

Table 1 (continued).

Name	Synonyms	Status of identification	Stability	Molecular species	Section
$\mu$	CS <sub>2</sub> -insoluble sulfur polymeric chains	Conclusive	Unstable	Catena-poly-S	IV. C.3.c
$\nu$	Term inconsistently used: $\mu$ with special properties	Inconclusive		Mixture	IV. C.3.d
$\xi$	Triclinic mod.	Ambiguous	Very unstable	Cyclo-octa-S	IV. C.2.h
$\omicron$	---	Ambiguous	Very unstable	Cyclo-octa-S	IV. C.2.g
$\pi$	Aten's modification	Incomplete	Unstable	Catena-octa-S	IV. C.3.a
$\rho$	a) here: unbound cyclo-hexa-S molecule b) often Aten's, Engel	Conclusive	Unstable	Cyclo-hexa-S	IV. C.5.g
$\tau$	---	Ambiguous	Unstable	Cyclo-octa-S	IV. C.2.i
$\phi$	a) Fibrous sulfur b) Erämetsä c) Plastic; mixture of $\omega$ & $\gamma$ d) Fibrous sulfur Stretched sulfur	Incomplete Ambiguous Ambiguous Ambiguous	Unstable Unstable Unstable Unstable	Catena-poly-S or mixture Cyclo-octa-S Mixture (?) Catena-poly-S	IV. C.3.e   IV. C.3.f
$\omega$	Insoluble sulfur, white sulfur, super-sublimation, Das modification	Incomplete	Unstable	Catena-poly-S and mixture	IV. C.4.a

Table 1 (continued).

Name	Synonyms	Status of identification	Stability	Molecular species	Section
m	Tricilinic	Inconclusive	Very unstable	Cyclo-octa-S	IV. C.5.d
n	See $\mu$		Unstable	Catena-poly-S	IV. C.3.c
Aten	Used for $S_{\epsilon}$ and $S_{\rho}$				
Brauns	Mixture, see $S_{\mu}$				
Engel	See $S_{\epsilon}$ and $S_{\rho}$				
Woehler	Colloidal	Conclusive	Metastable	Poly-catena-S	
Amorphous	See $S_{\mu}$				
Metallic	---	Inconclusive	Unstable		IV. C. 1.a
Photo-sulfur	---	Incomplete	Unstable	Mixture	IV. C. 2.a
Irradiation sulfur	---	Incomplete	Unstable	Mixture	IV. C. 1.b
Black	(a) Mitscherlich	Not elemental sulfur			IV. C. 4.c
	(b) Skyerven	Inconclusive	Unstable		
	(c) Rice-Schenk	Incomplete	Unstable	Catena-S	
Green					
Purple	Trapped sulfur	Incomplete	Unstable	Mixture of catena-S	IV. C.4.c-h
Violet					
Brown					
Red	(a) Trapped; condensation sulfur	Incomplete	Unstable	Catena-S, mixture	IV. C. 4. b
	(b) Irradiation sulfur	Incomplete	Unstable	Catena-S, mixture	IV. C. 1. b
	(c) Precipitation sulfur	Incomplete	Unstable	Mixture	IV. C. 5. c

### III. SELECTED GENERAL DATA

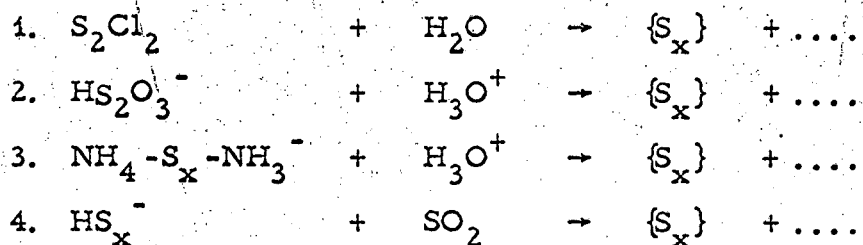
The general properties of elemental sulfur and many of its modifications are reviewed in references cited in Section VI; but the various allotropes differ so much in their behavior that general and over-all data have only limited value. It is the purpose of this chapter to indicate some common sulfur sources and then to discuss the problem of impurities.

#### A. Sulfur Sources

Commercial sulfur is derived from two principal sources. First, it can originate from the vast natural deposits of the element; second, it can be formed, generally as a byproduct, from compounds. Until 1914, most commercial sulfur came from volcanic sources. This sulfur forms large crystals of  $S_{\alpha}$  which are yellow-brownish, due to a rather large impurity concentration. A material containing up to 99.99% sulfur is now produced by the Frasch (115) method, which involves melting and recrystallizing of the element under water-vapor pressure. The main impurities in elemental samples are: Air inclusions, water, hydrosulfides, heavy-metal sulfides, sulfoxy acids and some arsenium, selenium, and tellurium. Commercial sulfur is generally a mixture of different allotropes, containing mainly orthorhombic  $S_{\alpha}$  and plastic  $S_{\mu}$  sulfur. Beside the stable  $S_{\alpha}$  form, two unstable (STP) modifications have been observed in nature:  $S_{\beta}$  and  $S_{\gamma}$ , both however only in small samples.

The most popular forms of sulfur are precipitated sulfur, sublimation sulfur, and sulfur flowers. They all are obtained from compounds which occur, for example, during the petroleum refining process as by products and contain the impurities mentioned above, and also contain organic sulfur compounds, dust, or solvent traces. In the laboratory, several methods are

used for precipitating the element. Probably the four most popular methods are the reactions of:



The mechanisms of these reactions (69, 239) always involve the formation of polysulfur chains in compounds which then degrade. During the wet preparation of the element, a variety of allotropes are formed and coprecipitate with sulfides, oxyacids, and solvents. It is hard to purify the element in this form because it can react with the contaminations during the purification process.

A new method has been developed by which sulfur can be released in precisely measured amounts from a sophisticated electrolytic cell (247, 248).

### B. Reactions

So far, reactions of unspecified mixtures of allotropes have been mainly studied, the composition of which can only be guessed from the reaction conditions and reaction media. Many reactions also involve allotropic transitions, and it is hard to isolate the rate determining species; but it has been demonstrated (17, 22) that the reactivity of sulfur depends very much upon the molecular structure and that the vapor composition depends upon the nature of the allotrope (28). Therefore, little quantitative data is available about the reactions of sulfur.

Under carefully selected conditions, sulfur can react with almost any element, but here only some selected reactions with impurities are listed. For a more complete discussion see references 123, 139, and 239.

The use of radio-active isotopes (45, 182) often facilitates the study of reaction mechanisms; but, so far, relatively little use has been made of this method (6, 17, 154, 155).

### 1. Elemental Sulfur Without Reactant

A great variety of intra and intermolecular arrangements have such a similar stability that the energy transport, even during careful handling, can bring about a transformation. Such allotropic transformations form the body of this review and are discussed in Sec. IV.

### 2. With Aqueous Solutions

The reaction of the element has been studied under different conditions (172). The mechanism is not yet known (239), but the products are highly water soluble and it is probable that they catalyze the reaction. Since sulfur is water insoluble, reactions are often performed in a mixture of an aqueous solution with an organic solvent.

### 3. In Organic Solvents

$S_a$  and almost all allotropes but  $S_\mu$  and  $S_\omega$  are fairly soluble in ethyl-alcohol, benzene, toluene, carbon disulfide, carbon tetrachloride, chloroform and many other solvents (157, 319). Reactions are brought about by introducing the reagent directly into the solution, or by mixing the solution with an acetic or alcoholic aqueous solution of the reagent. It is not yet clear how much the solvent partakes in such reactions, but they often form compounds with sulfur. Acetone with sulfur, for example, gives a deeply colored solution, and alcoholic solutions always smell of hydrogen sulfide, the formation of which is strongly enhanced by light (317). Polysulfides are also detected if sulfur is dissolved in hydrocarbons and in cumene heated to about  $112^\circ\text{C}$ . The last reaction probably involves open chains of the element

(239). Such chains have a free radical character (200) and make sulfur an excellent polymerization inhibitor (238, 294) for polystyryl (18), polyvinyl, polysulfenyl, and many other substances.

Nucleophilic reactions: Triphenylphosphine, the cyanogen ion and many weak bases (17, 18, 264) open the octa-sulfur ring and degrade (19) the chains under formation of the corresponding sulfur compounds. Ammonia and triethylamine, however, react with the  $S_8$  ring only in the presence of arylsulfide (20). The reaction with arylimines is not yet clearly understood.

The hydroxyl ion reacts quickly with sulfur at  $100^\circ\text{C}$  and leads to the formation of thiosulfate which then decomposes on further heating into sulfate and sulfite. At temperatures above  $200^\circ\text{C}$ , the sulfite ions are formed directly from the element.

The most important reaction for our discussion is that of the sulfide ion. The sulfide or polysulfide is often present as a primary impurity, or is easily produced through the reaction of hydrocarbon impurities with hot sulfur. It polymerizes to long polysulfide chains, which in many respects, react very similarly to the chains of the element; the components can, therefore, hardly be separated in a mixture of elemental and sulfide chains. This causes many of the confusing and contradictory observations assigned to the pure element, such as, for example, the data on the viscosity of liquid  $S_\mu$  (12, 103).

If sulfur colloids are stabilized with ammonia, sulfide ions are also present. Electrophilic attack on the sulfur ring has not been observed in solutions, but occurs in the presence of concentrated acids.

#### 4. Reactions at Elevated Temperatures

During the preparation and purification process, sulfur is either melted or evaporated. It reacts under such conditions with air (173), and almost any impurity. Organic contaminations decompose slowly and mainly

form sulfur dioxide which evaporates (202), hydrogen sulfide which is highly soluble in the melt (269), and carbon (202), which precipitates with a mixture of insoluble material (12). Such carbon deposits are black; they are a sensitive indication for the presence of impurities. Similar spots remain after the distillation of sulfur from glass bulbs (138). They are believed to come from the formation of silicium sulfide and other sulfides on the glass surface (which is quite reactive at the boiling point of sulfur). No reaction is observed when the element is vacuum distilled. Quartz glass does not react with sulfur vapor below 1000°C. Black deposits formed in pure sulfur have also been explained by the assumption that they are a new modification (271) (see "black sulfur").

#### 5. Other Reactions

The formation of deeply colored solutions of sulfur in inorganic liquids has already been pointed out. The dark blue solution in ammonia (133, 175) has a quasi-metallic character. With oleum or  $\text{SO}_3$ , a red solid crystallizes (158), which is believed to have the formula  $\{\text{SO}_3 \cdot \text{S}_x\}$ . In alkali-halide melts almost any color can be produced (144); the color remains after trapping at low temperatures for a long time (194). Some of these solutions are paramagnetic (158) and contain different active species, but only very little is known about such systems.

Sulfur and selenium can substitute for each other in crystals (145, 146) in chains (70) of the liquid, but not in rings (280). The Se-S system has been studied in the liquid (280) and gas (74) phases with the help of radioactive isotopes.

#### C. Purification Methods

Sulfur is often considered "pure" if contaminations cannot be observed or do not interfere with an arbitrarily selected set of tests. The purity



requirements however vary from one experiment to another, and the above definition is only sufficient if the tests are at least as sensitive to contaminations as the investigated properties: Crystallographic data and many other properties of sulfur can be studied accurately on volcanic crystals, but less than 0.1% contaminations already cause an inconsistent viscosity of the melt (13), and 0.002% of sulfur dioxide catalyzes the reaction with triphenylphosphine (21). Some methods which have been proposed to purify sulfur to different degrees are:

#### 1. Conventional Methods (138)

The most commonly used and most unsatisfactory purification procedure is to recrystallize sulfur from organic solvents. In this way one can obtain beautiful crystals (318) but they contain, besides solvent inclusions, still more than a 3% hydrogen sulfide and 0.08% sulfur dioxide (21). The carbon disulfide inclusions in a  $S_8$  crystal grown in this way have led to an erroneous assignment of the infrared spectrum (287).

Often sulfur is separated from insoluble impurities by being filtered through glass wool. This process does not remove any soluble impurities, helps to saturate the liquid with atmospheric gases, and frequently introduces dust.

Another method consists of washing sulfur with acids. If this treatment is not very carefully controlled and completed, it leads to a sample saturated with water, acid, and oxidized organic contaminations.

The distillation of sulfur (75) under atmospheric pressure cannot be recommended. The pyrex containers react at elevated temperature with the element, and many impurities are distilled in the same fraction with the sulfur and react to form new compounds.

## 2. New Methods

During recent years, two conventional methods have been sophisticated for the production of a very pure element. The first is zone melting and was used (188) to grow crystals of  $S_a$  and  $S_b$ . The second employs an electrolytic cell, Pt-Ag-AgS-AgI-Pt, from which sulfur can be released quantitatively (247, 248). Chromatographic methods (91) have also been proposed for the purification and separation of sulfur allotropes, using aluminum oxide and silica gel columns or paper and carbon disulfide or carbon disulfide-alcohol mixtures as solvent, but sulfur undergoes allotropic transformations and reacts with the column material (20). In addition, sulfur compounds and allotropes have on the material mentioned very similar  $f$ -values (262) and are therefore not suited for separation. Mass spectroscopy can be applied for the enrichment of isotopes and the separation of pure sulfur in small quantities, but the properties of this element make it undesirable in vacuum equipment.

## 3. Classical Methods

(a) Bacon and Fanelli (12, 13) prepared sulfur that has a reproducible viscosity over the whole temperature range of the melt: sulfur is boiled for 48 hours together with 2% MgO. The liquid is then filtered to remove precipitated impurities, and the whole process is repeated twice.

This method has been widely accepted and most data reported since 1943 have been obtained from samples purified in this way. There are, however, two drawbacks to this method. First, the material is saturated with atmospheric gases each time it is filtered, and second, an appreciable amount of magnesium salts (205), 0.02% hydrogen sulfide and 0.006% sulfur dioxide (21) are in the melt. If the sulfur is vacuum distilled after the preliminary treatment, both disadvantages are removed (180).

(b) Murphy, Calbaugh, and Gilchrist (205) use the following method. Sulfur and sulfuric acid are heated to 150° C, and nitric acid is slowly added over a period of 6 hours. The melt is then cooled and washed and heated under reflux with helium or dry nitrogen bubbling through it. The sample is afterwards cooled again and transferred into an ampulla. Water is added and the ampulla is sealed under nitrogen and heated to 125° C. The last process is repeated three times and the sulfur is then outgassed at 10-mm Hg nitrogen and finally sealed in an ampulla.

The authors indicate the testing methods used to determine the concentration of contaminations. The above procedure yields a high purity material on which the present values (211) of the melting points of sulfur are based (See Appendix). The method is, however, time consuming and requires several high-purity chemicals. In addition, the concentrated acid and the water treatments cause the formation of new compounds (172), which can only be removed through long and careful outgassing. This method has therefore to be combined with vacuum distillation to give the best result.

(c) A very simple and efficient method has been developed by v. Wartenberg (306, 307, 308). Sulfur is melted in a loosely covered roundflask and a red glowing quartz heater ( $\approx 700^{\circ}\text{C}$ ) is inserted into the melt. A carbon deposit is formed on the heater and should be removed daily. After one week the flask is connected with a pump-system and the sulfur is put under vacuum, distilled, and sealed into an ampulla.

This purification method is based upon the following processes. During the long heating time all material is brought into contact with the heater. The impurities either decompose completely and form volatile products, which escape, or insoluble carbon, which deposits on the heater. The bubbling of sulfur dioxide through the melt has been proposed to enhance the decomposition (270, 271) and to remove hydrogen sulfide. In the final vacuum distillation,

the sulfur is separated from the insoluble residue and outgassed. This last method seems the best way for purifying sulfur.

Methods for a quantitative determination of impurities are given in references 13, 138, and 205. Several qualitative tests indicate the presence of impurities: Clean sulfur is light yellow. At the melting point the liquid is pale yellow and has a lower viscosity than water. It does not wet the glass walls, nor does it smell. After it is heated, the yellow color of the solid is reproduced. As little as 0.04% oil produces black spots in the liquid. Precipitation comes from metal sulfides, dust, or silicosulfides.

Recently, high-purity sulfur became commercially available; 5N sulfur is now fairly cheap, and even 7N sulfur can be purchased.

## IV. ALLOTROPES

### A. Intramolecular and Intermolecular Allotropy

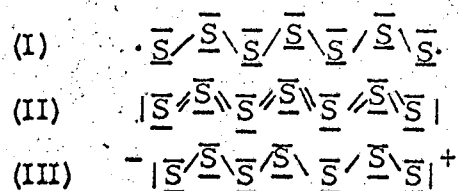
Berzelius (32) introduced the term allotrope for the different forms in which an element can exist. Several authors have since developed theories of allotropy (57, 59, 149, 177, 183, 279). Here a molecular point of view is taken and two sources for the variety of the appearance of sulfur are distinguished: first, the different ways in which the atoms can combine into molecules; second, the different manner in which the molecules can build up crystals. We discuss these intra- and intermolecular arrangements separately.

#### 1. Molecular Variety

Sulfur forms rings and unbranched chains. Molecules with one to ten atoms have been observed in sulfur vapor (27, 28, 35, 322). In liquid sulfur at a temperature between 159°C and the boiling point 444.6°C (186), polymer chains predominate. The average chain length varies between 8 and  $10^5$  atoms (295, 296). At the melting point, the liquid is a mixture of catena-octa-sulfur ( $S_{\pi}$ ) and cyclo-octa-sulfur ( $S_{\lambda}$ ). By means of sudden cooling, all of the molecules mentioned can be trapped as solids, but only cyclo-octa-S,  $S_{\lambda}$  is stable at room temperature. All others convert into the  $\lambda$  form with a half-life between about a millisecond and one year.

The comparable stability of a variety of different molecules is typical for sulfur. This has to do with the electron configuration which is similar to that of oxygen. Sulfur has however a full neon shell and empty d-orbitals available (214). It is generally assumed (3, 100, 217) that sulfur can activate these d-orbitals for the formation of  $d\sigma$  hybrids and  $d\pi$  bonds (320). This assumption requires a break-down of the octet rule, and it is believed, for example, that in carbon disulfide both electron octet and decet configurations can exist. Large chains have biradical character (124, 126) and therefore octet structure (I), while small chains might be stabilized by resonance

(187, 262)(see, however,  $S_{\pi}$ ):



Some authors believe (26), however, that the promotion energy for a decet might be much larger than the energy gain through a  $dp\pi$  bond (190). The ionic structure (III) has not been observed (222).

As useful way to discuss the stability of the different molecules is to compare the bond distance, the valence angle and the dihedral angle (217). Table 2 lists recent molecular data for cyclo-octa, cyclo-hexa and catena-poly-sulfur. The cyclo-octa molecule is the most stable and was, until recently, assumed to be torsion free (217). The stability of other molecules can be expressed through the bond strain, but early values seem to be too high. If one uses recent data (214) and computes a simple semi-empirical MO-LCAO model (26), the torsion energy of cyclo-octa-S ( $S_{\lambda}$ ) is not zero, but is rather small, being only about half as big as that for the cyclo-hexa-S ( $S_{\rho}$ ). Recent data for catena-poly sulfur and for cyclo-octa sulfur indicate similar values and make it probable that they are both nearly-torsion free.

The symmetry of cyclo-octa-S ( $S_{\lambda}$ ) is  $D_{4d}$ . The molecule is a puckered ring. The top four and the bottom four atoms each lie in the corner of a square. The two squares are parallel at a distance of 1.15 Å, and are concentrically turned against each other at an angle of 45°. The edges are 3.31 Å long; the S-S distance is 2.059 Å (see Fig. 1) (84). The cyclo-hexa molecules ( $S_{\rho}$ ) form a puckered ring with  $D_{3d}$  symmetry. The bond distance is 2.057 Å. The open chains of catena-poly-S ( $S_{\mu}$ ) form helices. Their structure is not yet fully known. They probably form spirals in which the bond angle and bond distance is very similar to that in  $S_{\lambda}$ . Many additional molecules such as

Table 2. Structural Data for  $S_\lambda$ ,  $S_\rho$ , and  $S_\mu$ .

Formula	$S_8 = S_\lambda$	$S_6 = S_\rho$	$S_x = S_\mu$
Name	Cyclo-octa-S;	Cyclo-hexa-S;	Catena-poly-S;
S-S bond length (in Å)	2.059 ± .002 or 2.048	2.057 ± 0.018	2.04
Valence bond angle	107° 54'	102.2 ± 1.6	
Dihedral angle	98.9 ± 0.7	74.5 ± 2.5	87°
Number of non-bonded neighbors - 3.5Å	6	12	
Molecular symmetry	$D_{4d}$	$D_{3d}$	$C_{2i}$

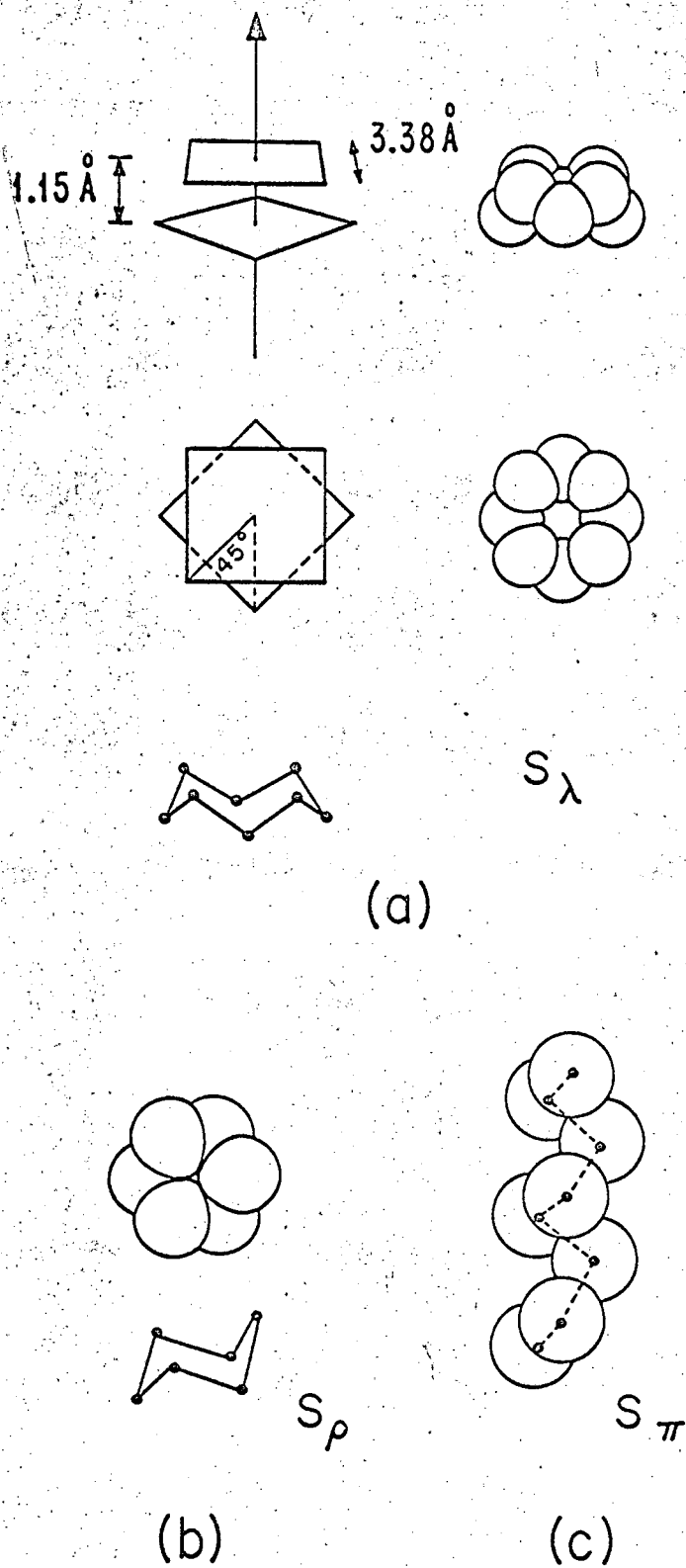


Fig. 1(a). The  $S_\lambda$  molecule (cyclo-octa-S), (b) The  $S_\rho$  molecule (cyclo-hexa-S), (c) The  $S_\pi$  molecule (catena-octa-S).



cyclo-tetra sulfur, cyclo-hepta sulfur and cyclo-deca sulfur are thermodynamically stable in the gas phase and have been observed (27, 28), but these particles are very unstable under normal conditions and are not important for the discussion of the properties of solid allotropes.

## 2. Intermolecular Structure

The sulfur molecules exert only short-range London forces upon each other. Sulfur therefore forms covalent crystals which have a low lattice energy. Optimum energy in such a solid can be accomplished by different intermolecular arrangements: each atom can either have few but close neighbors, each giving a high individual interaction energy, or have a high number of neighbors at an intermediate distance, each giving rather a low interaction energy. This explains why each sulfur molecule type can exist in many fairly stable polymorphs. Cyclo-octa sulfur has, for example, about ten such polymorphs. It is surprising that, of the two well-known allotropes,  $S_{\epsilon}$ --which is built up from unstable cyclo-hexa sulfur--has a higher number of close neighboring atoms than  $S_{\alpha}$ , which consists of the stable  $S_{\lambda}$ . The first allotrope has, therefore, a higher density and a more stable lattice than the latter.

Table 3 shows the way in which the different allotropes can be deduced from stable forms.

### B. Stable Allotropes

Under standard conditions, sulfur is thermodynamically stable only in one form as  $S_{\alpha}$ . The  $S_{\alpha}$  crystal is built up from cyclo-octa sulfur ( $S_{\lambda}$ ) molecules. Between 95.3°C and the melting point,  $S_{\beta}$  is stable. There are indications that other enantiotropic forms might exist (311), but no other stable allotrope has yet been observed. This review offers only a restricted discussion of stable allotropes, since their properties are well summarized in references 138, 168, and 215.

Table 3. Preparation of Allotropes.

The stable allotropes ( $S_\lambda$ ,  $S_\alpha$ ,  $S_\beta$ ) are formed from all other forms within a time varying from  $\approx 0.001$  sec to 1 year (See Sec.II). The unstable allotropes are here listed corresponding to their preparation method.

Section	Starting Material	Main Components	Unstable Allotropes	Stable Form (STP)
IV. C.1	Solid $S_\alpha$	Cyclo-octa-S ( $S_\lambda$ )	(a) Metallic-S (b) Irradiation-S (c) Orange-S	} In solution, $\lambda$ In lattice, $\alpha$
IV. C.2	$S_\lambda$ -solution	Cyclo-octa-S ( $S_\lambda$ )	(a) Photo-S, (b) $\gamma$ , (c) $\zeta$ , (d) $\eta$ , (e) $\delta$ , (f) $\nu$ , (g) $\phi$ , (h) $\xi$ , (i) $\tau$ , (k) $\chi$ (l) $\phi$ (m) $\psi$	
IV. C.3	Liquid sulfur	Cyclo-octa-S ( $S_\lambda$ ) Catena-octa-S ( $S_\pi$ ) Catena-poly-S ( $S_\mu$ )	(a) $\pi$ , (b) $\iota$ , (c) $\mu$ , (d) $\nu$ , (e) $\phi$ , (f) $\psi$	
IV. C.4	Sulfur vapor	$S_x$ : $1 < x < 10$	(a) $\omega$ , (b) m, (c) Yellow, (d) Black, (e) Purple, (f) Red, (g) Green, (h) Violet	
IV. C.5	Compounds	Sulfides and sulfoxy-acids as intermediates	(a) $\rho$ , (b) $\epsilon$ , (c) red, (d) $\nu$ , (e) $\omega$	
IV. C.6	Vapor and solvent		(a) Blue, (b) Maroon	

## 1. The $S_\lambda$ Molecule

The term  $S_\lambda$  was introduced by Berthelot (31), and it is the short name for the free cyclo-octa sulfur molecule. The structure of this particle has been discussed above.

The  $S_\lambda$  molecule is the lattice unit in the polymorphs of  $S_\alpha$ . It is also stable in solution and occurs in the melt and the frozen liquid. Kuester (178) discovered that  $S_\lambda$ , at higher temperature, is in equilibrium with  $S_\mu$ . It was later demonstrated that  $S_\pi$  is formed as an intermediate in this reaction. The equilibrium  $\lambda \rightleftharpoons \pi$  is photosensitive (316, 317) and favors at higher temperature  $S_\pi$ , which is a biradical and is the rate-determining particle in free-radical reactions of  $S_\lambda$ . The value for the homolytic ring scission is probably around 30 kcal/mol. (See Table 6b). In liquid sulfur the enthalpy of the overall reaction is 7 kcal/mol, but this includes secondary reactions, such as the solvation of  $S_\pi$  in  $S_\lambda$ . In the dark and at standard temperature, the  $S_\lambda$  ring can be broken by nucleophilic attack. As little as 0.004%  $H_2S$  or 0.002%  $SO_2$  catalyzes such reactions of  $S_\lambda$  with, for example, triphenylphosphine (21). If solutions are cooled or evaporated,  $S_\lambda$  crystallizes as the stable  $S_\alpha$  form or as one of its many unstable polymorphs. The ultraviolet (UV) (17-22, 54), infrared (IR)(16), and Raman (130) spectra of  $S_\lambda$  have only been partly analyzed, and the normal coordinate analysis is not yet complete (265, 266).

## 2. The $S_\alpha$ Modification

Since  $S_\alpha$  is the only stable sulfur modification at STP, all other allotropes convert ultimately into it. Broensted (46) discovered that the  $\alpha$  crystals contain  $S_8(S_\lambda)$  molecules (211). Burwell (49) determined the crystal structure (303, 305), which has since been restudied carefully (3, 5, 60, 298). The symmetry of the crystal is  $D_{2h}^{24}$ -Fddd, the symmetry of the

molecule is  $D_{4d}$  and the environmental symmetry is  $C_2-2$ . One hundred and twenty eight atoms form the unit cell. The lattice constants (210) are, after recent measurement (58) given with six significant figures:

$$a = 10.44349 \text{ \AA}$$

$$b = 12.84009 \text{ \AA} \quad a : b : c = 0.81335 : 1 : 1.9032$$

$$c = 24.43665 \text{ \AA}$$

The  $\alpha$  crystals often grow along unusual surfaces; for example, along an axis which is parallel to the  $\{101\}$  face diagonal (92, 93). Therefore microscopic observations of the crystal growth in solutions (see IV. C2) often lead to the discovery of different looking crystals, which have been frequently mistaken for other modifications, for example  $S_\gamma$ .

The melting point of  $S_\alpha$  is  $112.8^\circ\text{C}$ , but above  $95.31^\circ\text{C}$  (311) the stable modification is  $S_\beta$ . The transformation of  $\beta$  into  $\alpha$  has been studied by many authors (106, 150, 311) who reported contradictory results (65). It seems that the equilibrium with an enthalpy  $\Delta H_{368^\circ\text{K}} = 401.7 \text{ j/g}$ , is established slowly, sometimes only after a period of several weeks. In one case (65), the equilibrium was studied on crystals packed in celluloid films which were observed for many months. Many other properties of  $S_\alpha$  have been studied; among these are self-diffusion and the UV(23), IR (29, 30, 193), and Raman (130) spectra.

### 3. The $S_\beta$ Modification

The  $S_\beta$  crystal was discovered by Mitscherlich (201), and has since been studied often (165, 255); however, there is still a mysterious lack of information about this allotrope (211) which is stable in between  $95.31^\circ\text{C}$  and the melting point. It is found in nature and it is formed whenever sulfur solutions or liquid sulfur crystallize within this temperatures range. The "ideal" melting point of  $S_\beta$  is  $119.3^\circ\text{C}$  [compare Dufraisse et al. (87)  $122.0 \pm 0.5^\circ\text{C}$ ].

The liquid sulfur, however, disproportionates partly into  $S_{\pi}$ , which forms a self solution of sulfur in  $S_{\lambda}$ , and this leads to a melting point depression which causes the "natural" (131) melting point of  $S_{\beta}$  to be 114.6°C. The step-wise disentangling of this curious behavior of the melt will be discussed together with  $S_{\pi}$ .

Big crystals of  $S_{\beta}$  can be easily grown from boiling organic solvents (318). The symmetry of  $S_{\beta}$  was determined by Burwell (49):  $C_{2h}^5 - P2_1/a$ . Forty-eight atoms (6  $S_{\lambda}$  molecules)(211) seem to form a unit cell (220) with  $a : b : c \approx 0.995 : 1 : 0.999$ , but the details of the structure are not resolved. The X-ray data (304) is not yet conclusive, but it indicates that the structure of  $S_{\alpha}$  and  $S_{\beta}$  are closely related, and that the  $S_{\lambda}$  molecules might rotate in  $S_{\beta}$  and that they might be centrosymmetrically stacked. The density of  $S_{\beta}$  is between 1.96 and 1.93 gr/cm<sup>3</sup>, which indicates a looser packing of  $S_{\lambda}$  molecules than in  $S_{\alpha}$ .

### C. Unstable Allotropes

Some of the most important parameters needed for describing a sulfur system are the temperature of the sulfur source ( $T_{start}$ ), the formation mechanism, the preparation speed ( $dc/dt$ ), the observation conditions ( $T_{end}$ ), and the age of the sample. If not indicated otherwise, the observation conditions given in the following will be standard temperature and pressure. (STP)

#### 1. From $S_{\alpha}$ Without Solvent

New allotropes can be formed from  $S_{\alpha}$  by two processes: (a) by intramolecular rearrangement involving ring scission and leading to a lattice breakdown; and (b) by intermolecular rearrangement alone, with preservation of the  $S_{\lambda}$  molecule as the lattice unit. Both processes can be catalyzed by impurities.

(a) Metallic sulfur: Many authors hoped to prepare new allotropes by applying pressures of up to 100,000 atm., but no new properties or new

forms could be observed (43). Dynamic pressures (68, 147) of up to 230,000 atm have been applied to  $S_{\alpha}$  samples and a low electric resistance was observed. A metallic form was proposed as being responsible for this observation. It is however, still doubtful whether such a form really exists, and what the structure and properties of such a form should be. It has recently been indicated (25) that sulfur melts along the shock front and that the low conductivity could be caused by impurities.

(b) Irradiation Sulfur:  $\alpha$ ,  $\beta$ ,  $\gamma$  radiation (77, 141) and ultraviolet light (76) can break the S-S bond. Thus, the cyclo-octa molecules ( $S_{\lambda}$ ) are cut into catena-octa-sulfur ( $S_{\pi}$ ) or into smaller fragments. At STP, the recombination rate of all these unstable particles into  $S_{\omega}$  is so high that only a few free radicals can be accumulated, their concentration being roughly proportional to the intensity of irradiation. Because of this statistical chain scission and recombination equilibrium, all unstable allotropes reconvert under irradiation quickly into  $S_{\lambda}$  which then crystallizes as  $S_{\alpha}$ . Amounts of 75 mC of  $\beta$  radiation can consume small  $S_{\mu}$  samples within an hour (204). At  $-29^{\circ}\text{C}$  and below  $S_{\mu}$  (catena-poly-sulfur) is metastable (202). At these temperatures, small chains formed through irradiation can recombine to a mixture of  $S_{\lambda}$  and  $S_{\mu}$ , and at lower temperature, other smaller particles become metastable. Very few experiments have so far been performed with enough irradiation (72, 304) to produce substantial amounts of such unstable components. If  $S_{\alpha}$  is exposed to 40MR of  $\gamma$  radiation it turns red (246). Preliminary results on the electric conductivity (304) and the ESR Spectra (53) are now available. Several authors (17) use the name irradiation-sulfur as a synonym for photo-sulfur.

(c) Orange Sulfur: If rhombic or plastic sulfur is mixed with alumina and heated in the dark under vacuum (28) an orange product is formed which

is stable for about one day. The mass spectrum of this form is very different from that of other allotropes, but the X-ray pattern shows only lines belonging to  $S_\alpha$  and alumina. It seems that alumina is, therefore, an efficient catalyst for the conversion of sulfur allotropes in the solid as well as in solution (20).

## 2. From $S_\lambda$ in Solution

Sulfur is soluble in many organic solvents. At STP a stable solution contains cyclo-octa-S ( $S_\lambda$ ). Both an increase in concentration (adding or forming more sulfur) and a reduction of the solubility (changing of the temperature) bring about the crystallization of allotropes, all of which contain  $S_\lambda$  molecules. In a rough way, we can describe the conditions for the formation for different solids by comparing the precipitation rate ( $\{\dot{S}\}$ ) with the rate of the lattice growth of  $S_\alpha$  ( $\{\dot{S}_\alpha\}$ ). We shall discuss here three conditions. First, whenever we have  $\{\dot{S}\} \leq \{\dot{S}_\alpha\}$  the a modification is expected to crystallize. The higher the difference is between the two gradients, the bigger is the resulting alpha crystal. Second, in the extreme case, when we have  $\{\dot{S}\} \gg \{\dot{S}_\alpha\}$ , no crystals form, and the sulfur precipitates in amorphous form. Third, if we have  $\{\dot{S}\} \geq \{\dot{S}_\alpha\}$ , crystals nucleate in many places and in a variety of structures wherever some kind of lattice energy can be gained. Therefore, the crystal growth is irregular, and does not discriminate against unstable symmetries such as  $S_\gamma$  for example. All methods for the preparation of unstable crystalline allotropes are aimed at realizing case three. The change in  $[\dot{S}]$  and  $[\dot{S}_\alpha]$  is generally brought about by changing concentrations, mixing solutions, or varying the temperature. Since the concentration changes during the crystallization, many different allotropes are formed simultaneously. The systems in which unstable allotropes are prepared are, therefore, highly unequilibrated and it is not astonishing that the

preparation process is hard to duplicate or unreproducible. Often, rubber or solutions of other highly viscous materials are mixed with the solution containing the allotrope to increase the viscosity. This trick reduces the diffusion, makes locally high concentration gradients possible, and stimulates energy gains through the formation of unstable lattices in isolated pockets.

The lifetime of the unstable crystals can be quite high in such solutions but they eventually dissolve in favor of the growth of neighbor nuclei with higher stability, and finally convert into  $S_a$ . Many studies of crystallization in sulfur solutions have been made under a microscope (48, 156, 169, 90-99, 170, 171, 163). A great number of allotropes have been reported but generally, only their crystal shape, their behavior toward polarized light, their relative refractive index, and their relative stability can be measured. It has been repeatedly pointed out that often not enough information is available to ascertain the existence of new allotropes, and that many "new" forms might only be  $S_a$  crystallized along an unusual lattice face (92, 93, 237). The following stability order (138) for some polymorphs of  $S_a$  has been given:

$$\alpha > \beta > \gamma > \zeta > \eta > \xi > \delta > \theta > \tau > \kappa \text{ (see Table 4).}$$

(a) Photo-Sulfur. Lallemand (179) discovered that sulfur solutions become cloudy if they are exposed to light. Such suspensions (87, 241) of insoluble sulfur in a sulfur solution are called photosulfur. Wigand (316, 317) made an extensive study of the photosensitivity of allotropic forms and determined thermal data with a calorimeter, but his results have been overlooked and most work since does not take into account the important influence of light on systems containing sulfur. The composition and structure of photo-sulfur is not known (17, 22), but it was found that it is more reactive than  $S_\lambda$  and that it is probably a mixture. Recently studies of the influence of light on the formation of different allotropes indicate that the  $S_8$  ring breaks under



Table 4. Polymorphs of the Various Sulfur Molecules.

Molecule	Polymorphs
Cyclo-octa-sulfur ( $\lambda$ )	a, $\beta$ , $\gamma$ , $\delta$ , $\zeta$ , $\eta$ , $\lambda$ , $\rho$ , $\sigma$ , $\tau$ , $\kappa$
Catena-octa-sulfur ( $\pi$ )	None
Cyclo-hexa-sulfur ( $\rho$ )	$S_{\epsilon}$
Catena-poly-sulfur ( $\mu$ )	Amorphous: $\mu$ , $\gamma$ , $\phi$ , $\psi$ , $\omega$ , n. Threads: m, v
Mixture, multicomponent forms	$\phi$ , $\mu$ , black, green, red, purple, photo, in, Brauns, red. <sup>a</sup>

<sup>a</sup>Polymorphs in a free sense: they contain the same molecular species in a similar concentration.

the influence of light (76, 94, 95). The resulting biradical then attacks other rings and initiates other secondary reactions, in which the solvent is frequently involved. For the formation of photo-sulfur,  $S_\lambda$  in  $CCl_4$  is exposed to sunlight (110), or better, to the light of an uv lamp, such as a mercury pressure arc. Many authors report that the formation of photo sulfur is reversible, but alcoholic photo sulfur, for example, smells from hydrogen sulfide. The photochemistry of sulfur is a neglected field and very little is yet known about the effect of light on solutions and on allotropes. It seems that the catalytic action of hydrogen sulfide (21) and other secondary molecules is responsible for many reactions of photo sulfur. A report on the x-ray pattern (95) purports that the structure is similar to that of  $S_\omega$ .

(b)  $\gamma$ -Sulfur. This allotropes was discovered by Spica (286) and Gernez (134-136). These brilliantly glittering crystals (251), which grow in thin sheets (254), are also called mother-of-pearl and nacreus sulfur. The crystal symmetry is probably  $C_{2h}^4$ , with the eight cyclo-octa molecules stacked in a "sheared penny roll" (145) formation; however, details are not yet known. The lattice constants are reported as (82,145,210,291):

$$\begin{array}{l} a = 8.57 \text{ (275)} \\ a: b: c = 0.658 : 1 : 0.632 \quad b = 13.02 \\ c = 8.23 \end{array}$$

Older data (145, 146) seem incorrect. The melting point of this allotrope is  $106.8^\circ\text{C}$ , the density is  $2.041 \text{ g/cm}^3$ . This modification is unstable under normal conditions, but the crystals can exist for years if inbedded in a rubber solution, and they can withstand 40 hours of x-ray examination. The  $\alpha$  crystals catalyze their transformation and can reduce the lifetime of the  $\gamma$ -form to  $1/2$  min (152). Above  $75^\circ\text{C}$ ,  $\beta$ -sulfur is formed quickly. The transformation rate has been studied, and the possibility of enantiotropic transformation  $\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$  has been pointed out (149-154).

According to several reports,  $\gamma$ -crystals have been found in oil wells (290) and as Rosickyit mineral (267).  $\gamma$ -sulfur was proposed as a component in plastic sulfur. The  $\gamma$ -allotrope can be prepared through condensation of vapor, from an undercooled melt at  $90^{\circ}\text{C}$  (314), from an undercooled solution of sulfur in benzene, toluene or ethylalcohol, by evaporating an alcoholic solution of sulfur at  $70^{\circ}\text{C}$  (206, 214), and spontaneously from  $\alpha$ -sulfur. Also,  $\gamma$ -sulfur can be obtained during the production of the element from compounds if saturated solutions of potassium sulfate and sodium thiosulfate are carefully combined and diffuse slowly into each other, if ammonium polysulfide in an alcoholic solution is oxidized slowly in air, and if precipitated sulfur is dissolved in a mixture of alcohol, and if carbon disulfide is slowly evaporated at room temperature.

(c)  $\zeta$ -sulfur. Korinth (169-171) found reddish-brown monoclinic (?) crystals of  $\zeta$ -sulfur that are stable for about half a day. The  $\zeta$ -sulfur is less stable than  $\gamma$ , but more stable than  $S_8$ . The  $S_8$  allotrope crystallizes together with  $S_8$  and spontaneously forms  $S_8$ . It is formed in the presence of selenium from carbon disulfide and chloroform solutions, preferably in a mixture with a rubber solution. This form is very similar to a crystals growing along unusual faces (93, 94). The existence of this form has not yet been conclusively shown, and the crystals could be due to an impurity.

(d)  $\eta$  sulfur. Korinth (169) observed monoclinic (?) crystals of  $S_\eta$  during the preparation of  $\delta$  sulfur from rubber solutions containing sulfur and selenium. The experiments have been reproduced. This form has a lifetime of 10 minutes (91). It is an isomorph of Se. The data on this modification are inconclusive. Both an impurity and a coprecipitation of selenium and sulfur could be responsible for the formation of such crystals.

(e)  $\delta$  sulfur. Muthmann (206) listed  $S_\delta$  as the fourth sulfur allotrope (171). The crystals have been studied frequently (99, 156, 278, 290), but this form is very unstable and has not yet been conclusively described. It could be identical with one component of "Brauns" sulfur.

The symmetry of this form is either  $C_{3i}$  or  $C_{3i}^2$ . The crystals can be prepared in mixture with  $S_\alpha$  and  $S_\gamma$  by oxidizing an alcoholic ammonium polysulfide solution at  $\leq 15^\circ\text{C}$  in the open air. This preparation is similar to the preparation of the  $\gamma$ -form, and only about 1 in 1000 experiments leads to the formation of  $\delta$ .

The crystals can transform into  $\gamma$ ,  $\zeta$ ,  $\beta$ , or  $\alpha$  sulfur.

(f)  $S_\gamma$ .  $S_\gamma$  was first observed by Korinth (169). This allotrope was recently restudied (92). It crystallizes together with  $S_\gamma$  from a not too concentrated boiling solution of fenchonon,  $\alpha$ -pinene, and nitrobenzene; its preparation is somewhat haphazard. The yield is enhanced by the presence of a solution of rubber in carbon disulfide. The ditetragonal bipyramids (169) have a ratio  $a:b = 1 : 0.468$ . The crystals are unstable and dissolve after less than one minute; then,  $S_\gamma$ ,  $S_\beta$ , and finally  $S_\alpha$  are formed.

(g)  $S_\theta$ . Erämetsa (93) observed the formation of a new crystal when solutions of  $S_\delta$  were evaporated. This form is characterized by an extremely low refractive index. It converts within seconds into  $S_\gamma$ , and is the most unstable polymorph known.

(h)  $S_\xi$ . Korinth (169) described monoclinic spirals, which he called  $S_\xi$ . This form is either extremely unstable or does not exist. It might be identical with triclinic sulfur.

(i)  $S_\tau$ .  $S_\tau$  crystallizes in about 1 out of 1000 experiments if sulfur solutions of orthoxylol or menthenon are boiled. This form consists of cubic crystals which can exist for several hours (97).

(j) Brauns Sulfur (41). Gernez (133) and Quincke (240) identified this form as a mixture of  $S_\alpha$  and  $S_\phi$ .

(k)  $S_{\kappa}$ . Henkel (169) discovered this fairly stable monoclinic allotrope. The best yield is reported when a sulfur solution of orthoxylol at the boiling point is saturated (91). The crystals have such a high refraction index that they appear to be black in transmission and white in reflection. This allotrope is more stable than  $S_\gamma$ . The report that  $S_{\kappa}$  occurs in trapped liquid sulfur (125, 236), has been corrected. The name was used for a mixture of  $\alpha + \gamma$ .

(l)  $S_\phi$ . This name was recently used for a new allotrope which is similar to  $S_\delta$  (92), but much more stable. It has been prepared from  $\alpha$ -pinene solutions at a temperature of  $8^\circ\text{C}$  and has an unusually low refractive index.

(m)  $S_\psi$ . A crystal precipitated from an  $\alpha$ -pinene solution has been called  $S_\psi$  (92). Its refractive index is lower than that of the solution. Both  $S_\phi$  and  $S_\psi$  are difficult to prepare and it is not clear whether they represent new allotropes.

### 3. From Liquid Sulfur

The composition of liquid sulfur is complicated. We do not intend to present here a complete survey, but give only the data necessary for the understanding of the solid. References for the liquid phase are listed in the Appendix (see also references 164, 232, 234, 257, and 258). At the melting point, cyclo-octa sulfur is in equilibrium with catena-octa-sulfur  $S_\pi$ , which then polymerizes with  $S_\lambda$  into unbranched chains ( $S_\mu$ ). At  $159^\circ\text{C}$  (273) the polymerization increases so sharply that  $S_\mu$ , which had been a solvate, suddenly becomes the solvent. Most properties of the melt have a strong discontinuity at this temperature. Only the color (122, 181) does not follow this trend but instead changes smoothly from a pale yellow at the melting point to a dark, deep red (164) at the boiling point. The molecular variety of liquid

sulfur has been repeatedly discussed (277), and the viscosity (12, 13, 103, 104), the specific heat (38, 108, 184, 313), and the heat conductivity and density (165, 309) have been measured. Several authors (101, 229) have explained the polymerization process, which was recently formulated in a very simple and precise manner (88, 159, 160, 295, 296). The heat of polymerization for  $S_{\pi}$  is 3.17 kcal ( $\Delta S^{\circ} = 4.63$  eu) and the energy required for the chain scission (160, 161) is 32.8 kcal. ( $\Delta S^{\circ} = 23$  eu)(296). The free radical nature of long, open sulfur chains was pointed out (200), and later confirmed with the help of ESR (124, 126) equipment and a Faraday balance (226). Table 5 gives a comparison of ESR data for several allotropes. The average chain length varies between 158°C and 404°C from 8 to  $5 \times 10^5$  atoms. Statistical and other arguments make (101) the occurrence of macro-rings (175, 187) in the melt improbable. The properties of the melt are extremely sensitive to impurities. The viscosity, for example, is changed by very small amounts of trivalent elements and by the electric conductivity, which is the sum of two terms, these being the electronic conductivity of the liquid element and the electrophoretic conductivity caused by (sulfide) impurities.

The structure of the liquid has been studied by several investigators (137, 175, 232, 234, 260, 293). The bond length in the chains between the sulfur atoms seems to be slightly smaller (2.07 Å) than in solid samples. At low temperatures, the melt possibly shows some structure similar to  $S_{\gamma}$ . More data are necessary, however, before we have a conclusive picture of the composition of liquid sulfur. It seems, for example, that a fourth component has to be assumed to explain the color effect.

Table 6 contains some recent thermal data for the melt and other allotropes.

Table 5. Survey of ESR Studies

Material Studied	g-value	Band-width (G)	Spin concentration per mol	Ref.
Liquid	2.024±0.002	40-60	10 <sup>-3</sup> at 300°C (increased by 2.10 <sup>2</sup> from 190 to 375°C)	(124-126)
Plastic	2.0044	9.5	10 <sup>-5</sup>	(221)
S on Al <sub>2</sub> O <sub>3</sub>	≈2.0 ≈4			(28)
Green	2.010±0.002	8.8 at 78°K 2.2 at -78°C	5.10 <sup>-2</sup> (six components)	(51, 52)
Blue	2.025 four com- ponents			(53)
Purple	2.020	8.8	-	(245)
Black or dirt (see 256)	2.010	7	-	(124-126)
Free electron	2.0023			

Table 6. Thermal Data.

a. Specific Heat				
T = 298.16°K	$C_p^0$ (cal/deg-g-at)	$S^0$ (cal/deg-g-at)	$\Delta H^0$ F(kcal/g-at)	Reference
$\alpha$ (s)	5.4 <sup>a</sup>	7.62		(311)
$\beta$ (s)	5.65 <sup>b</sup>	7.78	0.009	(311)
$S_{at}$ (g)	5.66	40.1	53.11	(180)
$S_2$ (g)	7.76	54.5	30.85±0.15	(180)
$S_\lambda$ (g)	37.16	102.7	24.35	(180)

<sup>a</sup> 35-95°C:  $5.2688 + 0.006121T - 8.164 \times 10^{-6} T^2$  (Ref. 311).

<sup>b</sup> 101-115°C:  $5.2630 + 0.006857T + 0.08039/(115.176 - T^2)$  (Ref. 311).

Note:  $C_p$  decreases from 95-101°C (Ref. 311).



Table 6 (continued).

b. Transitions				
Transitions	T(°K)	$\Delta H$	$\Delta S$ (cal/g-at-deg)	Reference
$\alpha, \beta$	368.46±0.01	0.096 kcal/g-at <sup>a</sup>	0.261±0.002	(311)
$\beta, ?$	374.2	0.000383 kcal/g-at	7.93	
$\alpha$ -subl, $\lambda$	368.5	3.01 kcal/g-at	8.17	(34)
$\beta$ -subl, $\lambda$	368.5	2.92 kcal/g-at	7.93	
$\epsilon, \rho$	300	4.02 kcal/g-at	8.38	(30)
Fusion $\alpha, \lambda$	383	0.507 kcal/g-at		
Fusion $\beta, \lambda$	388.33	0.410, 5 kcal/g-at	0.75	(311)
$\lambda, \pi$	432	4.1 <sup>b</sup> kcal/g-at	2.88	(295, 296)
Polymer. $\lambda, \mu$	442.8	0.396 <sup>c</sup> kcal/g-at	0.58	(295, 296)
Vap. $\lambda, \lambda$	444.6000°C	2.5 kcal/g-at	3.5	
7/8 S $\lambda, S_7$	400°K	5.7 kcal/mol		(27)
3/4 S $\lambda, S_6$	400	6.2 kcal/mol		(27)
5/8 S $\lambda, S_5$	400	14.3 kcal/mol		(27)
1/2 S $\lambda, S_4$	400	20.5 kcal/mol		(27)
3/8 S $\lambda, S_3$	400	22.5 kcal/mol		(27)
1/4 S $\lambda, S_2$	400	23.5 kcal/mol		(27)

<sup>a</sup> 1 g-at S = 32.066 g

<sup>b</sup>  $K = (\pi)/(\lambda) = 1.137 \times 10^5 \exp(-16520/T)$

<sup>c</sup>  $K_3 = (\pi)/(\pi\lambda) = 10.43 \exp(-1596/T)$   
 $D_0(S_2) \approx 4.4 \text{ eV (27, 42)}$

This selection of recent values differs considerably from older selections (ref. 215, p. 852).

Table 6 (continued).

(c) Triple points (215)

(1) $\alpha$ , $\beta$ , vapor	95.31°C(311)	0.00376 mm Hg
(2) $\alpha$ , liquid, vapor	112.8	0.013 mm Hg
(3) $\beta$ , liquid, vapor	119.3	0.018 mm Hg
(4) $\alpha$ , $\beta$ , liquid	$\approx 152^\circ$	$\approx 1400$ atm

(d) Melting points (138, 215) $\alpha = 112.8^\circ\text{C}$  (ideal) $\beta = 119$  (natural mp) $= 114$  (ideal mp) $\gamma = 106.8$  $\epsilon \approx 100^\circ$ 

m: 330 sublimation (?)

Boiling point STP: 444.6000 °C(186)

(e) Bond strength ( $D_0$ ,  $S_2 = 102.4$  kcal)

		<u>Reference</u>
$\text{H}_2\text{S}$ up to $\text{H}_2\text{S}_6$	63.2 X n kcal	(107, 189, 231)
$\text{S}_2\text{Cl}_2$	64.4 kcal	(217)
$\text{S}_8$	64 kcal	(215)

(f) S-S stretch frequency

	<u>Reference</u>
440 to 550 $\text{cm}^{-1}$	(187)
680 $\text{cm}^{-1}$	(207)

From liquid sulfur, different solid allotropes can be formed with varying yields, depending upon the original temperature ( $T_S$ ), the speed of the cooling ( $dT/dt$ ), and the observation conditions ( $T_E$ ), but the solid always contains three fractions: (a) a crystalline part which consists of  $S_a$  or its polymorphs, (b) an active species which will be called  $S_\pi$ , and (c) a  $CS_2$ -insoluble polymer. The composition of this polymer is complicated and depends upon the preparation method, but many authors treat this solid or some fraction of it as a definable system. So little data are given for this fraction, generally, that one cannot compare results reported by different groups. Regardless of the nomenclature used in the original paper, we will choose the name  $S_\mu$  for this plastic  $CS_2$ -insoluble polymer, which is obtained if viscous liquid sulfur is quenched. The rigid  $CS_2$ -insoluble polymer, which is prepared by condensing sulfur vapor, will be called  $S_\omega$ .

In discussing the products, we distinguish between samples obtained by one of three different methods. First, slow cooling leads to pure  $\beta$  and  $\alpha$  sulfur, regardless of the temperature of the liquid. Second, if the hot liquid is poured into water,  $S_\pi$ ,  $S_\mu$ ,  $S_\lambda$ , and  $S_a$  are formed. The  $S_\pi$  converts within three days into  $S_a$  and  $S_\mu$ , but the  $S_\mu$  converts only slowly into  $\alpha$ , and its concentration, therefore, goes through a maximum after about three days (see  $S_\pi$ ). Third, if the liquid sulfur contains only  $S_\lambda$  and  $S_\pi$  (below  $158^\circ C$ ), the quenched sample crystallizes mainly to  $S_a$ , and  $S_\mu$  is formed only in a secondary reaction through the polymerization of  $S_\pi$ . Other particles might exist, but have not yet been observed in these solids; it is very hard to isolate small species, such as that which might cause the red color, because the heat capacity of the liquid is so high that even spraying of a thin stream onto a surface at  $20^\circ K$  does not give a high enough temperature gradient for trapping such particles. The trapping of highly reactive small molecules from the vapor

will be discussed in the next chapter. The following section deals with four allotropes prepared from the melt:  $S_\lambda$ ,  $S_\pi$ ,  $S_\mu$ , and  $S_\psi$ .

(a)  $S_\pi$ . Gernez (132) discovered that the melting point of sulfur changes during the melting process. The slow decrease (272) from the ideal melting point at  $119.3^\circ\text{C}$  to the natural melting point at  $114.5^\circ\text{C}$  has been explained by proposing the formation of a new unknown component which dissolves in the liquid and thus causes a melting point depression. Aten (7-10) called this particle  $S_\pi$  (24), a name which had been used before (191, 192) for a different allotrope. Above  $159^\circ\text{C}$  a third component (274), catena-poly-sulfur (177), becomes important. If liquid sulfur is quenched in cold water,  $S_\mu$  is always present regardless of whether the liquid was originally hotter or cooler than  $158^\circ\text{C}$ . This was first taken as a proof for  $S_\pi$  and  $S_\mu$  being identical. Molecular weight (39, 40, 228, 260, 261) calculations, however, using the melting point depression and the concentration of  $S_\mu$  in the solid, indicated that a much smaller particle had to be present in the liquid (24), which then on cooling could possibly polymerize into  $S_\mu$ . The  $S_\mu$  concentration (the  $\text{CS}_2$ -insoluble fraction in a frozen melt) first increases and goes through a maximum (258) after about three days. The  $S_\pi$ , with a lifetime of roughly one day, obviously partly polymerizes into  $S_\mu$ , which then converts into  $S_\alpha$  with a much higher lifetime, perhaps six months.

If liquid sulfur is quenched to  $-78^\circ\text{C}$  some of the  $S_\pi$  can be isolated. The  $S_\lambda$  is soluble in  $\text{CS}_2$  at room temperature but not at  $-78^\circ\text{C}$ ;  $S_\mu$  is  $\text{CS}_2$  insoluble, but  $S_\pi$  is soluble in  $\text{CS}_2$  at  $-78^\circ\text{C}$ . From the deep yellow  $S_\pi$  solution, Erämetsa (97) separated (with the help of chromatography) four components with different molecular weights. His results are, however, not quite conclusive, since it has been shown that the column material, alumina, catalyzes the conversion of allotropes. Schenk (262) could not repeat the separation of

the  $S_{\pi}$  fraction, but he used the method of Bartlett (17) to independently titrate different allotropes in a mixture; he discovered that the liquid content is 5.5%  $\pi$  at the mp (261), but that in the frozen melt only 60% of the  $S_{\pi}$  molecules polymerized, while the other 40% recombined directly to  $S_{\lambda}$ . Using this observation to recalculate the molecular weight of  $S_{\pi}$ , he came to the conclusion that this molecule is catena-octa sulfur.

In this review the name  $S_{\pi}$  is adopted for the catena-octa sulfur, in contrast to earlier authors who used this name for a product obtained by several preparation methods (230). There remain, however, several unexplained facts about this particle. A model that accurately describes the viscosity of the melt over the whole temperature range assumes that  $S_{\pi}$  is very unstable and polymerizes with  $S_{\lambda}$  to polymer chains (295). The  $S_{\pi}$  concentration is calculated at the melting point to be undetectably small; but Schenk (261, 262) obtains 5.5%  $S_{\pi}$  from measurements of the soluble part in the solid and the melting point depression. ESR measurements (126) indicate a very low free spin concentration at the temperature mentioned above, but this can be interpreted either as an indication that there is only very little  $S_{\pi}$ , or that the  $S_{\pi}$  has strong resonance stabilization of the chain. Such a resonance stabilization has been earlier assumed for small molecules (187).

(b)  $S_{\iota}$ . A fraction of  $S_{\pi}$  has been separated with the help of chromatography (97). Part of the dry  $S_{\pi_2}$  fraction turns into a white solid which is very similar to  $S_{\omega}$  but which supposedly has a different x-ray diffraction pattern. This form is not  $CS_2$  soluble and was called  $S_{\iota}$  (97).

(c)  $S_{\mu}$ . If liquid sulfur, a complex mixture of allotropes, is poured into ice water or cooled to  $-78^{\circ}C$ , an astonishingly homogeneous product is obtained (133). The reason for this is that most particles in liquid sulfur become so highly unstable when cooled that they convert immediately into the stable alpha form or the catena-poly form,  $S_{\mu}$ , which, under such conditions has a relatively high lifetime. The fading of the red color of the melt to a

white yellow in the solid demonstrates in a visible way this recombination of reactive particles. If a frozen melt is washed with  $\text{CS}_2$ , the stable alpha sulfur and the  $S_{\pi}$  dissolve and an insoluble part remains (73, 148). Both the viscous liquid sulfur and the carbon disulfide-insoluble solid (125, 178) are called  $S_{\mu}$ . The yield and the structure of  $S_{\mu}$  depend upon the composition of the liquid ( $T_{\text{start}}$ ), the speed with which the quenching is performed ( $\frac{dT}{dt}$ ), the temperature at which the material is collected ( $T_{\text{end}}$ ), the age of the unstable modification and the purity of the sulfur. Experiments are quite commonly performed with insufficiently defined liquid sulfur systems. Many authors, overwhelmed by the importance of one parameter, neglect others. One author for example can obtain plastic sulfur only from commercial samples, pure samples giving exclusively  $S_{\alpha}$  (256) while in another group pure sulfur always leads to 100%  $S_{\mu}$ , with crude samples giving up to 60% of it.

The  $S_{\mu}$  can also be prepared by slowly hydrolyzing disulfur dichloride, or by acidifying an aqueous thiosulfate solution. The mechanism of both reactions is discussed together with the formation of  $S_{\rho}$ . The  $S_{\mu}$  is unstable at room temperature. The transformation rate into  $S_{\alpha}$  depends upon the temperature, pressure, or stretching, and impurities. Light (61) and the presence of  $S_{\alpha}$  are believed to catalyze the conversion into the stable form. The presence of 0.04% oil, or 0.1% iodine and trivalent contaminations such as nitrogen or phosphorous can stabilize (289) plastic sulfur over a long period of time. Pure samples have been reported to be metastable below  $-29^{\circ}\text{C}$  (202) and can exist at room temperature for over a year. The exposure to ultraviolet light or to alpha, beta, or gamma radiation enhances the transformation by breaking long chains (204). The samples do not convert completely into the alpha form, but reach an equilibrium composition, where the scission and formation of chains and rings are in balance (see irradiation sulfur).

The x-ray diagram (293, 297, 298) of  $S_{\mu}$  looks very similar to that of  $S_{\alpha}$ . Alpha impurities have therefore been held responsible for the observed patterns, since the x-ray method does not strongly discriminate against different components or contaminations. Another interpretation proposes a similar structure for  $S_{\alpha}$  and  $S_{\mu}$ , but seems to be wrong (223) (see  $S_{\psi}$ ). Some authors believe that  $S_{\mu}$  is amorphous, some think it is a glass, and others report that it has a well-developed structure. It is possible that the chains are so long that crystalline and amorphous zones can exist at the same time in different parts of one molecule, as is observed in organic polymers. Most probably the chains are curled and form long helices. The molecules seem to be held together by statistical cohesion. This cohesion energy is often quite big for polymers and can explain the relative stability of the  $S_{\mu}$  form. The structure of  $S_{\mu}$  is not yet completely known, but it is possibly similar to the structure of stretched sulfur, which will be discussed with  $S_{\psi}$ .

Detailed discussions about  $S_{\mu}$  have been published (99, 218, 259, 273-277, 283-285). The terms  $\mu_1$  and  $\mu_2$  have been proposed for the soft and the hard fractions of plastic sulfur, and many other names are in use for various plastic products, but this does not help much in identifying the components of the mixture.

(d)  $S_{\nu}$  is a shorthand name for  $S_{\mu}$  (96-98).

(e)  $S_{\phi}$ . Von Weimann (309) discovered that plastic sulfur samples obtained by chilling liquid sulfur from above 250°C assume new properties if they are stretched. This material was studied by several groups (67, 199, 298, 235) with the help of x-rays. Neuberger (210) found the symmetry to be  $C_{2h}^2$ . Pauling (217) proposed a helical structure, similar to that of selenium, with 112 atoms in the unit cell. Prins and co-workers (232-237, 258) have devoted many investigations to this form. They found that it consists of two different components, namely  $S_{\psi}$  and  $S_{\gamma}$ . This discovery devaluated much of the earlier

work (199, 298). The present description (237) is based upon long sulfur helices that are packed together regularly with crystals of  $S_\gamma$ , which seems to be formed during the stretching. The c-axis of the gamma crystals is assumed to be parallel to the fiber. The  $S_\phi$  can be stored for several years.

(f)  $S_\psi$ . The name  $S_\psi$  is used for three different sulfur forms. Here it is mentioned only that  $S_\psi$  is often taken as a synonym for  $S_\phi$ , but that Neumann (211) introduced the term  $S_\psi$  for the crystalline part of  $S_\phi$ .

Prins and coworkers (236) designate with  $S_\psi$  the fibrous part of  $S_\phi$ . This is the reverse of Neumann's terminology. The symmetry of the fiber is  $C_{2h}^2$ , the same as that of  $S_\phi$ . A closed packed helical structure with a concentric arrangement has been proposed (219, 222, 223), analogous to an alpha sulfur structure. This proposal, however, is not convincing since the alpha structure mentioned is incorrect. The best present model (83, 235-238, 249, 250, 257, 258) assumes long helices containing  $3\frac{1}{3}$  atoms per turn. The unit cell then contains 10 atoms; a and b are 4.7 Å, and c is 13.7 Å. A possible superstructure giving the unit cell a length of 69 Å has recently been mentioned (237). Details of the  $S_\psi$  structure are not yet known.

#### 4. From the Vapor Phase

At the natural boiling point, sulfur vapor consists mainly of  $S_8$ , but the concentration of smaller particles increases rapidly with increasing temperature and decreasing pressure. Mass spectroscopic data (27, 28) indicates the presence of at least 10 different molecular species in the vapor. Staudinger (288) recognized the possibility of trapping small molecules such as  $S_2$  from hot vapor, but Rice (242, 243) was the first to observe frozen unstable particles. The solids obtained by cooling equilibrium vapor have a very complex composition. The vapor phase generally contains several



different molecules in comparable concentrations. On condensation, these different species are partly trapped and partly recombine into new molecules which in turn can be intermediates in the formation of other more stable molecules. Such recombination reactions occur even under extreme trapping conditions, for example, if a molecular beam of hot material is slowly condensed on a wall which is kept at 4°K. The reason for this is partly the high reactivity of small molecules and partly the local warming which occurs during the heat dissipation from condensing molecules through the frozen solid. Rice observed green (242) solids when he condensed  $S_{\lambda}$  vapor, and a blue (243) glass when he trapped vapor with a high  $S_2$  concentration. Several workers have repeated these and similar experiments and obtained different deeply colored samples. Many of the observations are contradictory and irreproducible because of insufficient definition of the conditions during the preparation of these multicomponent systems. Some experiments (194-198) performed under well-defined conditions have led to the identification of  $S_2$  in the solid. The same molecules have been trapped and studied in different rare gas matrices, but very little data is yet available about these solids which can show absorption spectra with well-developed structure similar to the spectra of the free molecules in the gas phase. The relative yields of metastable or unstable radicals depends on the deposition speed  $\{S\}$ , the temperature of the cold wall ( $T_E$ ) and the vapor composition ( $T_S$ ). The concentration of unstable particles is roughly proportional to  $\frac{T_S}{T_E \cdot \{S\}}$ .

Despite their complicated composition, most colored forms have a sharply defined stability range which is listed in Table 7. These multicomponent solid self-solutions are metastable and monotropic, i. e., they do not convert into a less stable form by cooling.

The relative stability of such colored products obtained from molecular

Table 7. Stability Ranges of Defined Colored Allotropes (198).

Solvent	Sulfur concentration	Preparation temperature (°K)	Observed stability range (°K)	Color	Identified species
A		35	35		
Kr	≤ 0.3%	4- 45	4 < T < 45	Maroon	≥ 90% S <sub>2</sub>
Xe		50	50		
A, Kr, Xe or none	≥ 0.5%	45 - 60	4 < T < 60	Violet	S <sub>2</sub> + ?
A, Kr, Xe or none	≥ 1%	60 - 170	4 < T < 170	Green	S <sub>2</sub> + ?
None	100%	170-240(?)	4 < T < 240	Yellow	S <sub>μ</sub> + S <sub>π</sub> + ?

beams of  $S_2$  in decreasing order is: a > plastic > yellow > green > purple.

First  $S_\omega$  and  $S_m$  are discussed. They are obtained from the sublimation of sulfur under atmospheric pressure. Later on, the colored condensation products are described. They are obtained from the vapor under reduced pressure.

(a)  $S_\omega$ .  $S_\omega$  is here defined as the carbon disulfide insoluble part of sublimated sulfur. Because of its color,  $S_\omega$  is also called "white sulfur" (62). This modification is similar to the commercial form "crystex" and "super-sublimation" sulfur (224) and is not a well-defined allotropes. Its properties have been carefully studied and it was found that it is stable for more than a year at STP and for 36 hours at  $88^\circ\text{C}$  (63, 64, 67). Bases, such as  $\text{NH}_3$ , catalyze the conversion of this form into  $S_\alpha$  (259). The density lies in between  $1.834$  and  $1.95 \text{ g/cm}^3$ .

The x-ray data are fairly similar to those of  $S_\mu$  and  $S_\alpha$  (66, 99). This was explained by the presence of  $S_\alpha$  impurities on the crystal surface (65), but other authors think that  $S_\omega$  is a mixture of different forms, partly polymers, partly crystallites, or that  $S_\omega$  is identical with  $S_\mu$ , or that  $S_\omega$  is built up from  $S_6$ , of which three molecules form a unit cell (228).

Another structure with  $10^4$  oriented chains in a particle was proposed, but the evidence is not conclusive (224). More work is needed before a final answer can be expected, and it is so far not even clear whether  $S_\omega$  is a pure modification, or whether it contains components identical with  $S_\mu$ .

The  $S_\omega$  can be prepared by different methods, and each method leads to a somewhat different form and yield of this rather vaguely defined allotrope (111, 228, 236). The best yield of  $S_\omega$  is obtained if sulfur flowers are sublimed (33, 102). Other procedures include the hydrolysis of disulfur dichloride with water, the reaction of hydrogen sulfide with sulfur dioxide, and the reaction of

polysulfide with disulfur dichloride with water, and the reaction of polysulfide with disulfur dichloride.

(b)  $S_m$ .  $S_m$  was isolated from the distillation products of  $S_w$  or through chromatography of red sulfur (98). The  $S_m$  has so far been characterized only by its x-ray diagram (95). The lattice ratios are estimated to be  $a:b:c = 0.672 : 1 : 0.064$ . This allotrope is said to sublime under dry nitrogen.

(c) Yellow sulfur. If hot sulfur vapor is condensed under reduced pressure on a cold surface at  $\leq -78^\circ\text{C}$ , the solid is most probably a mixture and is deep yellow (194-196). It contains a high concentration of  $S_\pi$ . All low-temperature forms convert monotropically into this yellow form at  $-100^\circ\text{C}$ .

(d) Black sulfur. Black sulfur has been observed in condensed vapors (259) of  $S_2$ . It seems to be similar to violet sulfur. This name is also used for the black deposit which forms during the purification of elemental sulfur with the method of von Wartenberg. This black material has been described (271) as containing a pure sulfur allotrope which is very stable in the dark, but which converts after about one week in sunlight suddenly into  $S_a$ . The existence of such a form was already proposed by Magnus (191), but the presence of impurities aroused doubt about the existence of such a sulfur allotrope. It is possible that polysulfides are responsible for the black color, and such polysulfides could then decompose in sunlight and form elementary sulfur.

(e) Purple Sulfur.  $S_2$  vapor condenses on a liquid nitrogen cooled trap with a purple color (242, 244). The color was assigned to the  $S_2$  radical. Later re-examination (194-196) proved however, that the  $S_2$  concentration in violet and green deposits are similar and most likely do not cause the color, which seems rather to depend on the deposition speed. Slow condensation yields green sulfur, fast deposition leads to purple samples. This form has a high magnetic susceptibility (117).

(f) Red and Brown sulfur. Three different red forms are discussed in this review: irradiation sulfur, precipitation sulfur and condensation sulfur. The latter and brown sulfur were produced by several authors (162, 194) by the condensation of hot vapor on targets held well below room temperature. It seems that a condensation of different vapor species of elemental sulfur can lead to almost any color. Such solids represent complicated multicomponent systems. Very little is known about their components.

Three such colored products can be prepared by condensing molecular beams of  $S_2$ . The formation of these colors is not yet known, and the experiments seem not to be reproducible. One group (162, 163) observed transitions of these forms by thermal effects at  $-70^\circ$ ,  $-60^\circ$ , and  $-55^\circ\text{C}$ .

(g) Green Sulfur. A green condensation product was reported in a liquid-air cooled trap (243) when  $S_\lambda$  was condensed. Green sulfur is also produced if molecular beams of  $S_2$  are slowly deposited upon a surface which is kept at  $-104^\circ\text{C}$  to  $-78^\circ\text{C}$ , or if purple sulfur is heated above  $80^\circ\text{K}$  (194-197). The preparation of this form has been thoroughly studied. Most of the  $S_2$  reacts after condensation under the formation of a statistical mixture of sulfur chains. During the formation of such chains, small molecules can be trapped in solid nonequilibrium self-solution between long curled chains. This solid has a complicated composition. The electrical conductivity, the UV and the IR spectrum of this multicomponent form have been studied (194), and the  $S_2$  particle could be identified in such mixtures with the help of the forbidden IR-spectrum. At least four different active species have been observed by their ESR spectrum (51-53, 245) during warm-up cycles of this green form. The ESR spectrum is similar to that of the red form obtained if  $S_\alpha$  is irradiated at  $78^\circ\text{K}$  (246).

It is not yet clear why this form is green. Rice held the  $S_{\pi}$  molecule responsible for this color, but  $S_{\pi}$  is known to be yellow. Another explanation is based upon the similarity of the color effect in colloid solutions. The color changes at  $100^{\circ}\text{C}$  into yellow.

(h) Violet Sulfur. If a molecular beam of  $S_2$  is slowly condensed on a surface at  $\leq 60^{\circ}\text{K}$ , a violet-purple solid forms. This solid has two absorption continua in the UV. At  $80^{\circ}\text{K}$  this form converts into green sulfur. The composition of violet sulfur is not known, but the presence of  $S_2$  has been demonstrated (194-196) and the color might be due to the same particle which causes hot liquid sulfur to be deep red (166).

A summary of the stability ranges of the metastable colored forms is given in Table 7 and in Fig. 2.

### 5. From Sulfur Compounds

In stoichiometric equations for the formation of elemental sulfur from compounds, atoms and small molecules are often assumed as intermediates. It is very unlikely that such unstable particles of the element occur in a solution. The allotropes form most probably through an internal displacement reaction or through an intramolecular rearrangement such as a ring closure or a chain scission from molecules which already contain the correct number of sulfur atoms. The most frequent intermediates are polysulfides or polysulfoxyacid ions in various oxidation states. The formation of  $S_{\rho}$  in acidified thiosulfate solution, for example, can be explained by the following reactions:

Fig. 2. Stability of allotropes =  $f(T_{\text{start}}, -(dT/dt), T_{\text{end}})$ .

This three-dimensional plot shows the stability range of allotropes, estimated as a function of the condensation speed, together with the temperature of the equilibrium sulfur system from which they can be prepared.

The various sulfur allotropes to which the symbols in the drawing refer are discussed in Section IV. C. 4. The z-form has not yet been observed.

At equilibrium ( $-dT/dt \ll$ ), only  $\alpha$  and  $\beta$  are stable solids. With an increasing temperature gradient, an increasing number of allotropes can exist in metastable form. The stability of allotropes generally decreases if the preparation temperature is raised, because of the increasing number of less stable particles.

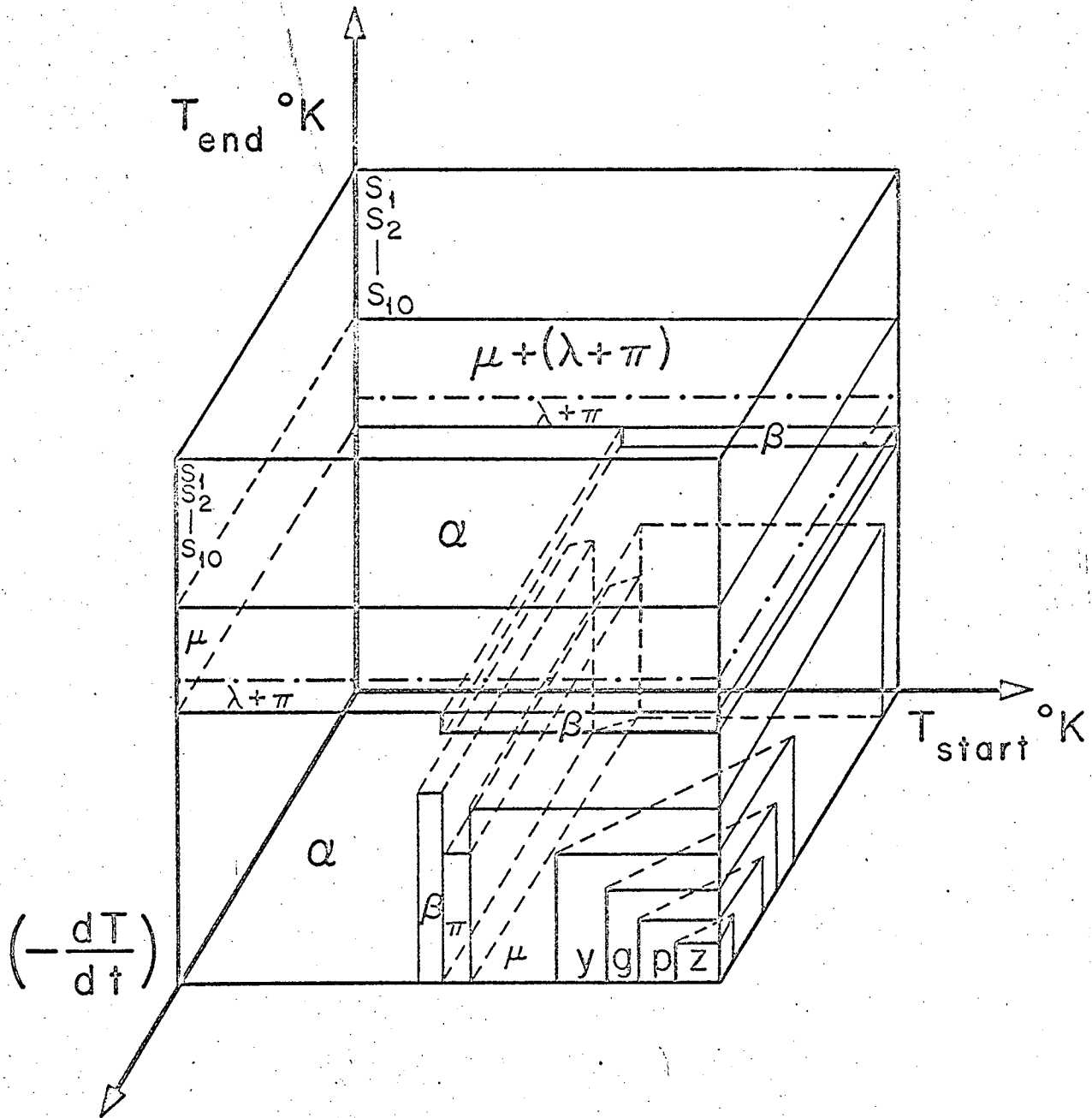
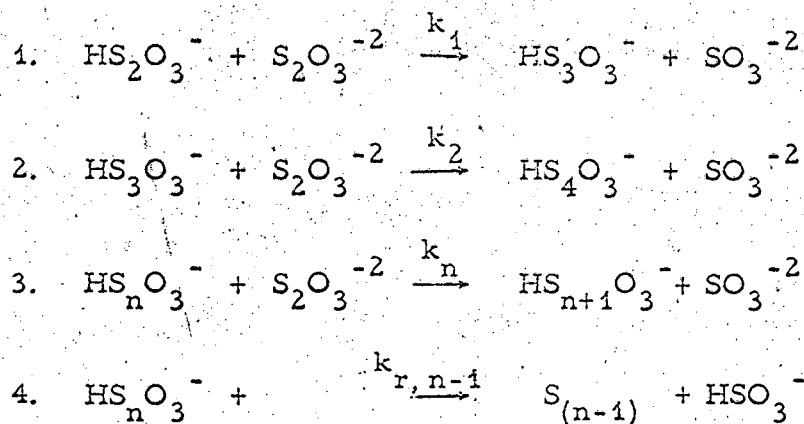


Fig. 2

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If reaction 3 prevails, long chains will form; reaction 4 represents the unimolecular formation of a ring.

The yield of different sulfur allotropes depends mainly upon two factors; first, upon the formation or displacement rate of the allotropes ( $k_r$ ) from an intermediate compound which has already the correct number of sulfur atoms, namely one more than the corresponding ring; and second, upon the formation rate  $k_n$  and the lifetime of the intermediate compound, which is dependent on  $k_{n+1}$ . The displacement reaction rate will depend mainly upon steric factors, and it is certainly higher for the torsion free  $\text{S}_8$  than for the  $\text{S}_6$  and the  $\text{S}_{10}$  ring. ( $k_{8r} > k_{6r}$ ). The formation rate of the intermediate compound and its lifetime will depend strongly upon the concentration, pH, temperature, and chain length. The formation of an allotrope will be favored whenever the formation rate of the allotrope is greater than the formation rate of the intermediate. If  $k_n$  for  $n > 5$  is assumed to have for all  $n$  about the same order of magnitude, three cases are of special interest:

$$1. \quad k_n \gg k_{8r} > k_{6r}$$

$$2. \quad k_{8r} > k_n > k_{6r}$$

$$3. \quad k_n \approx k_6$$

All three cases have been observed.

In warm concentrated solutions a fast pH change leads mainly to long chains which form  $S_\mu$ . Under mild conditions, the formation of  $S_\lambda$  will be favored. In cool solutions, slow acidification will yield an appreciable amount of  $S_6 = S_\rho$ . One cannot, however, obtain  $S_6$  through slow reaction at standard temperature, since the  $S_6$  is not stable enough. It can be concluded that the temperature coefficient of  $k_n$  is much greater than for  $k_r$ .

(a)  $S_\rho$ . Following an earlier suggestion (258) the term  $S_\rho$  is used here only for the unbound cyclo-hexa-sulfur molecule, and not as a synonym of  $S_\epsilon$ . The  $S_\rho$  molecule is thermodynamically unstable, but it can be preserved over extended periods of time (20), even at 60°C, if it is kept in solution and is carefully cleaned with potassium iodide, lead sulfide and potassium hydroxide.

It is best (22) prepared after the method of Engel (89, 90). Concentrated hydrogen chloride is slowly stirred into a concentrated solution of sodium thiosulfate at 0 to 10°C. The  $S_\rho$  is then, together with  $S_\lambda$ , extracted with toluene or benzene, and the yield is  $\leq 12\%$ . On evaporation or cooling of the solution,  $S_\rho$  crystallizes as  $S_\epsilon$ . Such solutions have been studied carefully (17, 20, 21, 22); it was found that  $S_\rho$  reacts roughly  $10^4$  times faster than  $S_\lambda$  with triphenylphosphine, cyanogen and the hydroxyl ion. This reaction is catalyzed by traces of  $H_2S$  and  $SO_2$ . The ultraviolet spectra (22, 243) and the IR (20) have been studied in  $CS_2$  and broad absorption bands around 2900 Å and 20 $\mu$  have been observed (See Appendix). The structure has been discussed earlier (85, 315).

(b)  $S_\epsilon$ .  $S_\epsilon$  is the only crystalline form of the cyclo-hexa-S molecule  $S_\rho$ . It was discovered by Engel (89, 90). The correct molecular composition was, however, reported only much later (10). In a recent publication,  $S_\epsilon$  has been erroneously considered to consist of long chains (85, 281).

The  $S_\epsilon$  is better known than the stable  $S_\rho$  form, and is by far the best understood unstable allotrope. The molecular symmetry ( $S_\rho$ ) is  $D_{3d}$ .

The environmental symmetry is  $C_{3i}$ . The crystal symmetry is  $C_{3i}^2$  (84).

The lattice constants are (82):

$$a = 10.818 \pm 0.002 \text{ \AA} \quad a : c = 1 : 0.396$$

$$c = 4.280 \pm 0.001 \text{ \AA}$$

Several authors studied the morphology (78, 80, 120, 121), the crystal symmetry, and other data (50). The melting point of  $S_\epsilon$  is estimated to be below  $100^\circ\text{C}$ . A remarkable property of  $S_\epsilon$  is the density. It is higher than that of any other allotrope so far studied, namely,  $2.135 \text{ gr/cm}^3$ . Each atom has twelve neighbors within a distance of  $\leq 3.5 \text{ \AA}$ . The high lattice stability of  $S_\epsilon$  becomes evident if the thermal data for the vaporization processes  $S_a - S_\lambda$  and  $S_\epsilon - S_\rho$  are compared (28). The vaporization entropy per mole of  $S_\epsilon$  is higher than that for  $S_8$ , and the enthalpy and free energy for this process are nearly equal. Computed per gram atom,  $\Delta S^\circ$ ,  $\Delta F^\circ$ , and  $\Delta H^\circ$  are, however, all greater for  $S_\epsilon$  than for  $S_8$ .

The production of  $S_\epsilon$  from boiling sulfur solution has been claimed, but this seems doubtful since it would necessitate the formation of  $S_\rho$  from the  $S_\lambda$ , i. e., the formation of an unstable ring with six atoms from a ring with eight atoms in a solution. This would require several intermediate steps including scission of the  $S_8$  ring. The  $S_\epsilon$  crystals convert within a few hours into  $S_a$  if the  $S_\rho$  is not carefully purified. The pure  $S_\epsilon$  is fairly stable at  $0^\circ\text{C}$ . Several authors report that  $S_\epsilon$  has been found in nature.

(c)  $S_{\text{red}}$ . Three different types of red sulfur exist. Here only one kind is discussed. It is prepared together with pink sulfur when ammonium polysulfide reacts with disulfur dichloride at pH 8. The precipitate (94) contains only 50% sulfur and has to be washed to be stable for more than 24 h. A chromatographic separation on aluminum oxide and silica gel leads to seven fractions, of which three contain 100% sulfur. These fractions have been characterized by their x-ray pattern and by their molecular weight, but it is not yet clear whether red sulfur really contains a new allotrope or is just a mixture of

already known allotropes with sulfur compound. It has been pointed out in the description of  $S_{\pi}$  that the chromatographic separation also catalyzes conversion of allotropes, and that the fractions after separation have, therefore, a different character, and have not yet been analyzed carefully enough.

Mitscherlich (201) and many other authors have reported further red sulfur forms that have later been clearly identified as impurities. All the forms mentioned above are multicomponent systems and are not well defined or understood.

(d)  $S_{\nu}$ .  $S_{\nu}$  is the name given to the pale insoluble residue of red sulfur (97) which is prepared by mixing disulfur dichloride with ammonium polysulfide solutions. Its lattice, x-ray spectrum, color, and sublimation temperature indicate that it might be identical with ammonium chloride.

(e)  $S_{\omega}$  can be prepared by hydrolyzing disulfur dichloride. It is described elsewhere in this report.

## 6. In Solid Solution

We have already discussed two cases of sulfur self-solutions: first, the metastable films which are obtained if molecular sulfur beams are trapped; and second, the quenched melt which is partly a solid solution of  $S_{\pi}$  in  $S_{\mu}$ . We list here two cases where sulfur allotropes have been studied in a solid foreign solvent:

(a) Polar solvents. Sulfur dissolves in ammonium (139), sulfur trioxide (158), and many other liquids, but the solvation is generally accompanied or caused by some chemical reaction. It seems, however, that sulfur does not react with alcalihalide melts (144). At 700°C, a deep blue solution is observed in an eutectic KBr-CsBr mixture. If the liquid is cooled slowly, the melt crystallizes with green sulfur inclusions, but if the melt is quenched

to 78°K, a metastable solution is trapped and remains colored even at standard temperatures for many days. It is easy to press pellets from this solid, but the IR spectra are complicated and are not yet fully understood. It is not clear what allotropes can exist under such conditions.

Recently, an attempt was made to produce and trap  $S_2$  in a water clathrate(140). It is very unlikely, however, that such an unstable molecule can be stabilized under the conditions described by the author, and it seems that the broad absorption spectra reported are due to hydrogen or organic sulfides and polysulfides.

(b) Nonpolar solvents. Homogeneous metastable solutions can be trapped by slow simultaneous condensation of a rare gas and of sulfur vapor (195). If 0.1%  $S_2$  is condensed in Ar, Kr, or Xe at a temperature below 25°K, very pure  $S_2$  solutions are obtained, and the spectra of such solutions are similar to the gas-phase spectrum.

## V. CONCLUSION

Sulfur has been known and used for several thousand years, but this review shows that many basic characteristics of this common element have not yet been explained and that only a few properties have been discovered. Due to the state of exploration, publications vary considerably in reliability and accuracy: Some properties are precisely known; for example, the lattice constant of  $S_\alpha$ ; but in the case of other allotropes it is not even clear whether they exist. In learning about elemental sulfur, the reader has to be constantly aware of drastic changes in accuracy and reliability, after concerning the properties of one single allotrope.

Only four of the over  $5 \times 10^5$  different sulfur particles have been obtained in pure form: (a) the cyclo-octa-S ( $S_\lambda$ ); (b) the cyclo-hexa-S ( $S_\rho$ ); (c) the  $S_2$  molecule, and (d) the S atom. Of these, only the diatomic molecule and the atom are well known. For the hexatomic and octatomic molecule, the spectroscopic data are incomplete and inconclusive and most of the thermal data are unknown. The study of polymers such as  $S_\mu$ ,  $S_\omega$  and  $S_\phi$  does not promise fast progress. They have been well studied, but their characteristic components, if there are any, have not yet been isolated. A further problem is that one does not yet know enough about their formation. Very little is known about  $S_\pi$  and it is not established what other particles might occur as intermediates in the formation of  $S_\mu$  and  $S_\omega$ .

It will, in the future be possible to isolate and study several of the small molecules: for example, catena-octa-S ( $S_\pi$ ),  $S_7$ ,  $S_4$ , and  $S_3$ . All can be trapped at lower temperatures because recently developed low-temperature techniques make it possible to trap such unstable particles in metastable form with purity and in quantities sufficient for observation.

The polymorphism of sulfur is a wide open field. Many different arrangements can yield a similar lattice energy and it is likely that for  $S_\lambda$  and  $S_\rho$  a great number of polymorphs will be found. Only polymorphs of  $S_\alpha$  have so far been investigated, and the existence of the 10 allotropes reported has not always been conclusively proved. Astonishingly, only two forms,  $S_\alpha$  and  $S_\gamma$ , have been clearly understood even though  $S_\beta$  is stable and has been frequently investigated.

The colored forms are complicated mixtures of allotropes. Most of them contain  $S_\mu$ , but their composition is very sensitive to the preparation conditions. From a chemical point of view, the colored forms are interesting because of their high reactivity. The sharp limit of their stability ranges is an indication that they might contain one particle as a predominant component.

Almost all sulfur allotropes are photosensitive but most experiments have been performed without regard to this fact. One of the future tasks will be to systematically investigate the influence of radiation on the sulfur system.

Another important task will be to establish a common terminology. The unstandardized terminology constitutes a very shaky ground for the exchange of observations; knowledge about sulfur allotropes would be greatly enhanced if a systematic nomenclature were to be developed.

Because of the large amount of specialized information available concerning elemental sulfur, this review was restricted to solid and unstable allotropes, but even this relatively small fraction of the whole field is so complex that many important problems could barely be touched. It was our general procedure to refer to information in the form of a guide to the literature, rather than to present a complete listing of data.

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## APPENDIX

References to Related Problems

References of fields related to sulfur allotropes are compiled in reversed chronological order in the following six paragraphs:

- (a) General reviews
- (b) Liquid sulfur
- (c) Sulfur vapor
- (d) Sulfur compounds and reactions of elemental sulfur
- (e) Photochemistry and photophysics
- (f) Spectral studies

(a) General reviews

The most comprehensive surveys are given by Pascal (215) 1960 and Gmelin (138) 1954. General information is reviewed by Pryor (239) 1962, Schmidt (263) 1962, Wells (310) 1962, Donohue (84) 1961, Gee (129) 1958, Gee (128) 1955, Feher (105) 1954, Tuller (299) 1954, and many others. The earlier surveys of Yost (319) 1944 and Schaefer (255) 1940 contain much obsolete data and employ a rather confusing terminology. The best review of old data has been compiled by Quincke (240) 1908.

(b) Liquid sulfur

Surveys are given by Schenk (258) 1957, Fairbrother (101) 1955, Gee (128) 1955 and Gee (127) 1952.

Theories have been developed by Tobolsky (295, 296) 1961, Gee (121) 1952, Jacobson (159, 160) 1950, and Powell (229) 1943.

The viscosity has been discussed by Powell (229) 1943, Bacon (13) 1943, Farr (104) 1928, and Kellas (165) 1918.

The structure has been described by Thompson (293) 1959, Prins (236) 1957, and Krebs (175, 176) 1953.

For electric conductivity data, see Gordon (142) 1954.

For heat capacity data, see Braune (39) 1954.

For specific heat data, see Feher (108) 1958, Braune (38) 1954, West (313) 1929, and Lewis (184) 1911.

The free-electron character is treated by Poulis (226) 1962, Gardner (126) 1956, and Feher (106) 1954.

The surface tension is discussed by Fanelli (103) 1950, and the color was discussed by Kelker (164) 1954 (see also spectral references).

(c) Sulfur vapor

Berkowitz (27, 28) 1964; Poulis (227) 1963; Budinikas (47) 1961; Jaeckle (161) 1961; Briske (44) 1960; Zietz (322) 1960; Feher (107) 1957; Bradt (35) 1956; Brewer (42) 1956; Bradley (34) 1954; Braune (36, 37) 1952; West (312) 1951; Cibronsky (55) 1949; Turell (300) 1947; Klemm (167) 1941; Neumann (211) 1934; West (313) 1929; Lewis (184) 1911.

(d) Sulfur compounds and reactions of elemental sulfur

Surveys: Pryor (239) 1962, Schmidt (263) 1962 and "Organic Sulfur Compounds," I, (84) 1961.

Special Problems: Feher (101-109) and 61 other contributions up to 1963; Nair (209) 1963; Schmidt (264) 1963; Kovalsky (174) 1962; Donohue (81) 1961; Foss (112-114) 1949-60; Koros (172) 1960; Kovalsky (173) 1960; Pryor (238) 1960; Fredga (116) 1958; Ingrahm (158) 1957; Garcia (123) 1958; Abrahams (1, 2, 4) 1953-56; Skirai (268) 1951; Aynsley (11) 1935; Lewis (185) 1918.

(e) Photochemistry and Photophysics

Studies have been made by: Bartlett (22) 1961; Erämetsä (93, 94) 1959; Bartlett (17) 1956; Dhar (76) 1948; Dufraise (87) 1946; Feigl (110) 1944; Wigand (316, 317) 1911; Rankin (241) 1907; and originally by Lallemand (179) 1870.

The photoconductivity, chemiluminescence and piezoelectricity were investigated by: Zhelndev (321) 1962; Dean (72) 1960; Chetkorov (54) 1960; Dorabialska (86) 1957; Fridkin (118) 1956; Sokolva (281) 1954; Nadzhakov (208) 1954; and Moss (203) 1951.

(f) Spectral studies

Vapor: The spectrum of  $S_2$  is being restudied carefully: R. F. Barrow et al. Proc. Roy. Soc. 83, 330 (1964), Can. J. Phys. 41, 419 (1963) and Can J. Phys. 40, 377 (1962), and Tanaka, Y. and Ogawa, M. J. Chem. Phys. 36, 726 (1962); a survey of earlier studies is listed in B. Rosen, "Données spectroscopiques concernant les molécules diatomiques," Hermann, Paris, 1951.

Polyatomic molecules have been studied by Kelker (164) 1954; Poulsen-Nautrup (228) 1954; Bass (23) 1953; Gerding (130) 1943; Fukuda (122) 1922; Graham (143) 1910; Gernez (131) 1872; and Salet (252, 253) 1871-72.

Solid Phase: Srb (287) 1962; Meyer (194-198) 1962; Rice (244) 1960; Barrow (16) 1953; Bernstein (29, 30) 1951; Gerding (130) 1943; Norris (212, 213) 1942; Venkateswarlu (303) 1940; Venkateswaran (301) 1936; Barnes (15) 1932; and Taylor (292) 1927.

Solutions: Clark (56) 1963; Bartlett (17-22) 1956-61; Barrow (16) 1953; Baer (14) 1949; Gerding (130) 1943; and for organic compounds, Passerini (216) 1960. Normal coordinate analyses have been performed by Scott (265, 266) 1963, Pistorious (224) 1959, and Venkateswarlu (302) 1940.

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