SOLID ALLOTROPES OF SULFUR

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I. INTRODUCTION

During the past 150 years a large amount of detailed information on elemental sulfur has been accumulated, and more than 30 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

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present knowledge (Jan., 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 labeling 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_λ), sometimes for modifications (*e.g.*, S_α), or even for complicated mixtures (*e.g.*, S_μ) 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_μ for which here only a few synonyms are listed: S_γ, S_x, S_n, S_ν, etc.

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

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 section 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 by-product, from compounds. Until 1914, most commercial sulfur came from volcanic sources. This sulfur forms large crystals of S_α 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 aresnic, selenium, and tellurium. Commercial sulfur is generally a mixture of different allotropes, containing mainly orthorhombic S_α and plastic S_μ sulfur. Besides the stable S_α form, two unstable (STP) modifications have been observed in nature: S_β and S_γ, 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

$$\begin{array}{lllllll}
\text{(a)} & S_2Cl_2 & + & H_2O & \rightarrow & \{S_x\} & + \; \ldots . \\
\text{(b)} & HS_2O_3^- & + & H_3O^+ & \rightarrow & \{S_x\} & + \; \ldots . \\
\text{(c)} & NH_4\text{–}S_x\text{–}NH_3^- & + & H_3O^+ & \rightarrow & \{S_x\} & + \; \ldots . \\
\text{(d)} & HS_x^- & + & SO_2 & \rightarrow & \{S_x\} & + \; \ldots .
\end{array}$$

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, mainly reactions of unspecified mixtures of allotropes, the composition of which can only be guessed from the reaction conditions and reaction media, have been studied. 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 are available about the reactions of sulfur.

TABLE I

NOMENCLATURE OF SULFUR ALLOTROPES

Name	Synonyms[a]	Status of identification	Stability	Molecular species	Section
α	1st mod., 1st Muthmann mod., orthorhombic	Conclusive	Only thermodynamically stable form at STP	Cycloocta-S	IVB3
β	2nd mod., 2nd Muthmann mod., monoclinic (I) sulfur, prismatic	Structure not known	Stable $\geq$95.6°	Cycloocta-S	IVB3
γ	3rd Muthmann mod., 2nd monoclinic, nacreus sulfur, mother-of-pearl sulfur, Gernez mod.	Incomplete	Metastable (?)	Cycloocta-S	IVC3b
δ	4th Muthmann mod., 3rd monoclinic, γ-monoclinic	Ambiguous	Unstable	Cycloocta-S	IVC3e
ϵ	Engel sulfur, Aten sulfur, rhombohedral mod., monoclinic Engel	Conclusive	Unstable	Cyclohexa-S	IVC5b
ζ	5th monoclinic	Ambiguous	Unstable	Cycloocta-S	IVC2c
η	4th monoclinic	Ambiguous	Unstable	Cycloocta-S	IVC2f
ϑ	Tetragonal	Ambiguous	Unstable	Cycloocta-S	IVC3e
ι	. . .	Inconclusive	Unstable	Cycloocta-S	IVC3e
λ	Free or bound cycloocta-S	Conclusive	Stable	Cycloocta-S	IVC1a
μ	CS$_2$-insoluble sulfur, polymeric chains	Conclusive	Unstable	Catenapoly-S	IVC3c
ν	Term inconsistently used: μ with special properties	Inconclusive		Mixture	IVC3d
ξ	Triclinic mod.	Ambiguous	Very unstable	Cycloocta-S	IVC2h
o	. . .	Ambiguous	Very unstable	Cycloocta-S	IVC2g
π	Aten's mod.	Incomplete	Unstable	Catenaocta-S	IVC3a
ρ	(a) Here: unbound cyclohexa-S molecule	Conclusive	Unstable	Cyclohexa-S	IVC5g
	(b) Often: Aten's, Engel				
τ	. . .	Ambiguous	Unstable	Cycloocta-S	IVC2i
ϕ	(a) Fibrous sulfur	Incomplete	Unstable	Catenapoly-S or mixture	IVC3e
	(b) Erämetsä	Ambiguous	Unstable	Cycloocta-S	
	(c) Plastic; mixture of ω and γ	Ambiguous	Unstable	Mixture (?)	
	(d) Fibrous sulfur, stretched sulfur	Ambiguous	Unstable	Catenapoly-S	IVC3f
ω	Insoluble sulfur, white sulfur, super-sublimation, Das mod.	Incomplete	Unstable	Catenapoly-S and mixture	IVC4a
m	Triclinic	Inconclusive	Very unstable	Cycloocta-S	IVC5d
n	See μ		Unstable	Catenapoly-S	IVC3c
Aten	Used for S$_\epsilon$ and S$_\rho$				
Brauns	Mixture, see S$_\mu$				
Engel	See S$_\epsilon$ and S$_\rho$				
Woehler	Colloidal	Conclusive	Metastable	Polycatena-S	
Amorphous	See S$_\mu$				
Metallic	. . .	Inconclusive	Unstable		IVC1a
Photosulfur	. . .	Incomplete	Unstable	Mixture	IVC2c
Irradiation sulfur	. . .	Incomplete	Unstable	Mixture	IVC1b
Black	(a) Mitscherlich	Not elemental sulfur			IVC4c
	(b) Skjerven	Inconclusive	Unstable		
	(c) Rice–Schenk	Incomplete	Unstable	Catena-S	
Green Purple Violet Brown	Trapped sulfur	Incomplete	Unstable	Mixture of catena-S	IVC4c–h
Red	(a) Trapped; condensation sulfur	Incomplete	Unstable	Catena-S, mixture	IVC4b
	(b) Irradiation sulfur	Incomplete	Unstable	Catena-S, mixture	IVC1b
	(c) Precipitation sulfur	Incomplete	Unstable	Mixture	IVC5c

[a] The abbreviation mod. means modification.

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 ref. 123, 139, and 239.

The use of radioactive 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 section 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_α and almost all allotropes but S_μ and S_ω 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 acetonic or alcoholic aqueous solution of the reagent. It is not yet clear how much the solvent partakes in such reactions, but the solvents 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°. The last reaction probably involves open chains of the element (239). Such chains have a free-radical character (200) and make sulfur a polymerization inhibitor (238, 294) for styrene (18), vinyl derivatives, sulfenyl compounds, and other monomers.

a. Nucleophilic Reactions. Triphenylphosphine, the cyanide ion, and many weak bases (17, 18, 264) open the octasulfur 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 an aryl sulfide (20). The reaction with arylimines is not yet clearly understood.

The hydroxyl ion reacts quickly with sulfur at 100° and leads to the formation of thiosulfate which then decomposes on further heating into sulfate and sulfite. At temperatures above 200°, 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_μ (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 of 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 silicon 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°. 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 SO_3, a red solid crystallizes (158), which is believed to have the formula $\{SO_3 \cdot S_x\}$. 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) and 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 follow.

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 3% hydrogen sulfide and 0.08% sulfur dioxide (21). The carbon disulfide inclusions in an S_α 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 perfected for the production of a very pure element. The first is zone melting and was used (188) to grow crystals of S_α and S_β. 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 by boiling sulfur for 48 hr. 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, Clabaugh, and Gilchrist (205) use the following method. Sulfur and sulfuric acid are heated to 150°, and nitric acid is slowly added over a period of 6 hr. The melt is then cooled, washed, and heated under reflux with helium or dry nitrogen bubbling through it. Afterward the sample is cooled again and transferred into an ampoule. Water is added and the ampoule is sealed under nitrogen and heated to 125°. The last process is repeated three times and the sulfur is then outgassed at 10 mm. with nitrogen and finally sealed in an ampoule.

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 be removed only 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 von Wartenberg (306–308). Sulfur is melted in a loosely covered round flask, and a red glowing quartz heater (~700°) is inserted into the melt. A carbon deposit is formed on the heater and should be removed daily. After 1 week the flask is connected with a pump system, and the sulfur is put under vacuum, distilled, and sealed into an ampoule.

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 precipitate as 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 ref. 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 silico sulfides.

Recently, high-purity sulfur became commercially available; sulfur with a purity of 99.999% is available from American Smelting and Refining Co. Also, sulfur with a purity of 99.99999% is available from several sources.

IV. ALLOTROPES

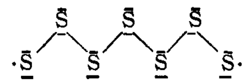
A. INTRAMOLECULAR AND INTERMOLECULAR ALLOTROPY

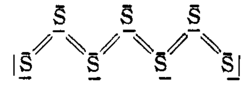
Berzelius (32) introduced the term allotrope for the different forms in which an element can exist. Several authors have since developed theories of allotropy (57, 59, 149, 177, 183, 279). Here a molecular point of view is taken, and two sources for the variety of the appearance of sulfur are distinguished: first, the different ways in which the atoms can recombine into molecules; second, the different manner in which the molecules can build up crystals. These intra- and intermolecular arrangements are discussed 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° and the b.p., 444.6° (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 catenaoctasulfur (S_π) and cyclooctasulfur (S_λ). By means of sudden cooling, all of the molecules mentioned can be trapped as solids, but only cycloocta-S (S_λ) is stable at room temperature. All others convert into the λ-form with a half-life between about 1 msec. and 1 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 dσ-hybrids and dπ-bonds (320). This assumption requires a breakdown 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_π).


(I)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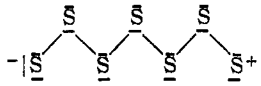
(III)

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

A 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 II lists recent molecular data for cycloocta-, cyclohexa-, and catenapolysulfur. The cycloocta 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 semiempirical MO-LCAO model (26), the torsion energy of cycloocta-S (S_λ) is not zero, but is rather small, being only about half as big as that for the cyclohexa-S (S_ρ). Recent data for catenapolysulfur and for cyclooctasulfur indicate similar values and make it probable that they are both nearly torsion free.

The symmetry of cycloocta-S (S_λ) is D_{4d}. The

TABLE II

STRUCTURAL DATA FOR S_λ, S_ρ, AND S_μ

	$S_8 = S_\lambda$ Cyclo-octa-S	$S_6 = S_\rho$ Cyclo-hexa-S	$S_x = S_\mu$ Catena-poly-S
S–S bond length, 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 ≤ 3.5 Å.	6	12	
Molecular symmetry	D_{4d}	D_{3d}	C_{2l}

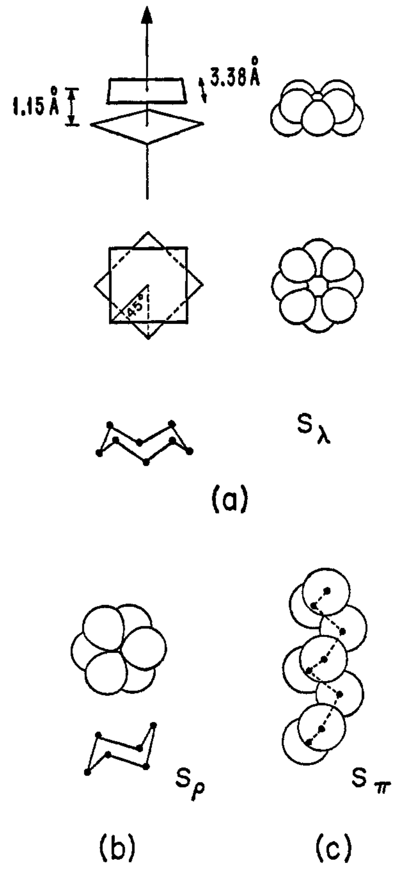

Fig. 1.—(a) The S_λ molecule (cycloocta-S), (b) the S_ρ molecule (cyclohexa-S), (c) the S_π molecule (catenaocta-S).

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 cyclohexa molecules (S_ρ) form a puckered ring with D_{3d} symmetry. The bond distance is 2.057 Å. The open chains of catenapoly-S (S_μ) form helices. Their structure is not yet fully known. They probably form spirals in which the bond angle and bond distance are very similar to those in S_λ. Many additional molecules such as cyclotetrasulfur, cycloheptasulfur, and cyclodecasulfur 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 either can 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. Cyclooctasulfur has, for example, about ten such polymorphs. It is surprising that, of the two well-known allotropes, S_ϵ—which is built up from unstable cyclohexasulfur—has a higher number of close neighboring atoms than S_α, which consists of the stable S_λ. The first allotrope has, therefore, a higher density and a more stable lattice than the latter.

Table III 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_α. The S_α crystal is built up from cyclooctasulfur (S_λ) molecules. Be-

TABLE III

PREPARATION OF ALLOTROPES[a]

Section	Starting material	Main components	Unstable allotropes	Stable form (STP)
IVC1	Solid S_α	Cycloocta-S (S_λ)	(a) Metallic-S, (b) irradiation-S, (c) orange-S	
IVC2	S_λ solution	Cycloocta-S (S_λ)	(a) Photo-S, (b) γ, (c) ζ, (d) η, (e) δ, (f) ϑ, (g) o, (h) ξ, (i) τ, (j) χ, (k) ϕ, (m) ψ	
IVC3	Liquid sulfur	Cycloocta-S (S_λ) Catenaocta-S (S_π) Catenapoly-S (S_μ)	(a) π, (b) ι, (c) μ, (d) ν, (e) ϕ, (f) ψ	In solution, λ
IVC4	Sulfur vapor	S_x, $1 < x < 10$	(a) ω, (b) m, (c) yellow, (d) black, (e) purple, (f) red, (g) green, (h) violet	In lattice, α
IVC5	Compounds	Sulfides and sulfoxy acids as intermediates	(a) ρ, (b) ϵ, (c) red, (d) ν, (e) ω	
IVC6	Vapor and solvent		(a) Blue, (b) maroon	

[a] The stable allotropes (S_λ, S_α, S_β) are formed from all other forms within a time varying from ~0.001 sec. to 1 year (see section II). The unstable allotropes are here listed corresponding to their preparation method.

tween 95.3° and the melting point, S_β 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 dicussion of stable allotropes, since their properties are well summarized in ref. 138, 168, and 215.

1. The S_λ Molecule

The term S_λ was introduced by Berthelot (31), and it is the short name for the free cyclooctasulfur molecule. The structure of this particle has been discussed above.

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

2. The S_α Modification

Since S_α is the only stable sulfur modification at STP, all other allotropes convert ultimately into it. Brønsted (46) discovered that the α-crystals contain S_8 (S_λ) 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^{24}_{2h}-Fddd, the symmetry of the molecule is D_{4d}, and the environmental symmetry is C_2-2. The unit cell is formed from 128 atoms. The lattice constants (210) are, after recent measurement (58), given with six significant figures: $a = 10.44349$, $b = 12.84009$, $c = 24.43665$ Å.; $a:b:c = 0.81335:1:1.9032$.

The α-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 section IVC2) often lead to the discovery of different looking crystals, which have been frequently mistaken for other modifications, for example S_γ.

The melting point of S_α is 112.8°, but above 95.31° (311) the stable modification is S_β. The transformation of β into α has been studied by many authors (106, 150, 311) who reported contradictory results (65). It seems that the equilibrium with an enthalpy $\Delta H_{368^\circ K} = 401.7$ joules/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_α have been studied; among these are self-diffusion and the ultraviolet (23), infrared (29, 30, 193), and Raman (130) spectra.

3. The S_β Modification

The S_β 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° and the melting point. It is found in nature and it is formed whenever sulfur solutions or liquid sulfur crystallize within this temperature range. The "ideal" melting point of S_β is 119.3° (compare Dufraisse, *et al.* (87), 122.0 ± 0.5°). The liquid sulfur, however, disproportionates partly into S_π, which forms a self-solution of sulfur in S_λ, and this leads to a melting point depression which causes the "natural" (131) melting point of S_β to be 114.6°. The stepwise disentangling of this curious behavior of the melt will be discussed together with S_π.

Big crystals of S_β can be grown easily from boiling organic solvents (318). The symmetry of S_β was determined by Burwell (49): C^5_h-$P2_{1/a}$. Forty-eight atoms (6 S_λ molecules) (211) seem to form a unit cell (220) with $a:b:c \sim 0.995:1:0.999$, but the details of the structure are not resolved. The X-ray data (304) are not yet conclusive, but indicate that the structures of S_α and S_β are closely related, and that the S_λ molecules might rotate in S_β and that they might be centrosymmetrically stacked. The density of S_β is between 1.96 and 1.93 g./cm.^{3}, which indicates a looser packing of S_λ molecules than in S_α.

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_α without Solvent

New allotropes can be formed from S_α 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_λ 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_α 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. α-, β-, and γ-radiation (77, 141) and ultraviolet light (76) can break the S–S bond. Thus, the cycloocta molecules (S_λ) are cut into catenaoctasulfur (S_π) or into smaller fragments. At STP, the recombination rate of all these unstable particles into S_ω 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_λ which then crystallizes as S_α. Amounts of 75 mc. of β-radiation can consume small S_μ samples within an hour (204). At −29° and below, S_μ (catenapolysulfur) is metastable (202). At these temperatures, small chains formed through irradiation can recombine to a mixture of S_λ and S_μ, 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_α is exposed to 40 mr. of γ-radiation it turns red (246). Preliminary results on the electric conductivity (304) and the e.s.r. spectra (53) are now available. Several authors (17) use the name irradiation sulfur as a synonym for photosulfur.

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 1 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_α 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_λ in Solution

Sulfur is soluble in many organic solvents. At STP a stable solution contains cycloocta-S (S_λ). 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_λ molecules. In a rough way, the conditions for the formation of different solids can be ascertained by comparing the precipitation rate ($\{\dot{S}\}$) with the rate of the lattice growth of S_α ($\{\dot{S}_\alpha\}$). Three conditions are: First, whenever $\{\dot{S}\} < \{\dot{S}_\alpha\}$, the α-modification is expected to crystallize. The higher the difference is between the two gradients, the bigger is the resulting α-crystal. Second, in the extreme case, when $\{\dot{S}\} \gg \{\dot{S}_\alpha\}$, no crystals form, and the sulfur precipitates in amorphous form. Third, if $\{\dot{S}\} \geq \{\dot{S}_\alpha\}$, 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_α, for example. All methods for the preparations 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_α. Many studies of crystallization in sulfur solutions have been made under a microscope (48, 90–99, 156, 163, 169, 170, 171). 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 be only S_α crystallized along an unusual lattice face (92, 93, 237). The following stability order (138) for some polymorphs of S_α has been given: $\alpha > \beta > \gamma > \zeta > \eta > \xi > \vartheta > o > \tau > \varkappa$ (see Table IV).

a. Photosulfur. 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

TABLE IV

POLYMORPHS OF THE VARIOUS SULFUR MOLECULES

Molecule	Polymorphs
Cyclooctasulfur (λ)	α, β, γ, δ, ζ, η, λ, ϑ, o, τ, $\varkappa$
Catenaoctasulfur (π)	None
Cyclohexasulfur (ρ)	S_ϵ
Catenapolysulfur (μ)	Amorphous: μ, γ, ϕ, ψ, ω, n Threads: m, ν
Mixture, multicomponent forms	ϕ, μ, black, green, red, purple, photo, Brauns, red[a]

[a] Polymorphs in a free sense; they contain the same molecular species in a similar concentration.

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 photosulfur are not known (17, 22), but it was found that it is more reactive than S_λ and that it is probably a mixture. Recent studies of the influence of light on the formation of different allotropes indicate that the S_8 ring breaks under 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 photosulfur, S_λ in CCl_4 is exposed to sunlight (110), or better, to the light of an ultraviolet lamp, such as a mercury pressure arc. Many authors report that the formation of photosulfur is reversible, but alcoholic photosulfur, 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 photosulfur. A report on the X-ray pattern (95) purports that the structure is similar to that of S_ω.

b. γ-Sulfur. This allotrope 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^4_{2h}, with the eight cycloocta 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): $a = 8.57$ (275), $b = 13.02$, $c = 8.23$; $a{:}b{:}c = 0.658{:}1{:}0.632$. Older data (145, 146) seem incorrect. The melting point of this allotrope is 106.8°; the density is 2.041 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 hr. of X-ray examination. The α-crystals catalyze their transformation and can reduce the lifetime of the γ-form to 0.5 min. (152). Above 75°, β-sulfur is formed quickly. The transformation rate has been studied, and the possibility of enantiotropic transformation $\alpha \rightleftarrows \beta \rightleftarrows \gamma$ has been pointed out (149–154).

According to several reports, γ-crystals have been found in oil wells (290) and as Rosickyit mineral (267). γ-Sulfur was proposed as a component in plastic sulfur. The γ-allotrope can be prepared through condensation of vapor, from an undercooled melt at 90° (314), from an undercooled solution of sulfur in benzene, toluene, or ethyl alcohol, by evaporating an alcoholic solution of sulfur at 70° (206, 211), and spontaneously from o-sulfur. Also, γ-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, if precipitated sulfur is dissolved in a mixture of alcohols, and if carbon disulfide is slowly evaporated at room temperature.

c. ζ-Sulfur. Korinth (169–171) found reddish brown monoclinic (?) crystals of ζ-sulfur that are stable for about half a day. The ζ-sulfur is less stable than S_γ, but more stable than S_δ. The S_ζ allotrope crystallizes together with S_δ and spontaneously forms S_δ. 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 α-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. η-Sulfur. Korinth (169) observed monoclinic (?) crystals of S_η during the preparation of δ-sulfur from rubber solutions containing sulfur and selenium. The experiments have been reproduced. This form has a lifetime of 10 min. (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. δ-Sulfur. Muthmann (206) listed S_δ 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^2_{3i}. The crystals can be prepared in mixture with S_α and S_γ by oxidizing an alcoholic ammonium polysulfide solution at $\leq 15°$ in the open air. This preparation is similar to the preparation of the γ-form, and only about 1 in 1000 experiments leads to the formation of δ.

The crystals can transform into γ-, ζ-, β-, or α-sulfur.

f. ϑ-Sulfur. S_ϑ was first observed by Korinth (169). This allotrope was recently restudied (92). It crystallizes together with S_γ from a not too concentrated boiling solution of fenchenone, α-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 1 min.; then, S_γ, S_β, and finally S_α are formed.

g. o-Sulfur. Erämetsä (93) observed the formation of a new crystal when solutions of S_δ were evaporated. This form is characterized by an extremely low refractive index. It converts within seconds into S_γ, and is the most unstable polymorph known.

h. ξ-Sulfur. Korinth (169) described monoclinic spirals, which he called S_ξ. This form is either extremely unstable or does not exist. It might be identical with triclinic sulfur.

i. τ-Sulfur. S_τ crystallizes in about 1 out of 1000 experiments if sulfur solutions in o-xylene or menthenone 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_α and S_ϕ.

k. $\varkappa$-Sulfur. Henkel (156) discovered this fairly stable monoclinic allotrope. The best yield is reported when a sulfur solution of o-xylol at the boiling point is saturated (91). The crystals have such a high refractive index that they appear to be black in transmission and white in refraction. This allotrope is more stable than S_γ. The report that $S_\varkappa$ occurs in trapped liquid sulfur (125, 236), has been corrected. The name was used for a mixture of $\alpha + \gamma$.

l. ϕ-Sulfur. This name was recently used for a new allotrope which is similar to S_δ (92), but much more stable. It has been prepared from α-pinene solutions at a temperature of 8° and has an unusually low refractive index.

m. ψ-Sulfur. A crystal precipitated from an α-pinene solution has been called S_ψ (92). Its refractive index is lower than that of the solution. Both S_ϕ and S_ψ 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 ref. 164, 232, 234, 257, and 258). At the melting point, cyclooctasulfur is in equilibrium with catenaoctasulfur (S_π) which then polymerizes with S_λ into unbranched chains (S_μ). At 159° (273) the polymerization increases so sharply that S_μ, 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_π is 3.17 kcal. ($\Delta S° = 4.63$ e.u.), and the energy required for the chain scission (160, 161) is 32.8 kcal. ($\Delta S° = 23$ e.u.) (296). The free-radical nature of long, open sulfur chains was pointed out (200), and later confirmed with the help of e.s.r. (124, 126) equipment and a Faraday balance (226). Table V gives a comparison of e.s.r. data for several allotropes. The average chain length varies between 158 and 404° from 8 to 5×10^5 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 electrical conductivity, which is the sum of two terms, these being the electronic conductivity of the liquid

TABLE V
SURVEY OF E.S.R. STUDIES

Material studied	g-value	Band width, gauss	Spin concentration per mole	Ref.
Liquid	2.024 ± 0.002	40–60	10^{-3} at 300° (increased by 2.10^2 from 190 to 375°)	124–126
Plastic	2.0044	9.5	10^{-5}	221
S on Al_2O_3	$\backsimeq 2.0$ $\backsimeq 4$			28
Green	2.010 ± 0.002	8.8 at 78°K.	5×10^{-2}, six components	51, 52
Blue	2.025, four components	2.2 at −78°C.		53
Purple	2.020	8.8	...	245
Black or dirt (see 256)	2.010	7	...	124–126
Free electron	2.0023			

TABLE VIa

THERMAL DATA: SPECIFIC HEAT

T, 298.16° K.	$C_p°$, cal./deg. g.-atom	$S°$, cal./deg. g.-atom	$\Delta H°_F$, kcal./g. atom	Ref.
$S_\alpha(s)$	5.4[a]	7.62		311
$S_\beta(s)$	5.65[b]	7.82	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

[a] 35–95°: $5.2688 + 0.006121T - 8.164 \times 10^{-6}T^2$ (ref. 311).

[b] 101–115°: $5.2630 + 0.006857T + 0.08039/(115.176 - T^2)$ ref. 311); note: C_p decreases from 95 to 101° (ref. 311).

TABLE VIc

OTHER THERMAL DATA

	Triple points (215)		
(1) α, β, vapor	95.31° (311)	0.00376 mm.	
(2) α, liquid, vapor	112.8°	0.013 mm.	
(3) β, liquid, vapor	119.3°	0.018 mm.	
(4) α, β, liquid	~152°	~1400 atm.	
	Melting points, °C. (138, 215)		
α, 112.8 (ideal)			
β, 119 (natural), 114 (ideal)			
γ, 106.8			
ϵ, 100			
m, 330 sublimation (?)			
B.p. (STP), 444.6000°	(186)		
	Bond strength (D_0, S_2 = 102.4 kcal.)		
			Ref.
H_2S up to H_2S_6	63.2 × n,	kcal.	107, 189, 231
S_2Cl_2	64.4	kcal.	217
S_8	64	kcal.	215
	S–S stretch frequency		
	440 to 550 cm.$^{-1}$		187
	680 cm.$^{-1}$		207

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_γ. 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.

Tables VIa–c contain some recent thermal data for the melt and other allotropes.

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_α or its polymorphs, (b) an active species which will be called S_π, 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_μ 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_ω. In discussing the products, we distinguish between samples obtained by one of three different methods. First, slow cooling leads to pure β- and α-sulfur, regardless of the temperature of the liquid. Second, if the hot liquid is poured into water, S_π, S_μ, S_λ, and S_α are formed. The S_π converts

TABLE VIb

THERMAL DATA: TRANSITIONS[a]

Transitions	Temp., °K.	ΔH	ΔS, cal./deg. g.-atom	Ref.
α, β	368.46 ± 0.01	0.096[b]	0.261 ± 0.002	31,1
β, ?	374.2	0.000383[b]	7.93	
α-Subl., λ	368.5	3.01[b]	8.17	34
β-Subl., λ	368.5	2.92[b]	7.93	
ϵ, ρ	300	4.02[b]	8.38	30
Fusion α, λ	383	0.507[b]		
Fusion β, λ	388.33	0.410[c]	0.75	311
λ, π	432	4.1[b,e]	2.88	295, 296
Polymer, $\lambda\pi$, μ	442.8	0.396[b,f]	0.58	295, 296
Vap. λ, λ	444.60000 (°C.)	2.5[b]	3.5	
$^7/_8$ S_λ, S_7	400	5.7[d]		27
$^3/_4$ S_λ, S_6	400	6.2[d]		27
$^5/_8$ S_λ, S_5	400	14.3[d]		27
$^1/_2$ S_λ, S_4	400	20.5[d]		27
$^3/_8$ S_λ, S_3	400	22.5[d]		27
$^1/_4$ $S\lambda$, S_2	400	23.5[d]		27

[a] This selection of recent values differs considerably from older selections (ref. 215, p. 852). [b] Units in kcal./g.-atom; 1 g.-atom of sulfur = 32.066 g. [c] Unit in 5 kcal./g.-atom. [d] Units in kcal./mole. [e] $K = (\pi)/(\lambda) = 1.137 \times 10^4 \exp(-16520/T)$. [f] $K_3 = (\pi)/(\pi\lambda) = 10\ 43 \exp(-1596/T)$; $D_0(S_2) \sim 4.4$ e.v. (27, 42).

within 3 days into S_α and S_μ, but the S_μ converts only slowly into S_α, and its concentration, therefore, goes through a maximum after about 3 days (see S_π). Third, if the liquid sulfur contains only S_λ and S_π (below 158°), the quenched sample crystallizes mainly to S_α, and S_μ is formed only in a secondary reaction through the polymerization of S_π. 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°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 section IVC4. The following section deals with four allotropes prepared from the melt: S_λ, S_π, S_μ, and S_ψ.

a. π-Sulfur. 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° to the natural melting point at 114.5° 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_π (24), a name which had been used before (191, 192) for a different allotrope. Above 159° a third component (274), catenapolysulfur (177), becomes important. If liquid sulfur is quenched in cold water, S_μ is always present regardless of whether the liquid was originally hotter or cooler than 158°. This was first taken as a proof for S_π and S_μ being identical. Molecular weight (39, 40, 228, 260, 261) calculations, however, using the melting point depression and the concentration of S_μ 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_μ. The S_μ concentration (the CS_2-insoluble fraction in a frozen melt) first increases and goes through a maximum (258) after about 3 days. The S_π, with a lifetime of roughly 1 day, obviously partly polymerizes into S_μ, which then converts into S_α with a much higher lifetime, perhaps 6 months.

If liquid sulfur is quenched to −78° some of the S_π can be isolated. The S_λ is soluble in CS_2 at room temperature but not at −78°; S_μ is CS_2 insoluble, but S_π is soluble in CS_2 at −78°. From the deep yellow S_π solution, Erämetsä (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_π fraction, but he used the method of Bartlett (17) to titrate independently different allotropes in a mixture; he discovered that the liquid content is 5.5% S_π at the melting point (261), but that in the frozen melt only 60% of the S_π molecules polymerized, while the other 40% recombined directly to S_λ. Using this observation to recalculate the molecular weight of S_π, he came to the conclusion that this molecule is catenaoctasulfur.

In this review, the name S_π is adopted for the catenaoctasulfur, 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_π is very unstable and polymerizes with S_λ to polymer chains (295). The S_π concentration is calculated at the melting point to be undetectably small, but Schenk (261, 262) obtained 5.5% S_π from measurements of the soluble part in the solid and the melting point depression. Electron spin resonance 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_π, or that the S_π has strong resonance stabilization of the chain. Such a resonance stabilization has been earlier assumed for small molecules (187).

b. ι-Sulfur. A fraction of S_π 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_ω but which supposedly has a different X-ray diffraction pattern. This form is not CS_2 soluble and was called S_ι (97).

c. μ-Sulfur. If liquid sulfur, a complex mixture of allotropes, is poured into ice water or cooled to −78°, 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 α-form or the catenapoly form (S_μ) 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 CS_2, the stable α-sulfur and the S_π dissolve, and an insoluble part remains (73, 148). Both the viscous liquid sulfur and the carbon disulfide-insoluble solid (125, 178) are called S_μ. The yield and the structure of S_μ depend upon the composition of the liquid (T_{start}), the speed with which the quenching is performed (dT/dt), the temperature at which the material is collected (T_{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_α (256), while in another group pure sulfur always leads to 100% S_μ, with crude samples giving up to 60% of it.

The S_μ 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_ρ. The S_μ is unstable at room temperature. The transformation rate into S_α depends upon the temperature, pressure, or stretching, and impurities. Light (61) and the presence of S_α 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 phosphorus can stabilize (289) plastic sulfur over a long period of time. Pure samples have been reported to be metastable below $-29°$ (202) and can exist at room temperature for over a year. The exposure to ultraviolet light or to α-, β-, or γ-radiation enhances the transformation by breaking long chains (204). The samples do not convert completely into the α-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_μ looks very similar to that of S_α. α-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_α and S_μ, but seems to be wrong (223) (see S_ψ). Some authors believe that S_μ 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_μ form. The structure of S_μ is not yet completely known, but it is possibly similar to the structure of stretched sulfur, which will be discussed with S_ψ.

Detailed discussions about S_μ have been published (99, 218, 259, 273–277, 283–285). The terms μ_1 and μ_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_ν is a shorthand name for S_μ (96–98).

e. ϕ-Sulfur. von Weimann (309) discovered that plastic sulfur samples obtained by chilling liquid sulfur from above 250° assume new properties if they are stretched. This material was studied by several groups (67, 199, 235, 298) with the help of X-rays. Neuberger (210) found the symmetry to be C^2_{2h}. 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_ψ and S_γ. 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_γ, which seems to be formed during the stretching. The c-axis of the γ-crystals is assumed to be parallel to the fiber. The S_ϕ can be stored for several years.

f. ψ-Sulfur. The name S_ψ is used for three different sulfur forms. Here it is mentioned only that S_ψ is often taken as a synonym for S_ϕ, but that Neumann (211) introduced the term S_ψ for the crystalline part of S_ϕ.

Prins and co-workers (236) designate with S_ψ the fibrous part of S_ϕ. This is the reverse of Neumann's terminology. The symmetry of the fiber is C^2_{2h}, the same as that of S_ϕ. A closed packed helical structure with a concentric arrangement has been proposed (219, 222, 223), analogous to an α-sulfur structure. This proposal, however, is not convincing since the α-structure mentioned is incorrect. The best present model (83, 235–238, 249, 250, 257, 258) assumes long helices containing $3^1/_3$ 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_ψ 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) indicate the presence of at least ten 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)

TABLE VII
STABILITY RANGES OF DEFINED COLORED ALLOTROPES (198)

Solvent	Sulfur concn., %	Prepn. temp., °K.	Obsd. stability range, °K.	Color	Identified species
Ar		35	35		
Kr	≤ 0.3	4–45	$4 < T < 45$	Maroon	$\geq 90\%$ S_2
Xe		50	50		
Ar, Kr, Xe, or none		35			
	≥ 0.5	45–60	$4 < T < 60$	Violet	S_2 + ?
Ar, Kr, Xe, or none	≥ 1	60–170	$4 < T < 170$	Green	S_2 + ?
None	100	170–240 (?)	$4 < T < 240$	Yellow	$S_\mu + S_\pi$ + ?

solids when he condensed S_λ 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 are 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 $\{\dot{S}\}$, the temperature of the cold wall (T_E), and the vapor composition (T_S). The concentration of unstable particles is roughly proportional to $T_S/(T_E\{\dot{S}\})$.

Despite their complicated composition, most colored forms have a sharply defined stability range which is listed in Table VII. 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 beams of S_2 in decreasing order is: $\alpha >$ plastic > yellow > green > purple.

First S_ω 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. ω-Sulfur. S_ω is here defined as the carbon disulfide-insoluble part of sublimated sulfur. Because of its color, S_ω is also called "white sulfur" (62). This modification is similar to the commercial form "crystex" and "super-sublimation" sulfur (221) and is not a well-defined allotrope. Its properties have been carefully studied, and it was found that it is stable for more than 1 year at STP and for 36 hr. at 88° (63, 64, 67). Bases, such as NH_3, catalyze the conversion of this form into S_α (259). The density lies between 1.834 and 1.95 g./cm.^{3}.

The X-ray data are fairly similar to those of S_μ and S_α (66, 99). This was explained by the presence of S_α impurities on the crystal surface (65), but other authors think that S_ω is a mixture of different forms, partly polymers and partly crystallites, or that S_ω is identical with S_μ, or that S_ω 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 (221). More work is needed before a final answer can be expected, and it is so far not even clear whether S_ω is a pure modification, or whether it contains components identical with S_μ.

The S_ω 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_ω 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.

b. *m*-Sulfur. S_m was isolated from the distillation products of S_ω or through chromatography of red sulfur (98). The S_m has been characterized so far 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 $\leq -78°$, the solid is most probably a mixture and is deep yellow (194–196). It contains a high concentration of S_π. All low-temperature forms convert monotropically into this yellow form at $-100°$.

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 1 week in sunlight suddenly into S_α. 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 reexamination (194–196) proved, however, that the S_2 concentrations 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, −60, and −55°.

g. Green Sulfur. A green condensation product was reported in a liquid air-cooled trap (243) when S_λ was condensed. Green sulfur is also produced if molecular beams of S_2 are slowly deposited upon a surface which is kept at −104 to −78°, or if purple sulfur is heated above 80°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 and the ultraviolet and infrared spectra 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 infrared spectrum. At least four different active species have been observed by their e.s.r. spectra (51–53, 245) during warm-up cycles of this green form. The e.s.r. spectrum is similar to that of the red form obtained if S_α is irradiated at 78°K. (246).

It is not yet clear why this form is green. Rice held the S_π molecule responsible for this color, but S_π is known to be yellow. Another explanation is based upon the similarity of the color effect in colloid solutions. The color changes at −100° into yellow.

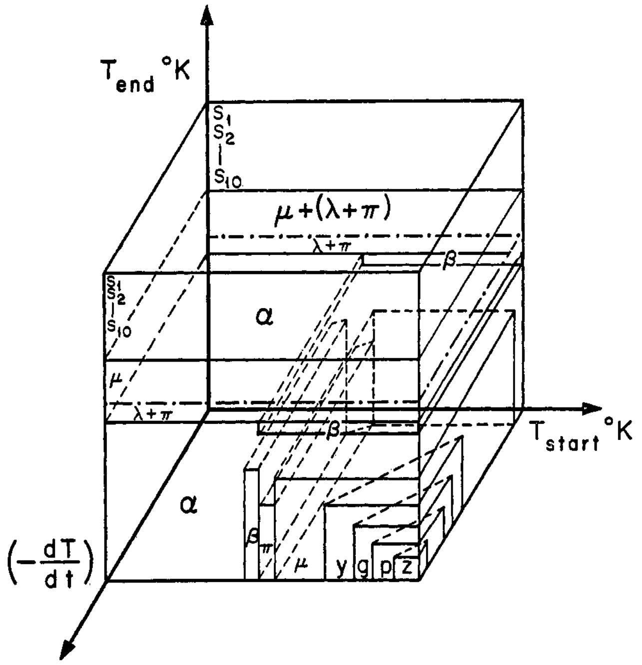

Fig. 2.—Stability of allotropes = $f(T_{start}, -(dT/dt), T_{end})$. This three-dimensional plot shows the stability range of allotropes, estimated as a function of the condensation speed, together with the temperature of the equilibrium sulfur system from which they can be prepared. The various sulfur allotropes to which the symbols in the drawing refer are discussed in section IVC4. The z-form has not yet been observed. At equilibrium ($-dT/dt \ll$), only α and β 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.

h. Violet Sulfur. If a molecular beam of S_2 is slowly condensed on a surface at ≤60°K., a violet-purple solid forms. This solid has two absorption continua in the ultraviolet. At 80°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 VII 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 polysulfoxy acid ions in various oxidation states. The formation of $S\rho$ in acidified thiosulfate solution, for example, can be explained by the following reactions.

$$HS_2O_3^- + S_2O_3^{-2} \xrightarrow{k_1} HS_3O_3^- + SO_3^{-2} \qquad \text{(Eq. 1)}$$

$$HS_3O_3^- + S_2O_3^{-2} \xrightarrow{k_2} HS_4O_3^- + SO_3^{-2} \qquad \text{(Eq. 2)}$$

$$HS_nO_3^- + S_2O_3^{-2} \xrightarrow{k_n} HS_{n+1}O_3^- + SO_3^{-2} \qquad \text{(Eq. 3)}$$

$$HS_nO_3^- \xrightarrow{k_{r,n-1}} S_{(n-1)} + HSO_3^- \qquad \text{(Eq. 4)}$$

If Eq. 3 prevails, long chains will form; Eq. 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 S_8 than for the S_6 and the 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.

$$k_n \gg k_{8r} > k_{6r}$$

$$k_{8r} > k_n > k_{6r}$$

$$k_n \sim k_6$$

All three cases have been observed.

In warm concentrated solutions, a fast pH change leads mainly to long chains which form S_μ. Under mild conditions, the formation of S_λ 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. ρ-Sulfur. Following an earlier suggestion (258), the term S_ρ is used here only for the unbound cyclohexasulfur molecule, and not as a synonym for S_ϵ. The S_ρ molecule is thermodynamically unstable, but it can be preserved over extended periods of time (20), even at 60°, 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°. The S_ρ is then, together with S_λ, extracted with toluene or benzene, and the yield is $\leq 12\%$. On evaporation or cooling of the solution, S_ρ crystallizes as S_ϵ. Such solutions have been studied carefully (17, 20, 21, 22); it was found that S_ρ reacts about 10^4 times faster than S_λ with triphenylphosphine, cyanogen, and the hydroxyl ion. This reaction is catalyzed by traces of H_2S and SO_2. The ultraviolet (22, 243) and the infrared (20) spectra have been studied in CS_2 and broad absorption bands around 2900 Å. and 20 μ have been observed (see Appendix). The structure has been discussed earlier (85, 315).

b. ϵ-Sulfur. S_ϵ is the only crystalline form of the cyclohexa-S molecule S_ρ. It was discovered by Engel (89, 90). The correct molecular composition was, however, reported only much later (10). In a recent publication, S_ϵ has been erroneously considered to consist of long chains (85, 281).

The S_ϵ is better known than the stable S_β form, and is by far the best understood unstable allotrope. The molecular symmetry (S_ρ) is D_{3d}. The environmental symmetry is C_{3i}. The crystal symmetry is C^2_{3i} (84). The lattice constants are (82): $a = 10.818 \pm 0.002$, $c = 4.280 \pm 0.001$ Å.; $a:c = 1:0.396$.

Several authors studied the morphology (78, 80, 120, 121), the crystal symmetry, and other data (50). The melting point of S_ϵ is estimated to be below 100°. A remarkable property of S_ϵ is the density. It is higher than that of any other allotrope so far studied, namely, 2.135 g./cm.^{3}. Each atom has twelve neighbors within a distance of ≤ 3.5 Å. The high lattice stability of S_ϵ becomes evident if the thermal data for the vaporization processes S_α–S_λ and S_ϵ–S_ρ are compared (28). The vaporization entropy per mole of S_6 is higher than that for S_8, and the enthalpy and free energy for this process are nearly equal. Computed per gram-atom, $\Delta S°$, $\Delta F°$, and $\Delta H°$ are, however, all greater for S_6 than for S_8.

The production of S_ϵ from boiling sulfur solution has been claimed, but this seems doubtful since it would necessitate the formation of S_ρ from the S_λ, *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_ϵ crystals convert within a few hours into S_α if the S_ρ is not carefully purified. The pure S_ϵ is fairly stable at 0°. Several authors report that S_ϵ has been found in nature.

c. Red Sulfur. 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 hr. 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 compounds. It has been pointed out in the description of S_π 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. ν-Sulfur. S_ν 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_ω can be prepared by hydrolyzing disulfur dichloride. It is described elsewhere in this report.

6. In Solid Solution

Two cases of sulfur self-solutions have been discussed: 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_π in S_μ. Two cases where sulfur allotropes have been studied in a solid foreign solvent are:

a. Polar Solvents. Sulfur dissolves in ammonium sulfide (139), sulfur trioxide (158), and many other liquids, but the solution is generally accompanied or caused by some chemical reaction. It seems, however, that sulfur does not react with alkali halide melts (144). At 700°, a deep blue solution is observed in a 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 infrared 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_α, 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, often concerning the properties of one single allotrope.

Only four of the over 5×10^5 different sulfur particles have been obtained in pure form: (a) the cycloocta-S (S_λ), (b) the cyclohexa-S (S_ρ), (c) the S_2 molecule, and (d) the S atom. Of these, only the diatomic molecule and the atom are well known. For the hexaatomic and octaatomic molecule, the spectroscopic data are incomplete and inconclusive, and most of the thermal data are unknown. The study of polymers such as S_μ, S_ω, and S_ϕ 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_π, and it is not established what other particles might occur as intermediates in the formation of S_μ and S_ω.

It will, in the future, be possible to isolate and study several of the small molecules, for example, catena-octa-S (S_π), 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_λ and S_ρ a great number of polymorphs will be found. Only polymorphs of S_α have been investigated so far, and the existence of the ten allotropes reported has not always been conclusively proved. Astonishingly, only two forms, S_α and S_γ, have been understood clearly even though S_β is stable and has been investigated frequently.

The colored forms are complicated mixtures of allotropes. Most of them contain S_μ, 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 investigate systematically 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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VI. APPENDIX

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

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 (127) 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

Sulfur vapor is discussed by the following authors: 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, Ciborowski (55) 1949, Turrell (300) 1947, Klemm (167) 1941, Neumann (211) 1934, West (313) 1929, and Lewis (184) 1911.

D. SULFUR COMPOUNDS AND REACTIONS OF ELEMENTAL SULFUR

Surveys. Pryor (239) 1962, Schmidt (263) 1962, and Kharasch (Ed.) (84) 1961.

Special Problems. Feher (105–109) and 61 other contributions up to 1963, Nair (209) 1963, Schmidt (264) 1963, Kowalski (174) 1962, Donohue (81) 1961, Foss (112–114) 1949–1960, Koros (172) 1960, Kowalski (173) 1960, Pryor (238) 1960, Fredga (116) 1958, Ingrahm (158) 1957, Garcia-Fernandez (123) 1958, Abrahams (1, 2, 4) 1953–1956, Skirai (268) 1951, Aynsley (11) 1935, and 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, Dufraisse (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 Zheludev (321) 1962, Dean (72) 1960, Chetkorov (54) 1960, Dorabialska (86) 1957, Fridkin (118) 1956, Sokolova (282) 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.* (London), **83**, 330 (1964); *Can. J. Phys.*, **41**, 419 (1963); **40**, 377 (1962)], and Y. Tanaka and M. Ogawa [*J. Chem. Phys.*, **36**, 726 (1962)]; a survey of earlier studies is listed in B. Rosen ("Données spéctroscopiques 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) 1871–1872.

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 (302) 1940, Venkateswaran (301) 1936, Barnes (15) 1932, and Taylor (292) 1927.

Solutions. Clark (56) 1963, Bartlett (17–22) 1956–1961, 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, Pistorius (224) 1959, and Venkateswarlu (302) 1940.

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