UCRL-10768

University of California

Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

UNSTABLE SOLID ALLOTROPES OF SULFUR

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to Chemical Reviews

UCRL-10768

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

UNSTABLE SOLID ALLOTROPES OF SULFUR

Beat Meyer

AUG 1963

Unstable Solid Allotropes of Sulfur

CONTENTS

ABSTRACT ii

I. Introduction 1

II. Nomenclature 3

III. General Data About the Element

1) Sources 4

2) Reactions 5

3) Purifications 8

IV. Allotropes

1) Intra and Inter Molecular Allotropy 12

2) Stable Allotropes 16

3) Unstable Allotropes 19

A. From S_α 19

B. From S_λ in solution 20

C. From the melt 26

D. From the vapor 33

E. From compounds 39

F. In solid solution 43

V. Conclusion 45

VI. Appendices

1. Nomenclature 47

2. Molecular Data 50

3. Polymorphic Forms 52

A. Stability of Low Temperature Forms

4. Selected Thermal Data 56

5. ESR Data 59

6. References for Related Problems 60

VII. Bibliography B-1

ABSTRACT

This report is a preliminary review of the allotropic forms in which elemental sulfur has been observed below 30°C. The nomenclature, purification, preparation and many properties of 33 molecules and modifications are discussed in the form of a guide to the extensive but uncoordinated literature in this field.

I. INTRODUCTION

More than 30 sulfur allotropes have been reported and a large amount of detailed information has been accumulated during the last 150 years, but many basic properties of sulfur are not yet known. Much data is so inconclusive or contradictory that it is difficult to establish the present status of our knowledge, and an inconsistent nomenclature hampers the coordination of observations. We find three causes for this situation:

1) Many authors assume that sulfur, being an element, should have a simple behavior pattern. Based upon this assumption, the interpretation of experimental data concentrates frequently upon expressing the observations in a very small number of parameters. This approach is wrong because the behavior of sulfur is complex and capricious and can only be reproduced in a well defined system. It has been observed, for example, that an allotrope can show different characteristics if it is studied by the same method, but by different investigators. It is tempting in this case to doubt the reliability of some of the observations and to select a single report as describing the situation correctly. However, the true cause for such a confusing situation is frequently the omission of a parameter. In the example cited above it is the aging of the sample, the time. In other cases minor disturbances such as sunlight,[72] recrystallization, etc., can cause the formation of a variety of allotropes which all have similar stability. The half life of many of these forms can be in the order of the time required for investigation and the sample changes its composition slowly under the hands of the investigator. It is hard or impossible to isolate one single allotrope in such a multi-component system. Often a mixture is so complex that it can be mistaken for a new homogeneous form.

2) Impurities are another source of confusion: the properties of sulfur depend critically upon contaminations.[13,20] Selenium,[265] hydrocarbons[225] and many other impurities react with the element already under mild conditions and cause time dependent observations. A satisfactory method for purifying S was developed only in 1943.[12,13] 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 which are uncorrelated to existing data, and, as a matter of fact, the same information has been frequently printed twice, but in different terminology. This situation could be improved if a survey of this field would be available.

This report represents a short and preliminary attempt to review our present (June 1963) knowledge about solid sulfur allotropes. In this context sulfur is considered solid at or below standard temperature. Wherever possible a systematic relationship between formation, structure and the origin of the different alltropes is indicated. It seem appropriate to refer occasionally to old literature since the work of recent years has confirmed some old observations which had been considered incorrect for a long time.

II. NOMENCLATURE

The lack of coordination of knowledge about the different sulfur allotropes shows clearly in the nomenclature. A systematic nomenclature does not exist[100] and there is not one generally accepted name for any allotrope. As a result of the many criteria which have been applied to the labelling of sulfur, most forms have several different names. 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 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 stand sometimes for molecules, (e.g. $S\lambda$), sometimes for modifications (e.g. $S\alpha$) or even for complicated mixtures (e.g. $S\mu$) either in the liquid or in the solid. A further difficulty encountered in the literature is the frequent renaming of allotropes with new or previously used symbols. Such a case of accidental or purposeful name-shifting is, for example, $S\mu$ for which we list here only a few synonyma: $S\gamma$, S_x, S_n, S_ν etc.

We will make use of the Greek letter system in the following and add other names only where considered important. Appendix I lists the common names of some allotropes.

III. SELECTED GENERAL DATA

The general properties of elemental sulfur and many of its modifications are reviewed in references cited in Appendix VI but the various allotropes differ so much in their behavior that general and over-all data have only limited value. It is the purpose of this chapter to indicate the sources and the reactions of the contaminations and then to mention the best purification methods.

1) Sulfur Sources

Commercial sulfur is derived from two sources. First, it can originate from the vast natural deposits of the element, and second, it can be formed, generally as a byproduct, from compounds. Until 1914, most commercial sulfur came from volcanic sources. This sulfur forms large crystals (S_α) which are yellow-brownish, due to a rather large impurity concentration. A material containing up to 99.9% sulfur is now produced by the Frasch[109] 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 As, Te and Se. Commercial sulfur is generally a mixture of different allotropes, containing mainly S_α and S_μ. Beside 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 and contain the impurities mentioned above, and often in addition dust or solvent traces. Some allotropes form only during the decomposition of sulfur compounds. In the Laboratory several methods are used for precipitating the element.

Probably the four most used methods are:

1) S_2Cl_2 + H_2O = $\{S_x\}$ + ...

2) $HS_2O_3^-$ + H_3O^+ = $\{S_x\}$ + ...

3) NH_4-S_x-NH_3^- + H_3O^+ = $\{S_x\}$ + ...

4) HS_x^- + SO_2 = $\{S_x\}$ + ...

The mechanisms of these reactions[66,225] (see Sec. IV, 3, E) involves always 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 preparation method has been reported by Rickert,[233,234] who has recently developed a sophisticated electrolytic cell from which sulfur can be released in precisely measured amounts.

2) Reactions

Sulfur reacts with almost any element, [illegible]

We refer here however only to some selected reactions with impurities. For a more complete discussion, see Ref. 117, 133, 225.

Bartlett[17-22] has demonstrated that the reactivity of sulfur depends very much upon the molecular structure, but so far only few forms have been studied. The bulk of observations reported refer to unspecified mixtures, the composition of which can only be guessed at from the reaction conditions and the reaction media. Often allotropic transitions are involved in a reaction mechanism, and it is hard to isolate the rate determining species. Only little is known therefore about the reactions of sulfur.

The use of radio-active isotopes[43,172] facilitates the study of reaction

mechanisms often, but relative little use has been made so far of this method.[6,17,147]

A) The pure element:

A great variety of intra and intermolecular arrangements have such a similar stability that even careful handling can bring about a transformation. Such allotropic transformations form the body of this report and will be discussed in Section IV.

B) With aqueous solutions:

The reaction of the element has been studied under different conditions.[164] The mechanism is not yet known,[225] but the products are highly water soluble and it is probably 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.

C) In organic solvents:

Sα and almost all allotropes but Sμ are fairly soluble in Ethyl-alcohol, benzene, toluene, CS_2, CCl_4, $CHCl_3$ and many other solvents.[150,303] 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 they often form compounds with sulfur: acetone, for example, gives with sulfur a deeply colored solution, and alcoholic solutions always smell from H_2S, the formation of which is strongly enhanced by light.[301] Polysulfides are also detected in hydrocarbons and if sulfur is dissolved in cumene and heated to ~112°. The last reaction involves probably open chains of the elements.[225] Such chains have free radical character[188] and make sulfur an excellent polymerization inhibitor[224,278] for polystiryl,[18] polyvinyl, polysulfenyl and many other substances.

Nucleophilic reactions: Even weak bases attack the sulfur molecules in solution and Ph_3P^-,[17] CH^-,[18] and $[(CH_3)_2Si]_2NN^a$,[250] for example, open the octa-S ring and degrade[19] the chains under formation of the corresponding S-compounds. Ammonia and triethylamine, however, react with the S_8 ring only in the presence of arylsulfide.[20] The reaction with arylimines is not yet clearly understood.

OH^- reacts with sulfur at 100° quickly and leads to the formation of thiosulfate which then decomposes on further heating into sulfate and sulfite. At temperatures above 200° the latter ions are formed directly from the element.

The most important reaction for our discussion is that of the SH^- ion. The SH^- or S_xH^- is often present as 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. A mixture of elemental and sulfide chains can hardly be separated. This is responsible for many of the confusing and contradictory observations assigned to the pure element. (See, for example, data on viscosity of liquid S_μ.[12,97])

If sulfur colloids are stabilized with NH_3, 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.

D) Reactions at elevated temperatures:

During the preparation and purification process sulfur is either melted or evaporated. It reacts under such conditions with air [165] and almost any impurity. Organic contaminations decompose slowly and form mainly SO_2 which evaporates,[191] H_2S which is highly soluble in the melt,[254] and carbon,[291] which deposits together with a mixture of insoluble material.[12] Such carbon deposits are black and a sensitive indication for the presence of impurities

(see page 11). Similar spots remain after the distillation of sulfur from glassbulbs.[132] They are believed to come from the formation of SiS and other sulfides on the glass surface which is quite reactive at the boiling point of sulfur. No reaction is observed when the element is vacuum distilled. Quartz glass does not react with sulfur vapor below 1000°C. Black deposits formed in pure sulfur have also been explained by assuming a new modification.[256] (See "black sulfur").

E) Other reactions:

Sulfur forms dark blue, quasi-metallic solution in ammonia[133,175] and other liquids. With oleum or SO_3 a red product is precipitated, which is believed to be $\{SO_3 \cdot S_x\}$.[151] In alkalihalide melts almost any color can be produced[137] and remains after trapping for a long time.[182] Some of these solutions are paramagnetic[151] and contain different active species, but only very little is known about such systems.

Sulfur and Selenium can be interchanged in crystals[138,139] and chains[67] but not in rings[265] and the Se-S system has been studied with the help of radio active isotopes in the liquid[265] and gas[71] phase.

3) 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 .1% contaminations cause already an inconsistent viscosity of the melt,[13] and .002% of SO_2 catalyze the reaction with triphenylphosphine.[21]

We will list here some methods which can be chosen to purify sulfur to the desired grade:

A) Conventional methods:[132]

The most commonly used and most unsatisfactory purification procedure is to recrystallize sulfur from organic solutions. In this way one can obtain beautiful crystals,[302] but they contain besides solvent inclusions still more than .3% H_2S and .08% SO_2.[21] The CS_2 inclusions in a Sα crystal grown in this way have lead to a wrong assignment of the infrared spectrum.[271]

Often sulfur is separated from insoluble impurities by filtering through glass wool. This process does not remove any soluble impurities, but 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 oxydized organic contaminations.

The distillation of sulfur under atmospheric pressure cannot be recommended. The pyrex containers react at elevated temperature with the element, and many impurities distill together with the sulfur, and react to form new compounds.

B) New Methods:

During recent years two conventional methods have been sophisticated for the production of a very pure element. The first is zone melting and was used[178] to grow crystals of Sα and Sβ. The second is an electrolytic method which was developed by Rickert.[233] He designed a Pt-Ag-AgS-AgI-Pt cell from which sulfur can be released quantitatively.[234]

Erämetsä[91] has proposed the use of Chromatography for the purification and separation of sulfur allotropes on Al_2O_3 and silica gel columns with CS_2 as solvent, but the reaction of sulfur with the column material[20] seems to

devaluate this otherwise elegant method. Schenk and coworkers[248] observed a very small f-value for the separation of different sulfur allotropes on paper with a CS_2-ROH mixture. Mass spectroscopy has been applied for the enrichment of isotopes and the separation of pure sulfur in small quantities.

C) Classical Methods:

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

This method has been widely accepted and most data reported since 1943 has been obtained from samples purified in this way. There are two drawbacks to this method. First, the material is saturated with atmospheric gases each time it is filtered, and second an appreciable amount of Mg-salts,[193] .02% H_2S and .006% SO_2 [21] are in the melt. If, however, the sulfur is vacuum distilled after the preliminary treatment, both disadvantages are removed.[180]

b) Murphy, Calbaugh and Gilchrist[193] use the following method. Sulfur and sulfuric acid are heated to 150°C, and nitric acid is slowly added over a period of 6 hours. The melt is then cooled and washed and heated under reflux with Helium or dry nitrogen bubbling through it. The sample is afterwards cooled again and transferred into an ampulla. Water is added and the ampulla is sealed under nitrogen and heated to 125°C. The last process is repeated three times and the sulfur is then outgassed at 10 mm Hg Nitrogen and finally sealed in an ampulla.

The authors indicate the testing methods used to determine the concentration of contaminations. The above procedure yields a high purity material on which the present values[295] of the melting points of sulfur are based.

(See App. VI). 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,[164] which can only be removed through long and careful outgassing. This method has therefore to be combined with vacuum distillation to give the best result.

c) A very simple and efficient method has been developed by v. Wartenberg.[290,291,292] Sulfur is melted in a loosely covered roundflask and a red glowing quartz heater (~700°C) is inserted into the melt. A carbon deposit is formed on the heater and should be removed daily. After one week the flask is connected with a pump-system and the sulfur is under vacuum distilled and sealed into an ampulla.

This purification method is based upon the following processes. During the long heating time all material is brought into contact with the heater. The impurities either decompose completely and form volatile products, which escape, or insoluble carbon, which deposits on the heater. Skjerven[255,256] proposes to bubbling SO_2 through the melt to enhance the decomposition and removal of H_2S. In the final vacuum distillation, the sulfur is separated from the insoluble residue and outgassed.

This last method seems to us the best way for purifying sulfur.

Methods for a quantitative determination of impurities are given by Murphy[193] and many others.[13,132] Several tests indicate quantitatively 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 heating the yellow color of the solid is reproduced. As little as .04% Oil produces black spots in the liquid. Precipitation comes from Metalsulfides, dust or silicosulfides.

IV. ALLOTROPES

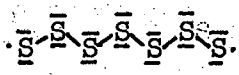
1) Berzelius[30] introduced the term allotrope for the different forms in which an element can exist. Smits,[264] de Leeuw,[173] Capisaroff,[56] Hartmann[142] and many others,[54,168] have developed theories of allotropy. We will take here a molecular point of view and distinguish in between two sources for the variety of the appearance of sulfur; first, the different ways in which the atoms can combine into molecules, and second the different manner in which the molecules can build up crystals. We will discuss these intra- and inter-molecular arrangements separately.

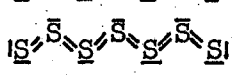
A. Molecular Variety

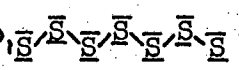
Sulfur forms rings and unbranched chains. Molecules with 1 to 10 atoms have been observed in sulfur vapor.[26,306,33] In liquid S, at a temperature between 159° and the boiling point (444.6°),[176] polymer chains predominate. The average chain length varies in between 8 and 10^5 atoms.[279] At the melting point the liquid is a mixture of catena-octa-sulfur (S_π) and cyclo-octa-sulfur (S_λ). By sudden cooling all of the molecules mentioned can be trapped as solids, but only cyclo-octa-S, S_λ, is stable at room temperature. All others convert into the λ-form with a half-life in between about a millisecond and one year.

The comparable stability of a variety of different molecules is typical for sulfur. This has to do with the electron configuration ((Ne)$3s^2 3p^4$) which is similar to that of Oxygen. Sulfur has however a full Neon shell and empty d-orbitals available. It is thus generally assumed[3,94,204] that sulfur can activate these d-orbitals for the formation of dσ hybrids and dπ bonds. This assumption requires a break-down of the octet rule, and it is

believed that both electron octet and decet (for example in CS_2) configurations can exist. Large chains have biradical character[118,120] and therefore octet structure, (I) while small chains might be stabilized by resonance.[177,248] (See however S_π)

I.) 

II.) 

III.) 

It has been indicated,[25] however, that the promotion energy for a decet might be much larger than the energy gain through a $dp\pi$ [179] bond. The ionic structure[209] (III) has not been observed.

Pauling[204] discussed the stability of the different molecules in terms of the bond distance, the valence angle and the dihedral angle. Appendix II lists recent molecular data for cyclo-octa, cyclo-hexa and catena-poly-sulfur and some average values deduced from various sulfur compounds. The cyclo-octa molecule is the most stable one and is assumed to be torsion free.[204] The stability of other molecules can be expressed through the bond stain, but Pauling's values seem to be too high. If one uses recent data (see App. II) and computes a simple semi-empirical MO-LCAO model as proposed by Bergson,[25] the torsion energy of cyclo-octa-S ($S\lambda$) is not zero, but is only about half as big as that for the cyclo-hexa-S (S_ρ). Recent data for catena-poly S and for cyclo-octa-S indicates similar values and makes it probable that they are both nearly torsion free.

The symmetry of cyclo-octa S (S_λ) is D_{4d}. The molecules 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 1.15Å , 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, App. II). The cyclo-hexa molecules (S_ρ) forms a puckered ring with D_{3d} symmetry. The bond distance is 2.057 Å. The open chains of catena-poly-S (S_μ) form helices. Their structure is not yet completely known, but it seems that a unit cell containing ten atoms in three turns is part of some superstructure.[223] This structure will be further explained together with S_μ. For other molecules, such as cyclo-tetra S and cyclo-deca S, structural data have not yet been measured. (See however ref. 177) These particles are very unstable and are not important for the discussion of the properties of solid allotropes.

B. Intermolecular Structure

The S molecules exert only short range London forces upon each other. Sulfur therefore forms covalent crystals which have a low lattice energy. Optimum energy in such a solid can be accomplished by different intermolecular arrangements: each atom can either have few but close neighbors, each giving a high individual interaction energy, or have a high number of neighbors at an intermediate distance, each giving rather a low interaction energy. This explains why sulfur can exist in many fairly stable polymorphs. (For the 10 polymorphs of Sλ, see IV,3,B.) It is interesting that of the two well known allotropes S_ϵ (built up from unstable cyclo-hexa-S (S_ρ)) has a higher number of close neighboring atoms than Sα, which consists of the stable Sλ. The first allotrope has, therefore, a higher density and a more stable lattice than the latter.

Table IV,1 indicates the order in which the different forms will be discussed.

TABLE IV,1 PREPARATION OF ALLOTROPES

The stable allotropes (S_λ, S_α, S_β) are formed from all other forms within a time varying from ~ 1/1000 sec to 1 year. (See Sec. II) The unstable allotropes are here listed corresponding to their preparation method.

Listed in Section	Starting Material	Main Components	Unstable Allotropes	Stable Form (STP)
3A	Solid Sα	Cyclo-octa-S (Sλ)	a) metallic-S b) irradiation-S	In solution, λ In lattice, α
3B	Sλ-solution	Cyclo-octa-S (Sλ)	a) photo-S, b) γ, c) ζ, d) η, e) δ, f) ν, g) o, h) ξ, i) τ, k) æ	
3C	Liquid sulfur	Cyclo-octa-S (Sλ) Catena-octa-S (S) Catena-poly-S (Sμ)	a) π, b) ι, c) μ, d) ν, e) φ, f) ψ	
3D	Sulfur vapor	Sx: 1 < x < 10	a) ω, b) m, c) yellow, d) black, e) purple, f) red, g) green, h) violet	
3E	Compounds	Sulfides and sulfoxy-acids as intermediates	a) ρ, b) ε, c) red, d) m, e) ν	
3F	Vapor and solvent		a) blue, b) maroon	

2) Stable allotropes:

At STP the stable sulfur allotropes are the cyclo-octa-S (S_λ) molecule and the S_α crystal. Between 95.3°C and the melting point S_β is stable. There are indications that other enantiotropic forms might exist, but no other stable allotrope has yet been observed.

A. S_λ

The term S_λ was introduced by Berthelot,[29] and it is the short name for the free Cyclo-octa-S molecule. The properties of this particle have been discussed above. Erämetsä[85-93] uses the name S_λ for 'the crystalline part of the melt'. This definition seems to refer to the fact that most crystalline modifications of sulfur are built up from this molecule.

The S_λ molecules is stable in solution and occurs in the melt and the frozen liquid. Kuester[169] discovered that S_λ is at higher temperature in equilibrium with S_μ. It was later demonstrated that S_π is formed as an intermediate in this reaction. The equilibrium $\lambda \leftrightharpoons \pi$ is photosensitive 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/mol (See App. IV). In liquid sulfur the enthalpy of the over-all reaction is 7 kcal/mol, 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 .004% H_2S or .002% SO_2 catalyze 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. (See Sec. 3B) The UV,[17-22,53] IR[16] and Raman[124] spectra of S_λ have been only partly analyzed.[211,251]

B. S_α

S_α is the only stable sulfur modification at STP and all other allotropes therefore convert ultimately into it. This modification is well known[160] and will not be fully described here. Broensted[44] discovered that the α-crystals contain $S_8(S_\lambda)$ molecules.[199] Burwell[46] determined the crystal structure, which has since been re-studied carefully.[3,5,57,282] The symmetry of the crystal is D_{2h}^{24} -Fddd, the symmetry of the molecule is D_{4d} and the environmental symmetry is C_2-2. One hundred and twenty eight atoms form the unit cell (Fig. 1-a) The lattice constants[198] are, after the most recent measurement,[55] six significant figures:

a = 10.44349 Å

b = 12.84009 a: b: c = .81335 : 1 : 1.9032

c = 24.43665

The α-crystals often grow along unusual surfaces; for example, along an axis which is parallel to the (101) face diagonal.[86,87] Therefore microscopic observations of the crystal growth in solutions (see 3B) often lead to the discovery of different looking crystals, which have been frequently mistaken for new modifications. (e.g. see S_γ)

The melting point of S_a is 112.8°, but above 95.31°C the stable modification is S_β. (ideal[126] mp 119.3) The 'natural' melting point of sulfur is 114.6°C. Melting points are generally studied by cooling down liquid sulfur. The transformation of β into α has been studied extensively.[94,143,295] The enantriotropic equilibrium $\alpha \leftrightharpoons \beta$ has a $\Delta H_{368°K}$ = 401.7 j/g. Das[62] re-examined this reaction and confirmed the fast conversion of undercooled S_β into S_α, but discovered that overheated S_α is converted only very slowly into S_β.

It seems that the formation of S_β from S_α has been studied rarely and this strange behavior cannot yet be explained. The self-diffusion of sulfur in S_α has been studied by Cuddeback.[57] The UV, IR and Raman spectra of this modification have been well studied. (See App. VI) The reactions of S_α and the conversion into other allotropes are discussed elsewhere. (page 19)

C. S_β

S_β was discovered by Mitscherlich,[189] and has since[240] been often studied,[158] but there is still a mysterious[199] lack of information about this allotrope which is stable in between 95.31°C and the melting point. It is found in nature and it is formed whenever sulfur solutions or liquid sulfur crystallize within this temperature range. Below 95.3°C[143,146,147] S_β converts in S_α. The equilibrium of these two forms has been well studied[94] and phase diagrams for S_β and S_α and the heat of transformation ($\Delta H_{368°K}$ = 401.7 j/g) are included in almost any Physical Chemistry textbook. Das[62] has studied this equilibrium by observing S-crystals packed in a thin cellophane film and has found that overheated S_α converts so slowly into β that this transformation cannot be observed. The 'ideal' melting point of S_β is 119.3°C (compare Dufraisse: 122. + 0.5°C). 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'[125] melting point of S_β to be 114.6°C. The stepwise disentangling of this curious behavior of the melt will be discussed together with S_π.

Big crystals of S_β can be easily grown from boiling organic solvents.[302] The symmetry of S_β was determined by Burwell:[46] C_{2h}^{25} - $P2_{1/a}$. Forty-eight atoms (6 S_λ molecules)[199] seem to form a unit cell with either

a: b: c = .99575 : 1 : .99903 or

.994 : 1 :1.005 , but the details of the structure are not yet understood. Some x-ray data[289] do not show any difference in between S_α and S_β while others indicate that the S_λ molecules rotate freely and that at least two of them are centro-symmetrically stacked. The density of S_β is between 1.96 and 1.93 gr/cm^3, which indicates a looser packing of S_λ molecules than in S_α.

3. Unstable Allotropes

We will now deduct the various allotropes by exposing stable sulfur forms under different conditions to various treatment. (Table IV 1). Several parameters are needed for the determination of an unstable sulfur system. Some of the most important ones 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.

A. Allotropes formed from S_α:

All the conversions of this allotrope which have so far been observed, involve a change in intremolecular structure, generally a transformation of S_λ into S_π or $S\mu$ chains, and transformations of $S\alpha$ into polymorphic forms, such as $S\beta$, have not yet been observed. The possibility of enantiotropic transformations $\alpha \leftrightharpoons \beta \leftrightharpoons \gamma \leftrightharpoons \alpha$, is discussed in Refs. 142-147.

a) Metallic sulfur - Bridgeman[41] exposed S_α to static pressures of up to 100,000 atmospheres, but no new properties or new forms could be observed. Hamann[65,140] and co-workers applied dynamic pressures of up to

230,000 atmospheres (T~1000°K) to S_α samples and observed a low electric resistance. They proposed a metallic form to be responsible for this observation. It is not clear whether such a form really exists, and what its structure and properties would be.

b) Irradiation Sulfur - α, β, and γ radiation[73,134] can break the S-S bond. Thus, the cyclo-octa-molecules (S_λ) are cut into catena-octa-sulfur (S_π) and possibly even into smaller fragments. At STP, the recombination rate of all these unstable particles into S_λ is so high that only 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. It has been observed that 75 mC of β radiation, 200 mR of α and 600 w of γ radiation can consume small S_μ samples within an hour.[192] At -29°C S_μ (catena-poly-sulfur) is metastable.[190] Below this temperature small chains formed through irradiation can recombine to a mixture of S_λ and S_μ, and at still lower temperature other particles become metastable. Very few experiments have so far been performed with enough irradiation[69,288] to produce substantial amounts of such unstable components. Rice[232] exposed S_α to 40MR of γ radiation and observed a red color. Other authors discuss the electric conductivity[288] of such samples. Dhar[72] believes that the sulfur bonds in S_α can even be broken by ultraviolet light.

Bartlett[17] and other authors used the name irradiation-S as a synonym for photosulfur (See IV,3,B,a).

B. Allotropes crystallizing from solutions of S_λ.

Sulfur is soluble in many organic solvents. At STP a stable solution contains cyclo-octa-S (S_λ). (For unstable forms see "photo sulfur".) 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 which all contain S_λ molecules. In a crude way, we can describe the conditions for the formation for different solids by comparing the precipitation rate ($\{\dot{S}\}$) with the rate of the lattice growth of S_α ($\{\dot{S}_\alpha\}$). We shall discuss here three cases. First, whenever $\{\dot{S}\} \leq \{\dot{S}_\alpha\}$, the α-modification is expected to crystallize. The higher the difference is between the two gradients, the bigger will be the size of the resulting alpha crystal. Second, in the extreme case, $\{\dot{S}_\rho\} \gg \{\dot{S}_\alpha\}$, no crystals will form at all, and the sulfur will precipitate in amorphous form. Third, if $\{\dot{S}_\rho\} \geq \{\dot{S}_\alpha\}$ crystals will nucleate in many places and in a variety of structures wherever some kind of lattice energy can be gained. The crystal growth will therefore be irregular, and not discriminate against unstable symmetries such as S_γ for example. All methods for the preparation of unstable crystalline allotropes are aimed at realizing case three. In this case many different allotropes are formed simultaneously because the concentration changes during the crystallization. Often, rubber or other material is mixed together with a solution to increase the viscosity. This trick reduces the difussion and makes locally high concentration gradients possible and makes energy gains possible through the formation of unstable lattices in isolated pockets. The unstable lifetime of the crystals can be quite high in such solutions because they are not dissolved in favor of the growth of neighbor nuclei with higher stability.

This simplified model explains not only the formation of unstable modifications, but also the observation that such samples consist of a mixture of small crystals with different symmetries. These allotropes or polymorphs

are not stable and slowly convert into S_α. Because of the small size of the crystals such a system can often be observed only under a microscope. Many studies of crystallizing solutions in sulfur have been made,[45,149,161,85,93,162,163] and a great number of allotrope have been reported but it has been repeatedly pointed out that many "new" forms might only be special crystals of S_α[86,87,221] which grow along an unusual lattice face. These allotropes, which all are polymorphs of S_α and have probably the following stability order:[132]

$$\alpha > \beta > \gamma > \zeta > \eta > \xi > \delta > \vartheta > o > \tau > \varkappa$$

a) Photo-Sulfur - Lallemand[170] discovered that sulfur solutions become cloudy, if they are exposed to light. Such suspensions[82,227] of insoluble sulfur in a sulfur solution are called photosulfur. Wigand[300,301] studied the photosensitivity of allotropic forms extensively and determined thermal data with a calorimeter, but his results have been overlooked and most work since does not take into account the important influence of light. See Ref.

Bartlett[17,22] found that photosulfur is more reactive than S_λ and Erämetsä[88,89] recently restudied the influence of light on the formation of different allotropes. It seems that the S_8 ring is broken under the influence of light. The resulting biradical then attacks other rings and initiates other secondary reactions, in which the solvent often is involved. Photo-sulfur is produced if S_λ in CCl_4 is exposed to light[104] but the yield is higher if the solution is irradiated with an UV pressure lamp. Many authors report that the formation of photo-S is reversible, but alcoholic photo-S, for example, smells from H_2S. 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 H_2S[21] and other secondary molecules is

responsible for many reactions of photo-S.

b) γ-Sulfur - This allotrope was discovered by Spica[270] and Gernez.[128-130] The brilliantly glittering crystals[237] which grow in thin sheets[240] are also called Mother-of-Pearl and nacreus sulfur. For other synonyma see Appendix I. The crystal symmetry is probably C_{2h}^{4}-P2/$_h$, with the eight cyclo-octa molecules stacked in a 'sheared penny roll'[138] formation (Fig. 2), but C_{2h}^{1}-P2/m, C_{2h}^{2}-P-2$_{1/m}$ and C_{2h}^{4}-P2/h [138] have also been proposed. Many contradictory values for the lattice constants appear in the literature:

a: b: c =	.646	.706	
a: b: c =	.0649 :1:	0.645	a = 8.57 or 8.50 (275)
	.658 :1:	0.6321	b = 13.02 or 13.16 (198)
			c = 8.23 or 9.26 (138)

β = 112°54' and
124°49'

other older data[138-139] have been excluded. The melting point of this allotrope is 106.8°C, 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 hours of x-ray examination. α-crystals catalize their transformation and can reduce the life-time of the γ-form to 1/2 min.[145] Above 75°C β-sulfur is formed quickly. The transformation rate has been studied by Hartshorne.[144,147]

According to several reports, γ-crystals have been found in oil wells[274] and as Rosickyit mineral.[252] γ-sulfur was proposed as a component in plastic sulfur (see S_μ). The γ-allotrope can be prepared after the following methods; through condensation of vapor; from an undercooled melt at 90°,[298] from an undercooled solution of sulfur in benzene, toluene or Ethylalcohol, by evaporating an alcoholic solution of sulfur at 70°,[194,199] and spontaneously from O-sulfur. γ-sulfur can be obtained also during the

production of the element from compounds. If K_2SO_4 saturated solutions of potassium sulfate and sodiumthiosulfate are carefully combined and diffuse slowly into each other, if ammoniumpolysulfide in an alcoholic solution oxidizes slowly in air, and if precipitated sulfur dissolved in a mixture of alcohol and carbon disulfide slowly evaporates at room temperature.

c) ζ-sulfur - Korinth[161-163] found monoclinic rhombic (?) crystals of this allotrope which are stable for about half a day. ζ-sulfur is less stable than γ, but more stable than S_δ.

The ζ-allotrope crystallizes together with δ and spontaneously from δ, and in the presence of Se from CS_2 solutions, or from other solvents, preferably in a mixture with a rubber solution.

Erämetsä[86,87] indicated the similarity of this form, to α-crystals of unusual growth. The existence of this form has not yet been conclusively shown, and the crystals could even be due to an impurity.

d) η-sulfur - Korinth[161] observed hexagonal-monoclinic (?) crystals of S_η during the preparation of delta-sulfur from rubber solutions containing sulfur and selenium. Erämetsä has repeated the experiments and obtained the same form which has a lifetime of 10 minutes. The η form is an isomorph of Se.

The data on this modification are inconclusive. Both an impurity and a coprecipitation of Se/S could be responsible for the formation of such crystals.

e) δ-sulfur - Muthmann[194] listed S_δ as the fourth sulfur allotrope. This form is very unstable and has not yet been conclusively described. It could be identical with one component of 'Brauns' sulfur. The crystals have been studied by Henkel,[149] Smith,[263] Strunz[274] and Erämetsä.[93]

The symmetry of this hexagonal (?) form could be either C_{3i} or $C^2_{3i-R_3}$.

The crystals can be prepared in mixture with α and γ by oxydizing an alcoholic ammoniumpolysulfide solution at ≤ 15°C 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. [illegible]

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

f) $S_{\gamma\!\!\!/}$ - $S_{\gamma\!\!\!/}$ was first observed by Korinth.[161] This allotrope was recently restudied[86]. It crystallizes from a boiling solution of fenchenon, a-pinene and nitrobenzene. The yield is enhanced by the presence of a solution of rubber in CS_2. The ditetragonal bipyramids have a:b = 1 : .46801.[161] The crystals are unstable and dissolve after about one minute and S_γ, S_β and finally S_α are formed.

g) o-sulfur - Erämetsä[93] observed the formation of a new crystal, S_o, when he evaporated solutions of S_δ. This form is characterized by an extremely low light refraction index. It converts within 2-3 sec. into S_γ, and is the most unstable polymorph known.

h) S_ξ - Korinth 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) S_τ - S_τ crystallizes in about one of 1000 experiments if sulfur solutions of o-Xylol or menthenon are boiled. This form consists of cubic crystals which can exist for several hours.

j) Brauns-Sulfur - Gernez and Quincke identified this form as a mixture of S_α and S_ϕ.

k) $S_\varkappa$ - 1) Henkel[161] discovered this fairly stable allotrope. Erämetsä[485] reports the best yield for it by saturating a sulfur solution

of o-Xylol at the boiling point. The crystals have such a high refraction index that they appear to be black in transmission and white in refraction.

2) Prins[119,221] described $S_{\varkappa}$ as occuring in frozen liquid, later he identified it as a mixture of $\alpha + \gamma$.

C. Allotropes Obtained 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. A list of references for the liquid phase is given in App. VI. For further discussion, see Refs. 157, 217, 219, 243, 244. At the melting point cyclo-octa-sulfur is in equilibrium with catena-octa-sulfur (S_{π}) which then polymerizes with S_{λ} into unbranched chains ($S\mu$). At 159°C[258] the polymerization increases so sharply that $S\mu$, before a solvate, suddenly becomes the solvent. Most properties of the melt have a strong discontinuity at this temperature. Only the color does not follow this trend but changes instead smoothly[116,171] from a pale yellow at the melting point to a dark, deep red[156] at the boiling point. The molecular variety of liquid sulfur has been repeatedly discussed,[262] and the viscosity,[12,13,97,98] the specific heat,[36,102,174,297], the heat conductivity and density[157,283] have been measured. Several authors[95,215] have explained the polymerization process which was recently formulated in a very simple and precise manner.[279,280] The heat of polymerization for S_{π} is 3.17 kilo-calories ($\Delta S° = 4.63$ e.u.) and the energy required for the chain scission[153,154] is 32.8 kilo-calories. ($\Delta S° = 23$ e.u.)[280] The free radical nature of long, open sulfur chains was pointed out,[188] and later confirmed with the help of ESR[118,120] equipment and a Faraday balance.[212]

The average chain length varies between 158°C and 404°C from 8 to 5 X 10^5 atoms. Statistical and other arguments make[95] the occurrence of makrorings[166,177] 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 the electric conductivity is the sum of two terms: One for the electronic conductivity of the liquid element and the other for the electrophorectic conductivity due to (sulfide-) impurities.

The structure of the liquid has been investigated by several groups.[217,131,219,244,166,277] 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 work is necessary, however, before we have a conclusive picture of the composition of liquid sulfur and much data is still lacking. It seems, for example, that a fourth component has to be assumed to explain the color effect.

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: 1) a crystalline part which consists of $S\alpha$ or its polymorphs, 2) an active species which will be called $S\pi$, and 3) a CS_2-insoluble polymer. The composition of this polymer is complicated and depends upon the preparation method, but many authors treat this solid or some fraction of it as a definable system. So little data are given for this fraction, generally, that one cannot compare results reported by different groups. Regardless of the nomenclature used in the original paper, we will choose the name $S\mu$ for this plastic, CS_2 insoluble polymer, which is

obtained if viscous liquid sulfur is quenched. The rigid, CS_2-insol. polymer, which is prepared by condensating sulfur vapor, will be called S_ω and will be discussed in section D. In discussing the products, we distinguish between samples obtained by 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 within three days into S_α and S_μ, but the S_μ converts only slowly into α, and its concentration, therefore, goes through a maximum after about three days (see S_π). Third, if the liquid sulfur contains only S_λ and S_π (below 158°C), the quenched sample crystallizes mainly to S_α, and S_μ is formed only in a secondary reaction throught the polymerization of S_π. Other particles have not yet been observed in these solids, but 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 the next chapter. The following section deals with four allotropes prepared from the melt: S_λ, S_π, S_μ, and S_ψ.

a) S_π - Gernez[126] discovered that the melting point of sulfur changes during the melting process. Smith[257] explained the slow decrease from the ideal (119.3°C) melting point to the natural melting point (114.5°C) 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 by Magnus[180,181] for a different allotrope. Above 159°C[258] a third component, catena-poly-sulfur,[168]

S_μ,[258] 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°C. This was first taken as a proof for S_π and S_μ being identical. Molecular weight[37,38,214,246,247] 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[244] after about three days. The S_π, with a lifetime of roughly one day, obviously partly polymerizes into S_μ, which then converts into S_α with a much higher lifetime, perhaps six months.

If liquid sulfur is quenched to -78°C some of the S_π can be isolated. S_λ is soluble in CS_2 at room temperature but not at -78°C, S_μ is CS_2 insoluble, but S_π is soluble in CS_2 at -78°C. From the deep yellow S_π solution Erämetsä[91] 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, Al_2O_3 catalyzes the conversion of allotropes. Schenk[248] 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 and discovered that the liquid content is 5.5% π[247] at the m.p. 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 catena-octa-sulfur.

We adopt here tha name $S\pi$ for the catena-octa-S. There remain, however, several unexplained facts about this particle. Tobolsky,[279] in a model

which accurately describes the viscosity of the melt over the whole temperature range, assumes that $S\pi$ is very unstable and polymerizes with $S\lambda$ to polymer chains. He calculates the $S\pi$ concentration at the melting point to be undetectably small, but Schenk[247,248] obtains 5.5% $S\pi$ from measurements of the soluble part in the solid and the melting point depression. ESR measurements[120] indicate a very low free spin concentration at the temperature mentioned above, but this can be interpreted either as an indication that there is only very little $S\pi$, or that the $S\pi$ has strong resonance stabilization of the chain. Such a resonance stabilization has been earlier assumed for small molecules.[177]

b) S_i - Erämetsä[91] separated different fractions of $S\pi$ with the help of chromatography. Part of the dry $S\pi_2$ fraction turns into a white solid which is very similar to S_ω but has a different x-ray diffraction pattern. This form is not CS_2-soluble and was called S_i.[91]

c) S_μ - If liquid sulfur, a complex mixture of allotropes, is poured into ice water or cooled to -78°C, an astonishingly homogeneous product is obtained.[127] The reason for this is that most particles in liquid sulfur become so highly unstable when cooled that they convert immediately into the stable alpha form or the catena-poly-form, ($S\mu$), which has under such conditions 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 alpha sulfur and the $S\pi$ dissolve and an insoluble part remains. Both the viscous liquid sulfur and the CS_2-insoluble[119,169] solid are called $S\mu$. The yield and the structure of $S\mu$ depend upon the composition of the liquid (T_{start}), the speed with which the quenching is performed

$(\frac{dT}{dt})$, 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,[242] while in another group pure sulfur always leads to 100% Sμ, with crude samples giving up to 60% of it.

Sμ can also be prepared by slowly hydrolizing S_2Cl_2, or by acidifying an aqueous thio-sulfate solution. The mechanism of both reactions will be discussed together with the formation of S_ρ. Sμ is unstable at room temperature. The transformation rate into S_α depends upon the temperature, pressure or stretching and impurities. Light[58] and the presence of Sα are believed to catalyze the conversion into the stable form. .04% oil, or .1% I_2 and tri-valent contaminations such as N or P can stabilize[273] plastic sulfur over a long period of time. Pure samples have been reported to be metastable below -29°C[190] and can exist at room temperature for over a year. The exposure to UV light or to alpha, beta or gamma radiation enhances the transformation by breaking long chains.[192] The samples do not convert completely into the alpha form, but reach an equilibrium composition, where the scission and formation of chains and rings are in balance. (See irradiation sulfur).

The x-ray diagram[277,281,282] of Sμ looks very similar to that of Sα. Alpha impurities have therefore been held responsible for the observed patterns, since the x-ray method does not strongly discriminate against different components or contaminations. Another interpretation proposes a

similar structure for S_α and Sμ, but seems to be wrong.[210] (See Sψ). Some authors believe that Sμ 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 Sμ form. The structure of Sμ is not yet completely known, but it is possibly similar to the structure of stretched sulfur, which will be discussed with Sψ.

Detailed discussions about Sμ have been published by Schenk,[245] and Smith.[258-262] 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.

d) S_ν - S_ν has been used for two allotropes: 1) Prins takes S_ν as a short hand name for Sμ.[90-92] 2) Eränetsä[90] labels a fraction of precipitated sulfur S_ν. (See IV.3.E.e)

e) S_ϕ

1) Von Weimann[293] discovered that plastic sulfur samples obtained by chilling liquid from above 250°C assume new properties if they are stretched. This material was studied by several groups[64,187,282,220] with the help of x-rays. Neuburger[198] found the symmetry to be C^2_{2h}. Pauling[204] proposed a helical structure, similar to that of Se, with 112 atoms in the unit cell. Prins[217-223] and co-workers[220,244] have devoted many investigations to this form. They found that it consists of two

different components, $\psi + \gamma$. This discovery devaluated much of the earlier work.[187,282] The present description[223] is based upon long sulfur helices that are packed together regularly with crystals of S_γ, which seems to be formed during the stretching (see Fig. 2d, App 2). The c-axis of the gamma crystals is supposedly parallel to the fiber. $S\phi$ can be stored for several years.

2) Erämetsä[86] calls a very unstable polymorph of S_α, S_ϕ.

f) $S\psi$ - The name $S\psi$ is used for different sulfur forms.

1) Erämetsä uses the term $S\psi$ for a very unstable polymorph of S_α.[86]

2) $S\psi$ is often a synonym for S_ϕ.

3) Neumann[199] introduced the term $S\psi$ for the crystalline part of S_ϕ.

4) Prins and co-workers[221] designate with $S\psi$ the fibrous part of S_ϕ (this is the reverse of 3). The symmetry of the fiber is C^2_{2h}, the same as that of S_ϕ. A closed packed helical structure with concentric arrangement has been proposed,[206,209,210] analagous to an alpha sulfur structure. This proposal, however, is not convincing since the alpha structure mentioned is incorrect. The best present model[79,220-223,235,236,243,244] assumes long helices containing $3\frac{1}{3}$ atoms per turn. The unit cell then contains 10 atoms; (a=b=4.7A) it is 13.7 Å long (c) and has a radius of .92Å. A possible super-structure giving the unit cell a length of 69Å has recently been mentioned.[223] Details of the $S\psi$ structure are not yet known (Fig. 2).

D. Allotropes Derived 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[26] indicates the presence of at least 10 different molecular species in the vapor. Staudinger[272] recognized the possibility of trapping small molecules such as S_2 from hot vapor, but Rice 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 different 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[228] solids when he condensed S_λ vapor, and a blue [229] glass when he trapped vapor with a high S_2 concentration. Several workers have repeated these and similar experiments and obtained many 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[182-185] performed under well defined conditions have lead to the identification of S_2 in the solid. The same molecules has been trapped and studied in different rare gas matrices, but very little data is yet available about these solids which can show absorption spectra with well developed structure. 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: $\frac{T_S}{T_E \cdot \{S\}}$.

Despite their complicated composition, most colored forms have a sharply defined stability range which is indicated in App. II, Fig. 3. 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: α > plastic > yellow > green > purple.

We will discuss here first S_ω and S_m which obtained from the sublimation of sulfur under atmospheric pressure and then the colored condensation products which are obtained from the vapor under reduced pressure.

a) S_ω - We define S_ω here as the CS_2 insoluble part of sublimated sulfur. Because of its color, S_ω is also called 'white sulfur'. This modification is similar to the commercial form "crystex" and 'super-sublimation' sulfur and is not a well defined allotrope. Das[60,61,64] studied the properties of S_ω carefully and found that it is stable for more than a year at STP and for 36 hours at 88°C.[62] Bases, such as NH_3, catalyze the conversion of this form into S_α.

The x-ray data show a distinctive similarity with S_μ and S_α. Das explained this by the presence of S_α impurities on the crystal surface, but Prins assumes that S_ω is a mixture of different forms, partly polymers, partly crystallites, and Pinkus thinks S_ω is identical with S_μ. Other[205] authors think that S_ω is built up from S_6 of which three molecules form a unit cell.[205] The density lies in between 1.834 and 1.95 g/cm^3.

$$a = 8.24 \text{ A}$$
$$b = 9.15 \text{ A}$$

The ESR spectrum of S_ω indicates a free spin concentration of 5.10^{-6} mol/l.[208] Another structure with 10^4 oriented chains in a particle was proposed, but the evidence is not conclusive.[208]

S_ω can be prepared by different methods, and each method leads to a somewhat different form[105,205,221] of this rather vaguely defined allotrope. The best yield of S_ω is obtained if sulfur flowers are sublimed.[31,96] Other procedures include the hydrolysis of S_2Cl_2 with water, the reaction of H_2S with SO_2, and the reaction of HS_4^- with S_2Cl_2 with water, and the reaction of HS_4^- with S_2Cl_2. From the later material, Erämetsä separates two other components, which he calls S_μ and S_ν.

b) S_m - Erametsa isolated S_m from the distillation products of S_ω, or through chromatrography of red sulfur (3 E.c). S_m has so far been characterized only by the x-ray diagram.[89] The lattice ratios are estimated to be

$$a:b:c = .672 : 1 : .064$$

c) Yellow sulfur - If hot sulfur vapor is condensed under reduced pressure on a cold surface, $\leq$ -78°C the solid is deep yellow.[182-184] It is likely that this sulfur contains a high concentration of S_π. All low-temperature forms convert into this yellow form at -100°C.

d) Black sulfur - 1) Schenk[245] observed black sulfur in condensed vapors of S_2. It seems to be similar to violet sulfur. 2) This name is also used for the black deposit which forms during the purification of elemental sulfur with the method of v. Wartenberg (Pg. 10). Skjierven[256] describes this black material as containing a pure sulfur allotrope which is very stable in the dark, but which converts after about one week in sunlight suddenly into S_α. The existence of such a form was already proposed by

Magnus,[180] 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 - Rice[228] observed that S_2-vapor condenses on a liquid nitrogen cooled trap with a purple color.[230] He assumed the color to be due to the S_2 radical. His work was later carefully re-examined,[182-184] and it was proved that the S_2 concentration in violet and green deposits are similar and do not cause the color. The color depends rather on the deposition speed. Slow condensation yields green sulfur, fast deposition leads to purple samples. A high magnetic susceptibility[111] of this form was quantitatively demonstrated.

f) Red and Brown Sulfur - Red and brown sulfur were produced by several authors.[155,182] 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. Kapustinsky[155] observed transitions of these forms by thermal effects at -70, -60 and -55°C.

g) Green Sulfur - Rice[229] reported a green condensation product in a liquid air cooled trap if S_λ was condensed. Green sulfur is also produced if molecular beams of S_2 are slowly deposited upon a surface which is kept[182-185] at 104°C, or if purple sulfur is heated above 80°K. The formation 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 non-equilibrium self-solution in between long curled chains. This solid has a complicated composition. At least four different active species have been observed by their ESR spectrum[49,50,231] during warm-up cycling of this green form. The electrical conductivity, the UV and the IR spectrum of this multicomponent form have been studied,[182] and the S_2 particle could be identified in such mixtures with the help of the (forbidden) IR-spectrum.

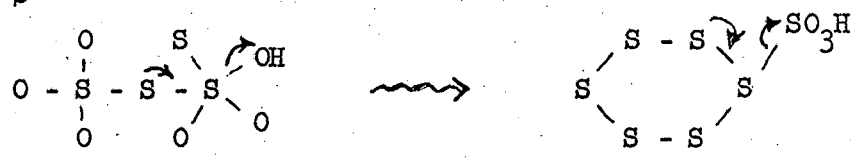
It is not yet clear why this form is green. Rice held the S_π molecule responsible for this color, but S_π is known to be yellow. (See S_π) Another explanation is based upon the similarity of the color effect in colloid solutions. The color changes at 100°C into yellow.

h) Violet Sulfur - If a molecular beam of S_2 is slowly condensed on a surface at $\leq$ 60°K, a violet-purple solid forms. This solid has two absorption continuous in the UV. At 80°K this form converts into green sulfur. The composition of purple sulfur is not known, but the presence of S_2 has been proven[182-184] and the color might be due to the same particle, which causes hot liquid sulfur to be deep red.[158]

The stability ranges of the metastable colored forms are listed on page 53 and indicated in Fig. 3 page 55.

E. Allotropes Prepared From Sulfur Compounds

In stochiometric 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 an intramolecular rearrangement such as a ring closure or a chain scission from molecules which contain already the correct number of sulfur atoms. The most frequent intermediates are polysulfides or polysulfoxyacid ions in various oxidation states. Davis[66] explained the formation of S_ρ in acidified Thio-sulfate solution, for example, by the following overall mechanism:



The yield of different sulfur allotropes depends mainly upon two factors; first, upon the formation or displacement rate of the allotropes ($[\dot{S}_n]$) from an intermediate compound which has already the correct number of sulfur atoms (In reaction II this number is n+1), and second, upon the formation rate ($[1\dot{C}_{n+1}]$) and the lifetime (const. x $[1\dot{C}_{n+2}]$) of the intermediate compound. 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. ($[\dot{S}_8] > [\dot{S}_6]$). The formation rate of the intermediate compound and it's 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 the temperature

coefficient of $[1\dot{C}_{n+x}] \gg [\dot{S}_x]$ and is more important than the chain length (n), three cases can be realized.

1) $[1\dot{C}_n] \gg [\dot{S}_8] > [\dot{S}_6]$.

In warm concentrated solutions a fast pH change leads mainly to long chains which form S_μ.

2) $[1\dot{C}_8] > [1\dot{C}_n] > [\dot{S}_6]$.

Under mild conditions, the formation of S_λ will be favored.

3) $[1\dot{C}_n] \sim [\dot{S}_6]$.

In cool solutions slow acidification will yield an appreciable amount of $S_6 = S_\rho$. One cannot, however, obtain S_6 thru slow reaction at standard temperature, since the S_6 is not stable enough.

All three molecules have been detected under the conditions mentioned above. S_λ has been discussed on page 16, S_μ on page 30 and we will now discuss S_ρ.

a.) S_ρ

We will use the term S_ρ only for the unbound cyclo-hexa-S molecule, and not as a synonym of S_ϵ (see S_ϵ). The S_ρ molecule is unstable (see page 13) and has been observed only during the decomposition of sulfur compounds.

It is best[22] prepared after the method of Engel[83, 84]. Concentrated HCl is slowly stirred into a concentrated solution of sodiumthiosulfate at 0-10°C. The S_ρ is then, together with S_λ, extracted with toluene or benzene, and the S_ϵ yield is $\leq 12\%$. Davis[66] has explained the formation of S_ρ during this reaction. On evaporation or cooling of the solution S_ϵ crystallizes. If they are carefully cleaned with KI_3, PbS and KOH[22],

S_ρ solutions are fairly stable even at 60°C.[20] Bartlett[17, 20, 22] has studied such solutions very carefully and found that S_ρ reacts roughly 10^4 times faster[21] than S_λ with $(Phenyl)_3P$, CN^- and OH^-. This reaction is catalized by traces of H_2S and SO_2. The ultraviolet spectra[22, 229] and the IR[20] have been studied in CS_2 and broad absorption bands around 2900 Å and 20μ have been observed. (See appendix 6.)

b.) S_ϵ

S_ϵ and S_ρ are often used as synonyms. We follow an earlier suggestion[244] and call the cyclo-hexa-S molecule S_ρ. This molecule has so far been observed only in one crystalline form, which we will call S_ϵ. S_ϵ has been discovered by Engel.[83, 84] The correct molecular composition was first reported by Aten.[10] 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} - $\bar{3}$. The crystal symmetry is C^2_{3i} - $\overline{R3}$.[80] The lattice constants are:[78]

$$a = 10.818 \mp .002 \text{ A} \qquad a : c = 1 : 0.396$$

$$c = 4.28 \quad .001$$

The morphology was first studied by Friedel[114] and the crystal symmetry was proposed by Frondel,[115] Donnay[74] and recently confirmed by Donohue[76]. Powder data and other x-ray data are reported in ref. 47. The melting point of S_ϵ is estimated to be below 100°C. The density of this allotrope is higher than that of any other: 2.135 gr/cm^3. Each atom has twelve neighbors within a distance of $\leq$ 3.5 A.

Several authors report that S_ϵ has been found in nature. The production of S_ϵ from boiling sulfur solution has been described, but this seems doubtful since it would nescessitate 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.

S_ϵ crystallizes if a solution of S_ρ is cooled or evaporated. The crystals convert within a few hours into S_α if the S_ρ was not carefully purified. The pure S_ϵ is at 0°C fairly stable.

c) S_{red} - Three different sulfur systems are labeled as red sulfur:

1) Eränetsä[88] prepared red and pink sulfur by combining CS_2Cl_2 with a $(NH_4)S_x^-$ soltuion at pH[8]. A chromatographic separation leads to two components which have been characterized by their x-ray diagram and by their molecular weight, as determined with an ebulloscopic method, but this form has not yet been ascertained.

2) Red sulfur is obtained if S_α is irradiated with α, β or γ radiation.[232]

3) Red sulfur can be obtained by trapping sulfur vapor (see pg.33). Mitscherlich[189] and many other authors have reported other red sulfur forms which have later been clearly identified as impurities. All the forms mentioned above are multicomponent systems and are not well defined or understood.

d) S_ν

1) See IV,3,C,d.

2) If Eränetsä s[91] red sulfur, prepared by combining S_2Cl_2 and $(NH_4)_2S_x$ is stored in the dark, a new allotrope is formed. Its lattice (CsCl), x-ray,

color, and sublimation temperature are very similar to NH_4Cl, but the author of this form studied S_ν carefully and was convinced that it was a sulfur allotrope.

F. Sulfur Allotropes in Solid Solution

We have already discussed two cases of S-self-solutions: first the metastable films which are obtained if molecular S-beams are trapped, and second the quenched melt which is partly a solid solution of S_π in S_μ. We will list here two cases where sulfur allotropes have been studied in a solid foreign solvent:

a) polar solvents:

Sulfur dissolves in NH_3,[133] SO_3,[151] and many other liquids, but the solvation is generally accompanied or caused by some chemical reaction. It seems, however, that sulfur does not react with alcalihalide melts.[137] At 700°C, a deep blue solution is observed in an eutectic KBr/CsBr mixture. If the liquid is cooled slowly, the melt crystallizes with green sulfur inclusions, but if the melt is quenched to 78°K, a metastable solution is trapped and remains colored even at standard temperatures for many days. It is easy to press pellets from this solid, but the IR spectra are complicated and are not yet fully understood. It is not clear what allotropes can exist under such conditions.

b) Non-Polar Solvents:

Homogeneous metastable solutions can be trapped by slow simultaneous condensation of a rare gas and of sulfur vapor.[183] Very pure solutions of S_2 in Ar, Kr and Xe have been prepared in this way.

If .1% S_2 is condensed in Ar, Kr or Xe at a temperature below 25°K, a very pure S_2-solutions is obtained, and the spectrum of such solutions is similar to the gas phase spectrum.[186]

V. CONCLUSION

Of the over 5.10^5 different sulfur particles observed, only four have been obtained in pure form: 1) the cyclo-octa-S ($S\lambda$); 2) the cyclo-hexa-S (S_ρ); 3) the S_2 molecule and 4) the S-atom. Of these last four particles, again, only the diatomic molecule and the atom are well known. For the hexatomic and octatomic molecule, the spectroscopic data is incomplete and inconclusive and most of the thermal data is unknown. The study of polymers such as S_μ, S_ω and S_ϕ does not promise fast progress from a molecular standpoint, and it seems that much future research will be concentrated on completing the data of the four molecules cited above. It will, however, also be possible to isolate and study several of the small molecules: Catena-octa-S (S_π), S_7, S_4 and S_3, for example, all can be trapped at lower temperatures because the recently developed low temperature techniques make it possible to trap such unstable particles in metastable form in purity and quantities sufficient for observation.

The polymorphism of sulfur is a wide open field. We indicated that many different arrangements can yield similar lattice energy and it is likely that for S_λ and S_ρ a great number of modifications will be found.

Only polymorphs of $S_\alpha(S_\lambda)$ have so far been investigated, and the existence of the 10 allotropes reported has not always been conclusively proved. Astonishingly only two forms, S_α and S_γ, have been clearly understood even though S_β is stable and has been frequently investigated.

Many modifications contain a complicated mixture of allotropes. The colored forms, for example, all contain S_μ, and their composition is very sensitive to the preparation conditions. These forms are also photosensitive.

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.

The polymeric forms S_μ and S_ω have been well studied, but their composition is not yet clear. One reason for this is that one does not yet know enough about their source. For example, the stability of S_π in liquid sulfur is not established and there might be more particles in the liquid than has been assumed.

Almost all sulfur allotropes are photosensitive but most experiments have been performed in the light and without control of this parameter. One of the future tasks seems to be to investigate the influence of radiation on the sulfur system.

It is not the purpose of this short and preliminary review to survey the methods of separation and identification of allotropes. We repeat here only that a standardization of methods could here, and in the entire field, facilitate the coordination of observations.

Because of the large amount of specialized information available concerning elemental sulfur, this review was restricted to solid and unstable allotropes, but even this relative 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 present a complete listing of data.

ACKNOWLEDGMENT

The author wishes to thank Dr. Leo Brewer.

Appendix I. Nomenclature of Sulfur Allotropes

Name	Synonyma	Present Status of Identification	Stability	Molecular Species	See Sec. IV Section
α	1st Modification 1st Muthmann modifica. orthorhombic	Conclusive	Only stable form at room temperature	Cyclo-octa-S	2,C
β	2nd. Modification 2nd. Muthmann Mod. monoclinic (I) sulfur prismatic	Structure not known	Stable $\geq$ 95.6°C	Cyclo-octa-S	2,C
γ	3rd Muthmann Mod. 2nd Monoclinic Nacreus sulfur Mother-of-Pearl sulfur Gernez Modification	Incomplete	Metastable (?)	Cyclo-octa-S	3,C,b
δ	4th Muthmann Modifi. 3rd monoclinic γ-monoclinic	Ambiguous	Unstable	Cyclo-octa-S	3,C,e
ε	Engel sulfur, Aten sulfur Rhombohedral modif. Monoclinic Engel	Conclusive	Unstable	Cyclo-hexa-S	3,E,b
ζ	5th Monoclinic	Ambiguous	Unstable	Cyclo-octa-S	3,B,c
η	4th Monoclinic	Ambiguous	Unstable	Cyclo-octa-S	3,B,d
ϑ	Tetragonal	Ambiguous	Unstable	Cyclo-octa-S	3,B,f
ι	--	Inconclusive	Unstable	Cyclo-octa-S	3,C,e
λ	Stands for unbound cyclo-octa-S	Conclusive	Stable	Cyclo-octa-S	3,A,a

Appendix I - Continued

Name	Synonyma	Present Status of Identification	Stability	Molecular Species	See Sec. IV Section
μ	Term designates CS_2-insoluble polymeric chains	Conclusive	Unstable	Catena-poly-S	3,C,c
ν	Term inconsistently used: for using part of μ with special properties	Inconclusive		Mixture	3,C,d
ξ	Tricilinic Mod.	Ambiguous	Very unstable	Cyclo-octa-S	3,B,h
o	---	Ambiguous	Very unstable	Cyclo-octa-S	3,B,g
π	Aten s Modification	Incomplete	Unstable	Catena-octa-S	3,C,a
	a) here: unbound cyclo-hexa-S molecule b) often Aten-S, Engel	Conclusive	Unstable	Cyclo-hexa-S	3,E,g
τ	--	Ambiguous	Unstable	Cyclo-octa-S	3,B,i
ø	Fibrous sulfur	Incomplete	Unstable	Catena-poly-S or mixture	3,C,e
	Used for 2 forms: a) Erämetsä b) Plastic-designates mixture of ω & γ	 Ambiguous Ambiguous	 Unstable Unstable	 Cyclo-octa-S Mixture (?)	
	Fibrous Sulfur Stretched Sulfur	Ambiguous	Unstable	Catena-poly-S or mixture	3,C,f
ω	Insoluble sulfur white sulfur super-sublimation Das modification	Incomplete	Unstable	Catena-poly mixture (?)	3,D,a

Appendix I Continued

Name	Synonyma	Present Status of Identification	Stability	Molecular Species	See page
m	Tricilinic	Inconclusive	Very unstable	Cyclo-octa-S	3,E,d
n	See μ		Unstable	Catena-poly-S	3,C,c
Aten	Used for S_ϵ or S_ρ				
Brauns	Mixture, see μ				
Engel	See S_ϵ and S_ρ				
Woehler	Colloidal	Conclusive	Metastable	Poly-catena-S	
Amorphous	See μ				
Metallic	-	Inconclusive	Unstable		3,A,a
Photo-sulfur	-	Incomplete	Unstable	Mixture	3,B,a
Irradiation sulfur	-	Incomplete	Unstable	Mixture	3,A,b
Black	a)Mitscherlich b)Skjerven c)Rice-Schenk	Not elemental sulfur Inconclusive Incomplete	 Unstable Unstable	 Catena-S	3,D,c
Green Purple Violet Brown	Trapped Sulfur	Incomplete	Unstable	Mixture of Catena-S	3,D,c-h
Red	a) Trapped S b) See irradiation c) -	Incomplete Incomplete Incomplete	Unstable Unstable Unstable	Catena-S Catena-S Mixture	3,D,b 3,A b 3,E,c

Appendix II. Some Molecular Data

Formula	$S_8 = S_\lambda$	$S_6 = S_\rho$	$S_x = S_\mu$
Name	Cyclo-octa-S;	Cyclo-hexa-S;	Catena-poly-S;
S-S bond length (in A)	2.059 ±.002	2.057 ±.018	2.04
Valence-bond angle =	1.076 ± .6 102(old)	102.2± 1.6 104(old)	107°
Dihedral angle =	98.9 ±.7	74.5±2.5 71 (old)	87°
Number of non-bonded distances _ 3.5A	6	12	
Molecular symmetry	D_{4d}	D_{3d}	C_{2i}

Torsion energy $E_T = S_\lambda = 2\ \delta$

Appendix II

Figure 1 (Caption)

1a) Structure of the Sλ molecule (cyclo-octa-S), symmetry D_{4d}. Page 16

1b) Structure of the Sρ molecule (cyclo-hexa-S), symmetry D_{3d}. Page 39

1c) Structure of the Sπ molecule (catena-octa-S). Page 29

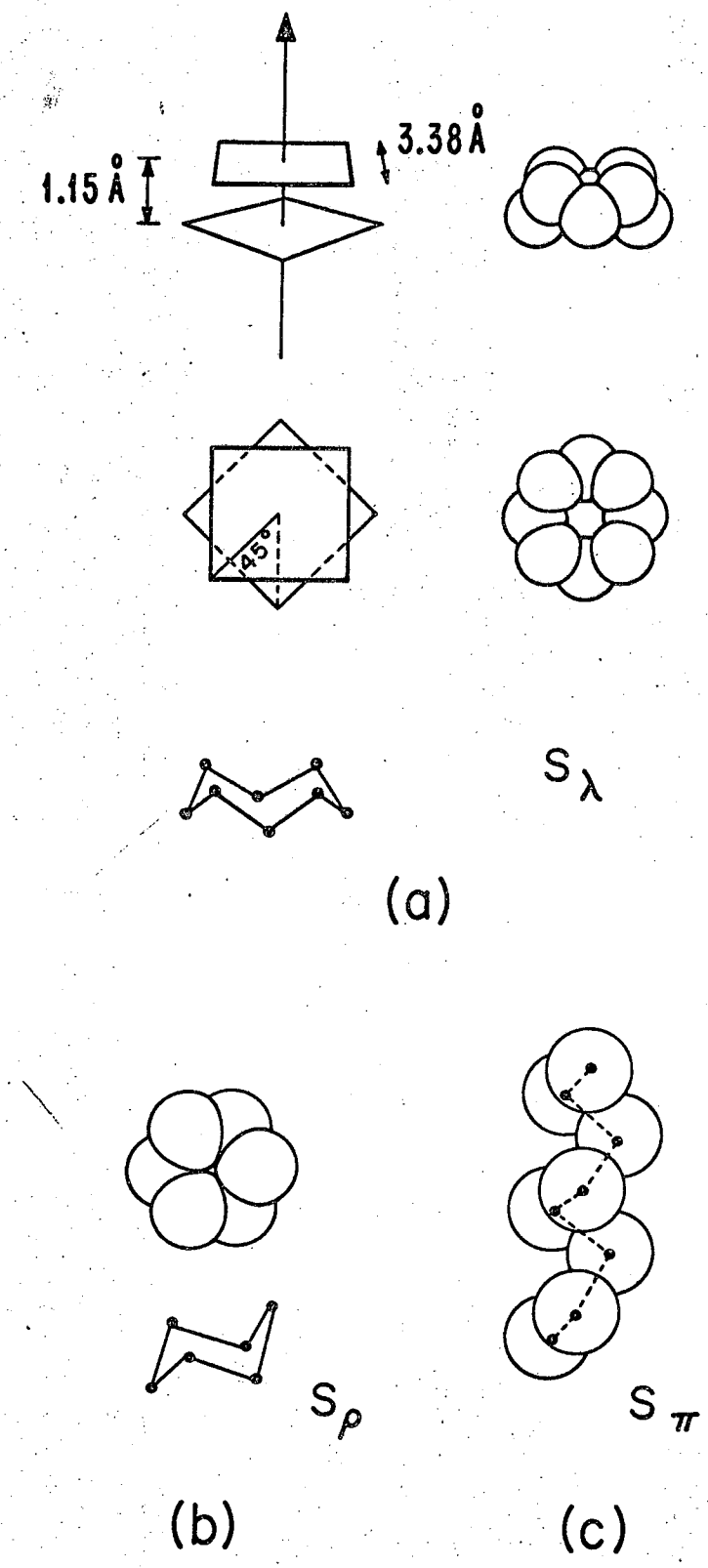


FIGURE 1

MU-31470

Appendix III. Polymorphs of the Various Sulfur Molecules

Molecule	Polymorphs
Cyclo-octa-sulfur (λ)	α, β, γ, δ , ζ, η , λ, ϑ, o, τ, $\varkappa$
Catena-octa-sulfur (π)	None
Cyclo-hexa-sulfur (ρ)	None
catena-poly-sulfur	Amorphous = μ , γ, ϕ, ψ, ω, n, threads m, ν
Mixture, multicomponent forms	(ϕ), (μ), black, green, red, purple, photo, in, Brauns, red.
Unidentified, metallic	[illegible]

Appendix III a - Stability Ranges of Defined Colored Allotropes

Solvent	S-Conc.	Prep. T. °K	Observed Stability Range, °K	Color	Identified Species
A Kr Xe	$\leq$.3%	4- 35 45 50	4< T< 35 45 50	Maroon	$\geq$90% S_2
A, Kr, Xe or none	$\geq$.5%	35 45 - 60 50	4< T< 60	Violet	S_2 + ?
A, Kr, Xe or none	$\geq$ 1%	60-170	4< T <170	Green	S_2 + ?
-	100%	170-240 (?)	4< T <240	Yellow	$S_\mu + S_\pi$?

Fig. 2- (Caption)

2a) Structure of $S\gamma$: sheared penny roll.

2b) Structure and unit cell of $S\alpha$.

2c) Structure of S_ϵ as seen along the c-axis.

2d) Structure of S_ϕ . S_γ crystals with their c-axis parallel to the $S\psi$ fiber fill the spaces in the helices of the latter. The structure of both $S\psi$ and S_ϕ is not yet completely established.

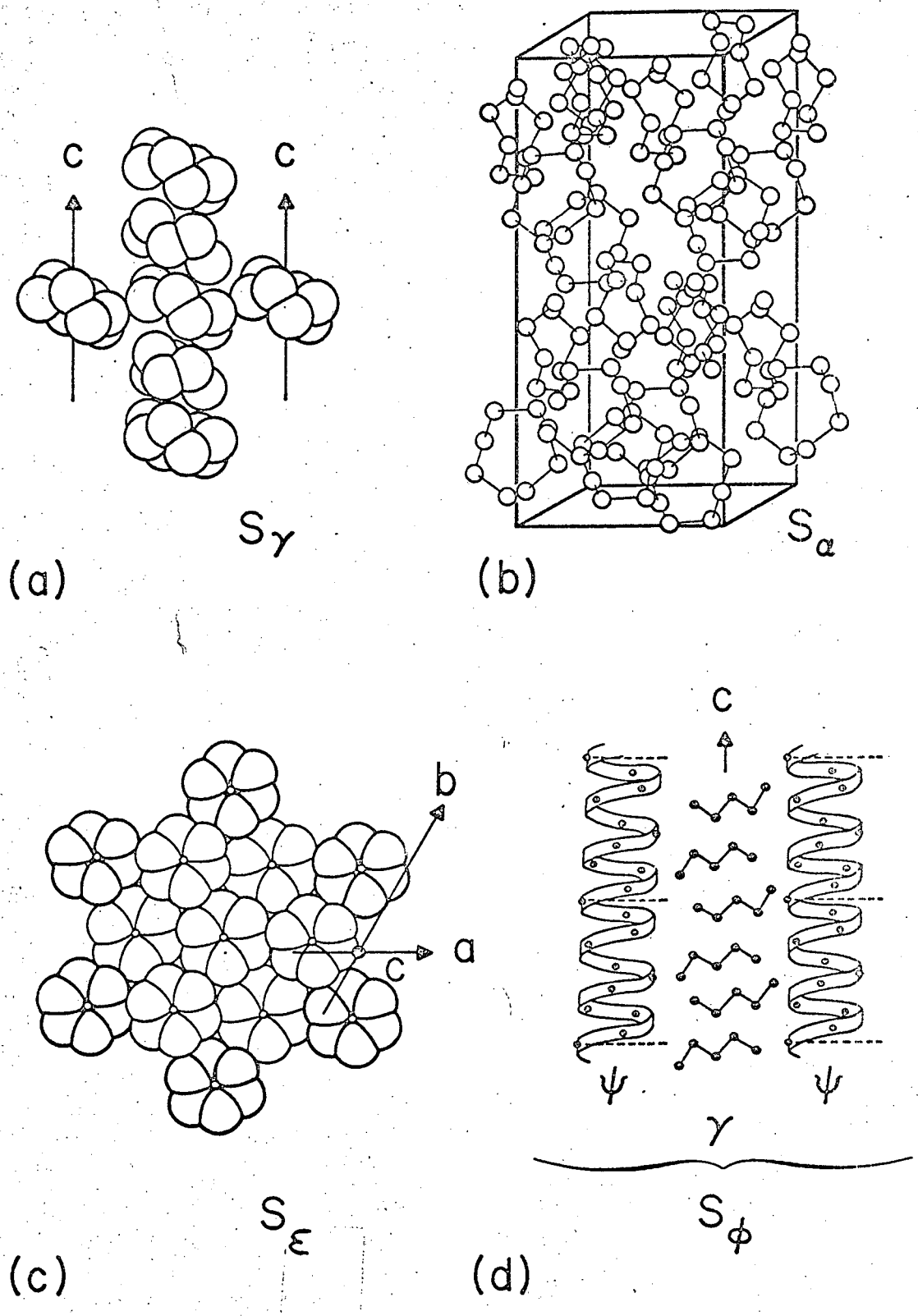


FIGURE 2

MU-31471

Fig. 3 - (Caption)

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

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

The various sulfur allotropes to which the symbols in the drawing refer are discussed in Section IV,3,d. The z-form has not yet been observed.

At equilibrium ($-dT/dt \ll$) only α and β are stable solids. With 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.

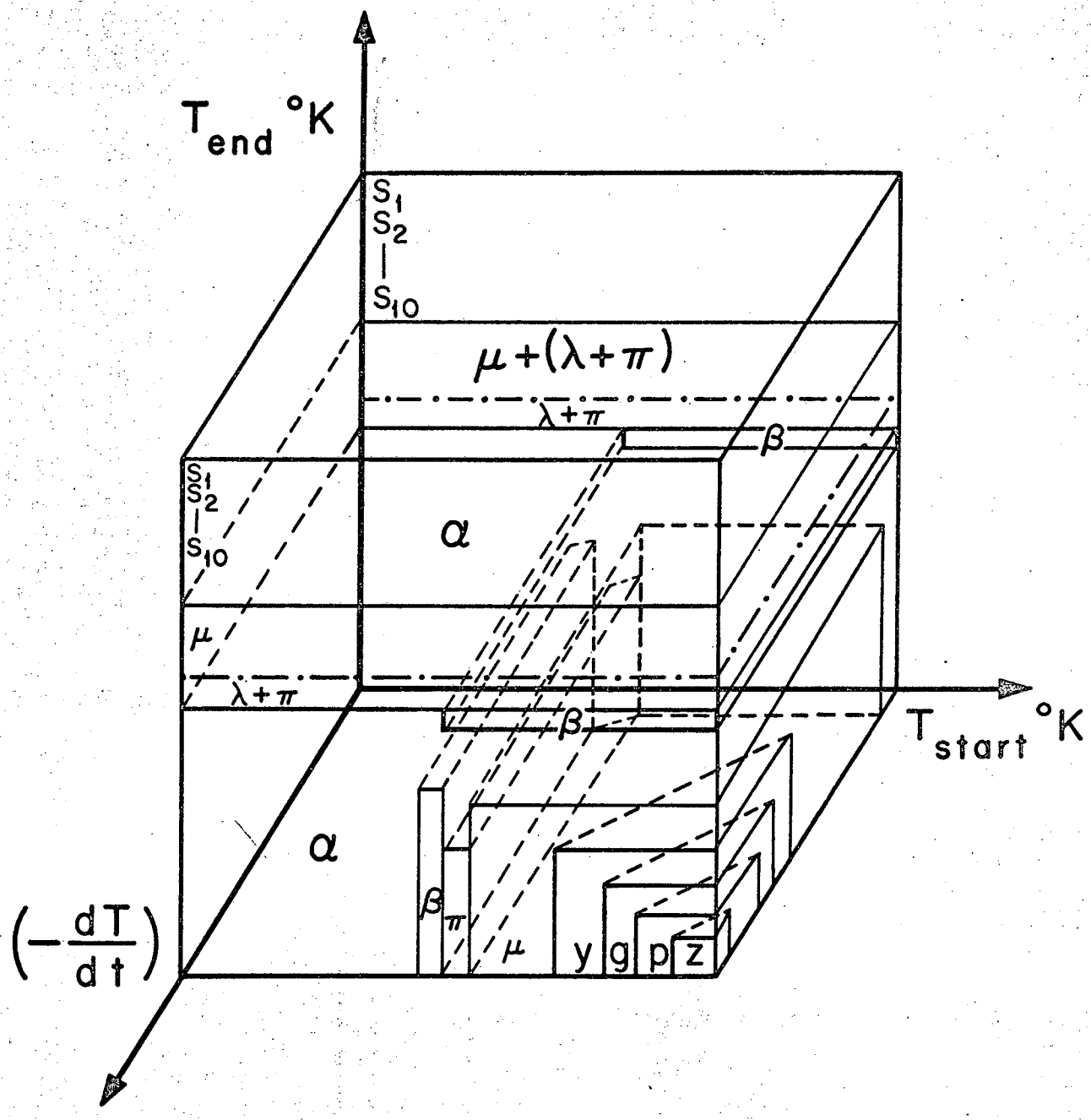


FIGURE 3

MU-31472

Appendix IV

1.) Specific Heat

T = 298.16°K	C°_p(Cal/deg.g.at.)	S°(Cal/deg.g.at.)	ΔH°_F(Kcal/g.at.)	Reference
α (s)	5.4*	7.62		295
β (s)	5.65**	7.78	.009	295
$S_{at.}$ (g)	5.66	40.1	53.11	Landolt-Bornstein Zahlenwerte und Funktionen, 6th Ed., Vol. II, pg. 184, 4. Springer, Berlin (1961)
S_2 (g)	7.76	54.5	30.85±0.15	"
S_λ (g)	37.16	102.7	24.35	"

* 35-95°C: $5.2688 + .006121T - 8.164 \times 10^{-6} T^2$ (Ref. 295)

**101-115°C: $5.2630 + .006857T + .08039/(115.176-T^2)$ (Ref. 295)

Note: Cp decreases from 95-101°C. (Ref. 295).

Appendix IV

2.) Transitions

Transition	T°K	ΔH		ΔS cal/g.at.°	Ref.
α-B	368.46 ± .01	.096, 16	Kcal/g.at.*	.261 ± 0.002	295
β-?	374.2	.000383	"	7.93	
α-subl - λ	368.5	3.01	"	8.17	32
β-subl - λ	368.5	2.92	"	7.93	
ε- ρ	300	4.02	"	8.38	+
fusion α-λ	383	.507	"		
fusion β-λ	388.33	.410, 5	"	.75	295
λ-π	432	4.1**	"	2.88	279-280
polymer. λπ-μ	442.8	.396††	"	.58	279-280
vap. λ-λ	444.6000°C	2.5	"	3.5	
7/8 Sλ-S_7	400°K	5.7	Kcal/mol		26
3/4 Sλ-S_6	400	6.2	"		26
5/8 Sλ-S_5	400	14.3	"		26
1/2 Sλ-S_4	400	20.5	"		26
3/8 Sλ-S_3	400	22.5	"		26
1/4 Sλ-S_2	400	23.5	"		26

* 1 g. at. S = 32.066 g.

\+ J. Berkowitz, W. A. Chupka, to be published

** $K = (\pi)/(\lambda) = 1.137 \times 10^5 \exp. (-16520/T)$

†† $K_3 = (\pi)/(\pi\lambda) = 10.43 \exp. (-1596/T)$

$D_oS_2 \simeq 4,4$, eV[26,40]

This selection of recent values differs considerably from older selections (ref. 202, pg. 852).

Appendix IV

3.) Triple points -[202]

1)	α, β, vapor	95.31°C [295]	.00376 mm Hg
2)	α, liquid, vapor	112.8	.013 mm Hg
3)	β, liquid, vapor	119.3	.018 mm Hg
4)	α, β, liquid	~ 152°	~ 1400 atm.

4.) Melting points -[132,202]

α = 112.8°C (ideal)

β = 119 (natural m.p.)

= 114 (ideal m.p.)

γ = 103.6 (?)

ϵ 100°

m: 330 subl.

boiling point SP: 444.6000 °C [176]

5.) Bond Strength: (D_oS_2 = 102.4 kcal)

		Reference
H_2S up to H_2S_6	63.2 x n	101
S_2Cl_2	64.4	204
S_8	64	202

6.) S-S Stretch Frequency 440-550 177

680 195

Appendix V

Survey of ESR Studies

Material Studied	g-value	band-width gauss	spin concent. per mol	Ref.
liquid	2.024 ± .002	40-60	10^{-3} at 300°C (increases by 2.10^{2} from 190 to 375°C)	Gardner, 118 -120.
plastic	2.0044	9.5	10^{-5}	Pinkus[208] (see 79)
green	2.010±.002	8.8 at 78°K 2.2 at -78°C	5.10^{-2} (six components)	Chatelain 49,50
purple	2.0 20	8.8	-	Rice[231]
black or dirt (see 256)	2.010	7	-	Gardner 118,120
free electron	2.0023			

Appendix VI

Survey of Related References

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

A) General Reviews

B) Liquid Sulfur

C) Sulfur Vapor

D) Compounds and Reactions

E) Photo chemistry and -physics

F) Spectra

A) General Review

The most comprehensive surveys are given by Pascal[202](1962) and Gmelin[132](1954). General information is reviewed by Pryor[225] (1962), Schmidt[249](1962), Wells (1962)[294], Donohue[80](1961), Gee[123](1958), Gee[122] (1955), Feher[99](1954), Tuller[283](1954), and many others. The earlier surveys of Yost[303](1944) and Schaefer[241](1940) contain much obselete data and a rather confusing nomenclature. The best review of old data has been compiled by Quicnke[226](1908).

B) Liquid Sulfur

Surveys are given by Schenk[244](1957), Gee[122](1955), Gee[121](1952) and Fairbrother[95](1955).

Theories have been developed by Tobolsky[279,280](1961), Gee (loc.cit) Powell[215](1943).

Viscosity has been discussed in Powell (loc. cit), Bacon[13](1943), Farr[98](1928) and Kellas[157](1918).

Appendix VI - Continued

Structure has been described by Thompson[277](1959), Prins[221](1957) and Krebs[167](1953).

Electric Conductivity data, see Gordon[135](1954).

Heat Capacity, Braune[37](1954).

Specific Heat, Feher[102](1958), Braune[36](1954), West[297](1929) and Lewis[174](1911).

The free electron character is treated by Poulis[212](1962), Gardner[120] (1956) and Feher[100](1954).

The surface tension by Fanelli[97](1950) and the color was discussed by Kelker[156](see also spectral references).

C) Data on the Vapor Phase

Berkowitz[26](63); Poulis[213](63); Jaeckle[154](61); Briske[42](60);Zietz[306](60); Feher[101](1957); Bradt[33](56); Brewer[40](1956); Bradley[32](54); Braune[34,35](52); West[296](51); Cibronsky[52](49); Turell[284](47); Klemm[59](41); Neumann[199](34); West[297](29); Lewis[174](11).

D) Sulfur Compounds and Reactions of Elemental Sulfur

Surveys: Pryor[225](1962), Schmidt[249](1962) and organic sulfur compounds Vol I. (see ref 80)(1961);

Special Problems: Feher[103](1963), Nair[197](1963); Schmidt[250](1963); Foss[106-108](1949-60); Koros[164](1960); Kovalsky[165](1960) Pryor[224](1960); Fredga[110](1958); Ingrahm[151](1957) Garcia[117](1958); Abrahams[1,2,4](1953-56) Skirai[253](1951), Aynsley[11](1935), Lewis[175](1918).

Feher[99-101] (61 contributions up to 1963).

E) [illegible]

E.) The Influence of Light:

Studies have been made by: Bartlett[22](61); Erämetsä[88,89](1959); Bartlett[17](1956) Dhar[72](1948); Dufraise[82](1946); Feigl[104](1944); Wigand[300,301] (1911) Rankin[227](1907) and originally by Lallemand[170](1870).

The photoconductivity, chemiluminiscences and piezoelectricity were investigated by: Zhelndev[305](1962); Dean[67](1960); Chetkorov[51](1960); Dorabialska[81](1957); Fridkin[112](1956) Sokolova[266](1954); Nadzhakov[196](1954) and Moss 191(1951).

F.) Spectral Studies:

Vapor: The spectraum of S_2 is being restudied carefully by R. F. Barrow and coworkers (Can. J. Phys. 41, 419 (1963) and Can. J. Phys. 40, 377 (1962)) and a new system (?) has been described by P. B. V. Haranath (Z. Physik. 173, 428 (1963)) a survey of earlier studies is listed in B. Rosen: Donnees spectroscopiques concernant les molecules diatomiques Hermann, Paris 1951.

Polyatomic molecules have been studied by Bass[23](1953); Graham[136](1910); Gernez[125](1872) and Salet[238,239](1871-72).

Kelker[156](1954); Poulsen-Nautrup[214](1954); Bass[23](1953); Gerding[124](1943) and Fukuda[116](1922).

Solid Phase: See Srb[271](1962); Meyer[182-186](1962); Rice[230](1960); Barrow[16](1953); Bernstein[50,51](1951); Gerding[124](1943); Norris[200,201](1942); Venkateswarlu[286](1940); Venkateswaran[285](1936) Barnes[15](1932) and Taylor[276] (1927).

Solutions: See Clark[53](1963); Bartlett[17-22](1956-61); Barrow[16](1953) Baer[14](1949) Gerding[124](1943) and for organic compounds, Passerini[203](1960). Normal coordinate analysis have been performed by Scott[251](1961) and Pistorius[211](1959) and Venkateswarlu(see 211).

BIBLIOGRAPHY

1. Abrahams, C. S.; Grison, E. — Acta Cryst. 6, 206 (1953).
2. Abrahams, C. S. — Acta Cryst. 7, 423 (1954).
3. Abrahams, C. S. — Acta Cryst. 8, 661 (1955).
4. Abrahams, C. S. — Quart. Rev. (London) 10, 407 (1956).
5. Abrahams, C. S. — Acta Cryst. 14, 311 (1961).
6. Ames, D. P.; Willard, J. E. — J. Am. Chem. Soc. 73, 164 (1951).
7. Aten, A. H. W. — Z. Physik. Chem. 81, 257 (1912).
8. Aten, A. H. W. — Z. Physik. Chem. 83, 442 (1913).
9. Aten, A. H. W. — Z. Physik. Chem. 86, 1 (1914).
10. Aten, A. H. W. — Z. Physik. Chem. 88, 321 (1914).
11. Aynsley, E. E.; Robinson, P. L. — J. Chem. Soc. 1935, 58.
12. Bacon, R. F.; Fanelli, R. — Ind. Eng. Chem. 34, 1043 (1942).
13. Bacon, R. F.; Fanelli, R. — J. Am. Chem. Soc. 65, 639 (1943).
14. Baer, J. E.; Carmack, M. — J. Am. Chem. Soc. 71, 1215 (1949).
15. Barnes, R. B. — Phys. Rev. 39, 570 (1932).
16. Barrow, G. M. — J. Chem. Phys. 21, 219 (1953).
17. Bartlett, P. D.; Meguerian, G. — J. Am. Chem. Soc. 78, 3710 (1956).
18. Bartlett, P. D.; Trifian, D. S. — J. Polymer Sci. 20, 475 (1956).
19. Bartlett, P. D.; Davis, R. E. — J. Am. Chem. Soc. 80, 2513 (1958).
20. Bartlett, P. D.; Lohaus, G.; and Weis, C. D. — J. Am. Chem. Soc. 80, 5064 (1958).
21. Bartlett, P. D.; Davis, R. E.; and Cox, E. F. — J. Am. Chem. Soc. 83, 103 (1961).
22. Bartlett, P. D.; Colter, A. K.; Davis, E. R.; and Roderick, W. R. — J. Am. Chem. Soc. 83, 109 (1961).

23. Bass, A. M. — J. Chem. Phys. 21, 80 (1953).

24. Beckmann, E.; Paul, R.; and Liesche, O. — Z. Anorg. Allgem. Chem. 103, 189 (1918).

25. Bergson, G. — Arkiv Kemi 16, 315 (1960).

26. Berkowitz, J.; Marquart, J. R. — J. Chem. Phys. 39, 275 (1963).

27. Bernstein, H. J.; Powling, J. — J. Chem. Phys. 18, 1018 (1950).

28. Bernstein, H. J.; Powling, J. — J. Chem. Phys. 19, 139 (1951).

29. Berthelot, M. — Ann. Chim. (Phys.) 49, (3) 481 (1857).

30. Berzelius, J. J. — Jahresber. 20, (Sec. 2) 13 (1841).

31. Boullé, A. — Ann. Agron. 17, (2) 575 (1947).

32. Bradley, R. S. — Trans. Faraday Soc. 50, 1182 (1954).

33. Bradt, P.; Mohler, F.; and Dibeler, V. H. — J. Res. Nat. Bur. Std. A, 57, 223 (1956).

34. Braune, H.; Peter, S.; and Neveling, V. — Z. Naturforsch. 6a, 32 (1951).

35. Braune, H.; Steinbacher, E. — Z. Naturforsch. 7a, 486 (1932).

36. Braune, H.; Moeller, D. — Z. Naturforsch. 9a, 210 (1954).

37. Braune, H. — Diss. Hannover, 1954.

38. Braune, H. — Colloquium of the Sect. for Inorg. Chem. of the Intern. Union for Pure and Appl. Chem., Muenster (Westfahlen) 1954, Sept. 2-4 (1954) Ver lag fuer Chemie, Weinheim, 1954, p. 113.

39. Brauns, R. A. — N. Jb. Mineral Beil. I 13, 39 (1900).

40. Brewer, L. — J. Chem. Phys. 31, 1143 (1955).

41. Bridgeman, P. W. — Phys. Rev. 48, 841 (1935).

42. Briske, C.; Hartshorne, N. H.; and Starnks, D. R. — J. Chem. Soc. 1960, 1200.

43. Briske, C.; Hartshorne, N. H.; and Starnks, D. R. — Inorg. Syn. 7, 116 (1963).

44. Broensted, J. N. — Z. Physik. Chem. 55, 371 (1906).

45. Buetschli, O. — Untersuchungen uebev Mikrostrukturen des erstarrten Schwefels, Leipzig, 1900 (C.A. 3994, (1943)).

46. Burwell, J. T. Z. Krist. 97, 123 (1937).

47. Caron, A.; Donohue, J. J. Phys. Chem. 64, 1767 (1960).

48. Caron, A.; Donohue, J. Acta Cryst. 14, 548 (1961).

49. Châtelain, A.; Buttet, J. Helv. Phys. Acta 35, 253 (1962).

50. Châtelain, A.; Buttet, J. Helv. Phys. Acta 35, 503 (1962).

51. Chetkorov, M. L. Izv. Fiz. Inst. s Aneb, Bulgar. Akad. Nauk 8, 33 (1960).

52. Ciborowski, J. Roczniki Chem. 23, 361 (1949).

53. Clark, L. B. Thesis, University of Washington (1963).

54. Cloz, M. S. Compt. Rend. 46, 485 (1858).

55. Cooper, A. S. Acta Cryst. 15, 578 (1962).

56. Copisaroff, M. J. Am. Chem. Soc. 43, 1870 (1921).

57. Cuddeback, R. B.; Drickamer, H. G. J. Chem. Phys. 19, 790 (1951).

58. Daguin, M. Compt. Rend. 20, 1665 (1845).

59. Das, S. R.; Gosh, M. Science and Culture (Calcutta) VI, 1, 784 (1936).

60. Das, S. R.; Ray, K. Science and Culture (Calcutta) VI, 2, 650 (1937).

61. Das. S. R. Indian J. Phys. 12, 163 (1938).

62. Das, S, R. Science and Culture (Calcutta) VI, 4, 665 (1939).

63. Das, S. R.; Gosh, M. Indian J. Phys. 13, 91 (1939).

64. Das, S. R. See Ref. 38, p. 113.

65. David, H. G.; Hamann, S. D. J. Chem. Phys. 28, 1006 (1958).

66. Davis, R. E. J. Am. Chem. Soc. 80, 3565 (1958).

67. Davis, R. E. Proc. Indiana Acad. Sci. 70, 100 (1960).

68. Dawson, B. Acta Cryst. 13, 409 (1960).

69. Dean, P. J.; Royce, B. S.; and Champion, F. C. Proc. Phys. Soc. (London) 75, 119 (1960).

70. Deville, Ch. (St. Claire) Compt. Rend. 26, 117 (1848).

71. Devyatykh, G. G.; Runovskaya, I. V. Zh. Neorgan. Khim. 8, 149 (1963).

72. Dhar, N. R.; Raghaven, B. V. S. Proc. Natl. Acad. Sci., India 17a, 7 (1948).

73. Doelter, C. Monatsh. 30, 179 (1909).

74. Donnay, J. D. H. Acta Cryst. 8, 245 (1955).

75. Donohue, J.; Schomaker, V. J. Chem. Phys. 16, 92 (1948).

76. Donohue, J.; Caron, A.; and Goldish, E. Nature 182, 518 (1958).

77. Donohue, J.; Caron, A.; and Goldish, E. Acta Cryst. 14, 548 (1961).

78. Donohue, J.; Caron, A.; and Goldish, E. J. Am. Chem. Soc. 83, 3748 (1961).

79. Donohue, J.; Caron, A.; and Goldish, E. J. Polymer Sci. 50, S-17 (1961).

80. Donohue, J. "The Structure of Elemental Sulfur" in Org. Sulfur Compounds, Vol. I., Pergamon, London 1961, N. Karash edited.

81. Dorabialska, A.; Krok, J. Zeszyty Nauk. Polytech. Lodz-Chem. No. 5 (57) 3.

82. Dufraisse, C.; Pinazzi, C.; and Baget, J. Compt. Rend. 222, 497 (1946).

83. Engel, M. R. Bull. Soc. Chim. 6, (3) II, 12 (1891).

84. Engel, M. R. Compt. Rend. 112, 866 (1891).

85. Erämetsä, O. Suomen Kemistilehti, B31, 237 (1958).

86. Erämetsä, O. Suomen Kemistilehti, B31, 241 (1958).

87. Erämetsä, O. Suomen Kemistilehti, B31, 246 (1958).

88. Erämetsä, O. Suomen Kemistilehti, B32, 15 (1959).

89. Erämetsä, O. Suomen Kemistilehti, B32, 47 (1959).

90. Erämetsä, O. Suomen Kemistilehti, B32, 97 (1959).

91. Erämetsä, O. Suomen Kemistilehti, B32, 233 (1959).

92. Erämetsä, O. Suomen Kemistilehti, B35, 154 (1962).

93. Erämetsä, O. Suomen Kemistilehti, B36, 6 (1963).

94. Eyring, H.; Cagle, F. W. J. Phys. Chem. 57, 942 (1953).

95. Fairbrother, F.; Gee, G.; and Merall, Z. T. J. Polymer Sci. 16, 459 (1955).

96. Faivre, R.; Chandreau, G. Proc. Intnatl. Congr. Pure Appl. Chem. (London) 11, 87 (1947).

97. Fanelli, R. J. Am. Chem. Soc. 72, 4016 (1950).

98. Farr, C. C.; McLeod, D. B. Proc. Roy. Soc. (London) A118, 534 (1928).

99. Feher, F. See Ref. 38, p. 81.

100. Feher, F. See Ref. 38, p. 112.

101. Feher, F. Z. Anorg. Allgem. Chem. 292, 210 (1957).

102. Feher, F.; Hellwig, E. Z. Anorg. Allgem. Chem. 294, 63 (1958).

103. Feher, F. Z. Anorg. Allgem. Chem. 322, 172 (1963).

104. Feigl, F. J. Chem. Educ. 21, 479 (1944).

105. Ferreira, R. C. J. Chem. Educ. 25, 54 (1948).

106. Foss, O. Acta Chem. Scand. 1, 307 (1947).

107. Foss, O. Acta Chem. Scand. 4, 404 (1950).

108. Foss, O. "Structures of Compds. Containing Sulfur-Chains" in Adv. Inorg. Chem. and Radio-Chem., II. Academic Press, N. Y. 1960.

109. Frasch, H. Mineral Res. of the U.S. 29 (1903).

110. Fredga, A. Acta Chem. Scand. 12, 891 (1958).

111. Freund, T.; Adler, S.; and Sparrow, C. J. Chem. Phys. 21, 180 (1953).

112. Fridkin, V. M. Kristallografiya 1, 557 (1956).

113. Friedel, C. Bull. Soc. Chim. (2), 32, 113 (1879).

114. Friedel, C. Compt. Rend. 112, 834 (1891).

115. Frondel, C.; Whitfield, R. E. Acta Cryst. 3, 242 (1950).

116. Fukuda, M. Chem. News 125, 209 (1922).

117. Garcia-Fernandez, H. Bull. Soc. Chim. 1958, 265.

118. Gardner, D. M.; Fraenkel, G. K. J. Am. Chem. Soc. 76, 5891 (1954).

119. Gardner, D. M. Thesis, Columbia University (1955).

120. Gardner, D. M.; Fraenkel, G. K. J. Am. Chem. Soc. 78, 3279 (1956).

121. Gee, G. Trans. Faraday Soc. 48, 515 (1952).

122. Gee, G. Sci. Progr. (London) 193, No. 170 (1955).

123. Gee, G. Chem. Soc. (London) Spec. Publ. No. 12 (1958).

124. Gerding, H.; Westrik, E. Rec. Trav. Chim. 62, 68 (1943).

125. Gernez, M. D. Compt. Rend. 74, 804 (1872).

126. Gernez, M. D. Compt. Rend. 82, 115 (1876).

127. Gernez, M. D. Compt. Rend. 97, 1477 (1883).

128. Gernez, M. D. Compt. Rend. 98, 144 (1884).

129. Gernez, M. D. Compt. Rend. 100, 1584 (1885)

130. Gernez, M. D. J. Phys. Radium (2) 4, 349 (1885).

131. Gingrich, N. S. J. Chem. Phys. 8, 29 (1940).

132. Gmelin, L. "Hanbuch der anorg. Chemie," 8th ed. Vol. 9a, Verlag Chemie, Weinheim, 1954.

133. Goehring, M. See Ref. 38, p. 121.

134. Goldstein, E. Chem. News 111, 27 (1915).

135. Gordon, C. K. Phys. Rev. 95, 306 (1954).

136. Graham, J. I. Proc. Roy. Soc. (London) A84, 311 (1910).

137. Greenberg, J.; Sundheim, B. R. J. Chem. Phys. 29, 461 (1958).

138. de Haan, Y. M. Physica 24, 855 (1958).

139. Halla, F.; Mehl, E.; Bosch, F. X. Z. Physik. Chem. B12, 377 (1931).

140. Hamann, S. D. Australian J. Chem. II, 391 (1958).

141. Hammick, D. L.; Cousins, W. R.; and Langford, E. J. J. Chem. Soc. 797 (1928).

142. Hartmann, P. Koninkle. Ned. Akad. Wetenschap. Proc. Sec. B 55, 134 (1952).

143. Hartshone, N. H.; Roberts, M. H. — J. Chem. Soc. 1951, 1097.

144. Hartshone, N. H.; Bradley, R. S.; and Thackray, M. — Nature 173, 400 (1954).

145. Hartshone, N. H.; Briske, C. — Discussions Faraday Soc. No. 23, 196 (1957).

146. Hartshone, N. H.; Thackray, M. — J. Chem. Soc. 1957, 2122.

147. Hartshone, N. H. — Chem. Soc. (London) Spec. Publ. No. 12, 252 (1958).

148. v. d. Heijde, H. B. — See Ref. 38, p. 154.

149. Henkel, M. — Diss. Giessen, 1931.

150. Hildebrand, J. H.; Jenks, C. A. — J. Am. Chem. Soc. 43, 2172 (1921).

151. Ingrahm D. J. E.; Symons, M. C. R. — J. Chem. Soc. 1957, 2437.

152. Jacobson, H.; Stockmayer, W. H. — J. Chem. Phys. 18, 1600 (1950).

153. Jacobson, H.; Stockmayer, W. H. — J. Chem. Phys. 18, 1607 (1950).

154. Jaeckle, R.; Peperle, W. — Z. Physik. Chem. 217, 321 (1961).

155. Kapustinskii, A. F.; Mal'tsev, A. K.; and Mill, B. V. — Tr. Mosk. Khim.-Tekhonol. Inst. 1961, No. 35, 73-81.

156. Kelker, H. — See Ref. 38, p. 113.

157. Kellas, A. M. — J. Chem. Soc. 113, 903 (1918).

158. Kendrick, N. S.; Miller, J. E.; and Crawford, G. W. — Phys. Rev. 99, 1631 (1955).

159. Klemm, W.; Kilian, H. — Z. Physik. Chem. B49, 279 (1941).

160. Koester, H. M. — Beitr. Mineral. und Petrog. 6, 199 (1959).

161. Korinth, E. — Diss. Jena, 1928.

162. Korinth, E.; Linck, G. — Z. Anorg. Allgem. Chem. 171, 312 (1928).

163. Korinth, E. — Z. Anorg. Allgem. Chem. 174, 57 (1928).

164. Koros, E.; Maros, L.; and Schulek, E. — Ann. Univ. Sci. Budapest Sect. Chim. 2, 163 (1960).

165. Kowalski, W. — Chem. Stosowana 4, 407 (1960).

166. Krebs, H. — Angew. Chem. 65, 293 (1953).

167. Krebs, H.; Weber, E. F. — A. Anorg. Allgem. Chem. 272, 288 (1953).

168. Kruyt, H. R. — Z. Physik. Chem. 65, 486 (1909).

169. Kuester, F. W. — Z. Anorg. Allgem. Chem. 18, 365 (1898).

170. Lallemand, M. A. — Compt. Rend. 70, 182 (1870).

171. Lange, B.; Cousins, W. R. — Z. Physik. Chem. 143, 135 (1939).

172. Leddicotte, G. W. — "The Radio Chemistry of Sulfur" NAS-NS 3054 (1962).

173. de Leeuw, H. L. — Z. Physik. Chem. 83, 245 (1913).

174. Lewis, G. L.; Randall, M. — J. Am. Chem. Soc. 33, 476 (1911).

175. Lewis, G. L.; Randall, M. and Bickowsky, F. R. — J. Am. Chem. Soc. 40, 356 (1918).

176. Lovejoy, D. R. — Nature 197, 353 (1963).

177. Luft, N. W. — Monatsh. 86, 474 (1955).

178. Lutsiv, P. B.; Pashkowskii, M. V.; and Savitskii, I. V. — Doporidi. L'vivsk Derzh. Univ. 1961, No. 9, Pt. 2, 42.

179. Maeda, K. — Bull. Chem. Soc. Japan 34, 785 (1961).

180. Magnus, G. — Pogg. Ann. 92, 312 (1854).

181. Magnus, G. — Pogg. Ann. 99, 151 (1856).

182. Meyer, B. — Diss. Zuerich 1960.

183. Meyer, B.; Schumacher, E. — Helv. Chim. Acta 43, 1333 (1960).

184. Meyer, B.; Schumacher, E. — Nature 186, 801 (1960).

185. Meyer, B. — J. Chem. Phys. 37, 1577 (1962).

186. Meyer, B.; Brewer, L. — to be published.

187. Meyer, K. H.; Go, Y. — Helv. Chim. Acta 17, 1081 (1934).

188. Meyer, K. H. — "Natural and Synthetic High Polymers" 2nd Ed. Interscience, N.Y., 1950, p. 96.

189. Mitscherlich, E. — Ann. Chim. Phys. 24, 264 (1823).

190. Mondain-Monval, P. — Compt. Rend. 198, 1413 (1934).

191. Moss, T. S. — Proc. Phys. Soc. (London) 69A, 590 (1951).

192. Mueller, H.; Schmid, E. — Monatsh. 85, 719 (1954).

193. Murphy, T. J.; Clabough, W. S.; and Gilchrist, R. — J. Res. Natl. Bur. Std. 69A, 355 (1960).

194. Muthmann, W. — Z. Krist. 17, 336 (1890).

195. Myers, R. J.; Blukis, U. — Private communication. (1959).

196. Nadzhakov, G.; Kashukeer, N. T. — Compt. Rend. Acad. Bulgare Sci. 7, No. 9 (1954).

197. Nair, C. G.; Ramachandran, G.; and Murphy, A. R. V. — Monatsh. 94, 134 (1963).

198. Neuberger, M. C. — Z. Krist. 93, 20 (1936).

199. Neumann, K. — Z. Physik. Chem. 171, 399 (1934).

200. Norris, R. — Proc. Indian Acad. Sci. 13A, 291 (1941).

201. Norris, R. — Proc. Indian Acad. Sci. 16a, 287 (1942).

202. Pascal, P. — "Nouveau Traite de Chim. Minerale, XIII," Masson, Paris (1960).

203. Passerini, R. C. — "UV Spectra of Org. Sulfur Compounds," in "Org. Sulfur Compounds" (see Ref. 80)

204. Pauling, L. — Proc. Natl. Acad. Sci. U.S. 35, 495 (1949).

205. Peter, S. — Z. Elektrochem. 57, 289 (1953).

206. Pinkus, A. G.; Concilio, C.; McAttee, J. L.; and Kim, J. S. — J. Am. Chem. Soc. 79, 4566 (1957).

207. Pinkus, A. G.; Concilio, C.; McAttee, J. L.; and Kim, J. S. — J. Am. Chem. Soc. 81, 2652 (1959).

208. Pinkus, A. G.; Piette, L. H. — J. Phys. Chem. 63, 2086 (1959).

209. Pinkus, A. G.; Concilio, C. B.; McAttee, J. L.; and Kim, J. S. — J. Polymer Sci. 40, 581 (1959).

210. Pinkus, A. G. — Chem. Eng. News 38, No. 36, 44 (1960).

211. Pistorius, C. W. F. T. — J. Mol. Spectry. 3, 101 (1959).

212. Poulis, J. A.; Massen, C. H.; and v. d. Leeder, P. — Trans. Faraday Soc. 58, 52/474 (1962).

213. Poulis, J. A.; Derbyshire, W. — Trans. Faraday Soc. 59, 559 (1963).

214. Poulsen-Nautrup, E. Diss. Hannover 1954. (See also Ref. 38).

215. Powell, R. E.; Eyring, H. J. Am. Chem. Soc. 65, 648 (1943).

216. Preuner, G.; Schupp, W. Z. Physik. Chem. 68, 129 (1909).

217. Prins, J. A.; Poulis, N. J. Physica 15, 696 (1949).

218. Prins, J. A. See Ref. 38.

219. Prins, J. A. Physica 20, 124 (1954).

220. Prins, J. A.; Schenk, J.; and Hospel, P. A. M. Physica 22, 770 (1956).

221. Prins, J. A.; Schenk, J.; and Wachters, L. H. J. Physica 23, 746 (1957).

222. Prins, J. A.; Tuinstra, F. Physica 29, 329 (1963).

224. Pryor, W. A. J. Am. Chem. Soc. 82, 2715 (1960).

225. Pryor, W. A. "Mechanism of Sulfur Reactions," McGraw-Hill, N. Y., 1962.

226. Quinke, G. Ann. Phys. 26, (4) 631 (1908).

227. Rankin, G. A. J. Phys. Chem. 11, 1 (1907).

228. Rice, F. O.; Sparrow, C. J. J. Am. Chem. Soc. 75, 848 (1953).

229. Rice, F. O.; Ditter, J. J. J. Am. Chem. Soc. 75, 6066 (1953).

230. Rice, F. O.; Ingalls, R. B. J. Am. Chem. Soc. 81, 1856 (1959).

231. Rice, F. O.; Radford, H. E. J. Chem. Phys. 33, 774 (1960).

232. Rice, F. O. "Advances in Chemistry; Free Radicals in Inorg. Chem.", Am. Chem. Soc. publ. No. 36, (1962), p. 5.

233. Rickert, H. Z. Electrochem. 65, 463 (1961).

234. Rickert, H.; Birks, N. Ber. Bunsenges. Physik. Chem. 67, 97 (1963).

235. Ripamonti, A.; Vacca, C. Ric. Sci. Rend. 28, 1880 (1958).

236. Ripamonti, A.; Liquori, A. M. Ric. Sci. Rend. 29, 2186 (1959).

237. Sabatier, P. Compt. Rend. 100, 1346 (1885).

238. Salet, M. G. Compt. Rend. 73, 559/872 (1871).

239. Salet, M. G. Compt. Rend. 74, 804/865 (1872).

240. Salomon, W. Z. Krist. 30, 605 (1891).

241. Schaefer, H. F.; Palmer, G. D. J. Chem. Educ. 17, 473 (1960).

242. Schenk, J.; Poulis, J. A. Nature 172, 957 (1953).

243. Schenk, J. Thesis, Delft 1956.

244. Schenk, J. Physica 23, 325, 546 (1957).

245. Schenk, P. W. Angew. Chem. 65, 325 (1953).

246. Schenk, P. W. Z. Anorg. Allgem. Chem. 280, 1 (1955).

247. Schenk, P. W.; Thuemmler, U. Z. Electrochem. 63, 1002 (1959).

248. Schenk, P. W.; Thuemmler, U. Z. Anorg. Allgem. Chem. 315, 271 (1962).

249. Schmidt, M. Chapter 3, p. 98 in "Inorganic Polymers," F. G. A. Stone, ed. Academic Press, N. Y., 1962.

250. Schmidt, M.; Scherer, O. Naturwiss. 50, 302 (1963).

251. Scott, D. W.; McCullough, J. P. J. Mol. Spectry 6, 372 (1961).

252. Sekanina, J. Z. Krist. 80, 174 (1931).

253. Skirai, T. J. Chem. Soc. Japan Pure Chem. Sect. 72, 696 (1951).

254. Skjerven, O. Kolloid-Z. 152, 75 (1957).

255. Skjerven, O. Z. Anorg. Allgem. Chem. 291, 325 (1957).

256. Skjerven, O. Z. Anorg. Allgem. Chem. 314, 206 (1962).

257. Smith, A.; H lmes, W. B. Z. Physik. Chem. 42, 469 (1903).

258. Smith, A.; Holmes, W. B.; and Hall, E. S. Z. Physik. Chem. 52, 602 (1905).

259. Smith, A.; Holmes, W. B. Z. Physik. Chem. 54, 257 (1906).

260. Smith, A.; Carson, C. M. Z. Physik. Chem. 57, 698 (1907).

261. Smith, A.; Carson, C. M. Z. Physik. Chem. 61, 200 (1908).

262. Smith, A.; Brownlee, R. H. Z. Physik. Chem. 61, 209 (1908).

263. Smith, A.; Carson, C. M. Z. Physik. Chem. 77, 661 (1911).

264. Smits, A. Z. Physik. Chem. 83, 221 (1913).

265. Soklakov, A. I.; Illarionov, V. V. Russ. J. Inorg. Chem. English Transl. 6, 647 (1961).

266. Sokolova, E. A. Trudy Vsesoyerz Naud. Issleddovatel Instr. Metr. 24, 122 (1954).

267. Specker, H. Z. Anorg. Allgem. Chem. 261, 116 (1950).

268. Specker, H. Kolloid-Z. 125, 106 (1952).

269. Specker, H. Angew. Chem. 65, 299 (1953).

270. Spica, P. Z. Krist. 11, 409 (1884).

271. Srb, I.; Vasko, A. J. Chem. Phys. 37, 1892 (1962).

272. Staudinger, H.; Kreis, W. Helv. Chim. Acta 8, 71 (1925).

273. Stauffer, Chem. Corp. US Patent 2460365 (1954).

274. Strunz, H.; Herka, E. Naturwiss. 48, 596 (1961).

275. Strunz, H.; Herka, E. Naturwiss. 49, 9 (1962).

276. Taylor, A. M.; Rideal, E. Proc. Roy. Soc. (London) A115, 589 (1927).

277. Thompson, C. W.; Gingrich, N. S. J. Chem. Phys. 31, 1598 (1959).

278. Tinyakova, E. I.; [illegible], E. A. Dolyoplosk, B. A.; and Tikhomolova, M. P. J. Gen. Chem. USSR Eng. Transl. 25, 1333 (1955).

279. Tobolsky, A. V.; Eisenberg, A. J. Am. Chem. Soc. 81, 780 (1959).

280. Tobolsky, A. V.; Eisenberg, A. J. Am. Chem. Soc. 82, 289 (1960).

281. Trillat, J. J.; Forestier, J. Compt. Rend. 192, 559 (1931).

282. Trillat, J. J.; Forestier, J. Bull. Soc. Chim. France 51, 248 (1932).

283. Tuller, W. N. "The Sulfur Data Book" McGraw-Hill, N. Y., 1954.

284. Turrell, F. M. Science 105, 434 (1947).

285. Venkateswaran, C. S. Proc. Indian Acad. Sci. 4A, 345 (1936).

286. Venkateswarlu, K. Proc. Indian Acad. Sci. 12A, 453 (1940).

287. Ventriglia, U. Periodico Mineral. (Rome) 20, 237 (1951).

288. Vul, B. M. Fiz. Tverdoga Tela 3, 2264 (1961).

289. Warren, B. E.; Burwell, J. T. J. Chem. Phys. 3, 6 (1935).

290. v. Wartenberg, H. Z. Anorg. Allgem. Chem. 251, 166 (1943).

291. v. Wartenberg, H. Z. Anorg. Allgem. Chem. 286, 243 (1956).

292. v. Wartenberg, H. Z. Anorg. Allgem. Chem. 297, 226 (1958).

293. v. Weimann Kolloid-Z. 6, 250 (1910).

294. Wells, A. F. "Structural Inorganic Chem." Oxford Univ. Press, 1962, 3rd Ed., p. 411.

295. West, E. D. J. Am. Chem. Soc. 81, 29 (1959).

296. West, J. R. J. Phys. (and Coll.) Chem. 55, 402 (1951).

297. West, W. A.; Menzies, A. W. C. J. Phys. Chem. 33, 1880 (1929).

298. Whitaker, H. J. Phys. Chem. 29, 399 (1925).

299. Whitfield, R. E. Thesis, Harvard University, 1949.

300. Wigand, A. Z. Physik. Chem. 65, 442 (1909).

301. Wigand, A. Z. Physik. Chem. 77, 423 (1911).

302. Wolf, M. G. J. Chem. Educ. 28, 427 (1951).

303. Yost, D. M.; Russel, H. "Systematic Inorg. Chem." Prentice Hall 1944, N. Y., p. 276.

304. Zackrisson, M. Acta Chem. Scand. 15, 1785 (1961).

305. Zhelndev, I. S.; Fridkin, V. M. Fiz. Dielektrikov Sbornik 1960, 1939 (CA 56, 1276, 1962).

306. Zietz, M. C. Thesis, Univ. Calif. Berkeley 1960 (UCRL-9277).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.