Elemental Sulfur

BEAT MEYER*

Chemistry Department, University of Washington, Seattle, Washington 98195, and Inorganic Materials Research Division, Lawrence Berkeley Laboratory, University of California Berkeley, California 94720

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I. Introduction

A. General Background

During the last 10 years 12 new elemental sulfur rings have been synthesized, the structure of the third solid cyclooctasulfur allotrope has been determined, and much has been learned about the molecular composition of solid, liquid, and gaseous sulfur. Many bulk properties are more accurately known, and the color of liquid and gaseous sulfur can now be explained. The purpose of the present review is to discuss these recent discoveries, and to present an up-to-date picture of our present knowledge of elemental sulfur.

Elemental sulfur has been known and used for several thousand years. Until 1880, the most important source of industrial sulfur was the volcanic soil of Sicily. Since 1891, the patents of Frasch[1] permitted mining of ever-increasing volumes of very pure elemental sulfur from salt domes in North America. In 1971 almost 10 million tons of Frasch sulfur was produced in the U.S. In contrast, and despite the excellent process of Claus,[2] 1882, chemical recovery of sulfur from smelting and refining operations remained comparatively insignificant, until the recent demand for energy forced the recovery of by-product sulfur from natural gas. In 1971, for the first time, chemical production of Claus sulfur exceeded mining of Frasch sulfur.[3] Parallel to this historic transition from mining to chemical production, recent interest in environmental quality attracted many to study sulfur chemistry and the recovery of sulfur from sulfur dioxide in combustion gases. However, despite 10 years of intensive efforts, the best known processes are still inefficient and uneconomical applications of limestone. The basic chemistry of the dry limestone process was patented by Clegg[4] in 1815 with the goal of reducing boiler corrosion. The chemistry of the wet limestone process, used to recover SO_2 from producer's and water gas, was described in a patent by Philips[4] in 1814. Obviously, much opportunity exists to apply progress in sulfur chemistry to develop new production methods, and much sulfur research remains to be undertaken to improve chemical production and use of this element, of which 40 million tons was consumed last year, and a comparable amount was released into the atmosphere.

This review is primarily concerned with progress during the last 10 years. The most reliable and extensive summary of old research can be found in Gmelin.[5] Since then, several summaries of specialized areas have appeared. The properties of solid allotropes have been reviewed in this journal.[6] Donohue[7] has described the discovery of the structure of the solid allotropes; Schmidt[8] reviewed general properties of sulfur, as well as the eight new metastable allotropes[9] which his group synthesized, and the late Tobolsky[10] summarized his contribution to the present understanding of the polymer. Harris[11] discussed the composition of the melt, Berkowitz[12] that of the vapor, and Scott[13] and Wiewiorowski[14] that of solutions. Many chemical and physical properties[15] of solid, liquid, and gaseous sulfur have been reviewed. The properties and reactions of sulfur compounds are treated in volumes edited by Nickless,[16] Senning,[17] Tobolsky,[18] and Karchmer.[19] Further reviews have been published by Schmidt,[20] and others.[21] The structure of polysulfides has been discussed by Rahman,[22] and organic reactions of elemental sulfur are included in the classical series by Reid[23] and Kharasch.[24] The reaction mechanisms have been discussed by Pryor.[25]

Since the last review, high-purity elemental sulfur has become commercially available and is now almost universally used. Research on ultrapure sulfur has been quite successful,[26] and analytical methods[27] for impurities in sulfur, and traces of sulfur, are established. Furthermore, highly enriched sulfur isotopes have become available. ^{34}S is now being separated both by thermodiffusion in liquid CS_2, and by exchange between SO_2 and HSO_3^-. It has been estimated[28] that 90% enriched ^{34}S will be available for about $100/g, i.e., about a 1000 times cheaper than up to now.

Most chemists are now aware of the unusual molecular complexity of elemental sulfur, and the fact that the physical and chemical properties of solid sulfur are dependent on its temperature history. However, the nomenclature of sulfur species is still unsatisfactory[7,15] and confusing.

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* Address correspondence to author at the University of Washington address.

TABLE I. Guide to Nomenclature

Name	Synonyms	Molecular species	Designation used in this review	Section or ref
α (alpha)	Rhombic, orthorhombic, Muthmann's I	Cycloocta-S	Orthorhombic-α	III.B
β (beta)	Monoclinic I, Muthmann's II, prismatic	Cycloocta-S	Monoclinic-β	III.B
γ (gamma)	Monoclinic II, Muthmann's III, nacreus, mother-of-pearl, Gernez	Cycloocta-S	Monoclinic-γ	III.B
δ (delta)	Monoclinic III, Muthmann's IV, γ-monoclinic	Cycloocta-S	Allotropes of S_8	6, 7
ϵ (epsilon)	Engel, Aten, rhombohedral, monoclinic Engel	Cyclohexa-S	Rhombohedral	6, 7
ζ (zeta)	5th monoclinic, Korinth	Cycloocta-S	Allotrope of S_8	6, 7
η (eta)	4th monoclinic, Korinth	Cycloocta-S	Allotrope of S_8	6, 7
θ (theta)	Tetragonal, Korinth	Cycloocta-S	Allotrope of S_8	6, 7
ι (iota)	Erämetsä	Cycloocta-S	Allotrope of S_8	6
κ (kappa)	Erämetsä	Cycloocta-S	Allotrope of S_8	6
λ (lambda)		Cycloocta-S	Cycloocta-S_8	6
μ (mu)	(a) Insoluble	Catenapoly-S	Solid or liquid	III.C
	(b) Polymeric		Polymeric-S	IV.B
ν (nu)	μ	Mixture	Solid polymeric	III.C
ξ (xi)	Triclinic, Korinth	Cycloocta-S	Allotrope of S_8	6, 7
ο (omicron)	Erämetsä	Cycloocta-S	Allotrope of S_8	6, 7
π (pi)	(a) Aten, Erämetsä	Ring mixture	Frozen liquid	IV.A
	(b) Catenaocta-S			6
ρ (rho)	Aten, Engel	Cyclohexa-S	Cyclohexa-S	III.B
τ (tau)	Erämetsä	Cycloocta-S	Allotrope of S_8	
ϕ (phi)	Fibrous	Mixture	Fibrous	III.C, D
φ (phi)	Fibrous, plastic	Polycatena-S	Fibrous	III.C, D
χ (chi)	Plastic	Mixture	Polymeric	III.C
ψ (psi)	Fibrous	Mixture	Fibrous	III.C, D
ω (omega)	Insoluble, white, Das supersublimation	Mixture	Polymeric	III.C
m	Triclinic	Cycloocta-S	Allotrope of S_8	6
n	μ		Solid Polymeric	III.C
Aten	See ϵ, ρ	Cyclohexa-S	Rhombohedral	III.B
Braun	See μ	Mixture	Solid, Polymeric	6
Engel	See ϵ, ρ	Cyclohexa-S	Rhombohedral	III.B
Korinth	See ξ, η, θ, ζ	Cycloocta-S		6
Muthmann	See α, β, γ, δ	Cycloocta-S		6
Schmidt	See orthorhombic-S_{12}	Cyclododeca-S		III.B
Amorphous	ω, μ	Mixture	Solid, polymeric	III.C
Cubic	High pressure cubic plastic		High pressure forms	III.D
Fibrous	ψ, ϕ, phase II	Catenapoly-S	Fibrous	III.C, D
Insoluble	"Crystex," supersublimated	Mixture	Insoluble	III.C
Laminar	Phase I, white, ω, μ, χ	Catenapoly-S	Laminar	III.C, D
Metallic	High pressure metallic	?	High pressure forms	III.D
Photosulfur	Insoluble	?	Photosulfur	VI
Black	(a) Skjerven	?	Quenched liquid	III.E
	(b) Rice, Schenk	Mixture	Trapped vapor	
Brown	Maltsev	Mixture	Trapped vapor	III.E
Green	Rice	Mixture	Trapped vapor	III.E
Orange	Erämetsä			6
Purple	Rice	Mixture	Trapped vapor	III.E
Red	(a) Rice	Mixture	Trapped vapor	III.E
	(b) Erämetsä	Mixture	Trapped vapor	III.E
Violet	Rice	Mixture	Trapped vapor	III.E
E, F, G	Erämetsä's red	Mixture	Allotrope of S_8	6
I, K, L, M	Orange			6

TABLE II. Orbital Ionization Potential (I_V), Electron Affinity (E_V), and Mulliken's Electronegativity (χ) of Atomic Sulfur[a]

Configuration	Orbital	I_V	E_V	χ
s^2p^2pp	p	12.4	2.4	7.4
$(sp^3)^2(sp^3)^2sp^3sp^3$	sp^3	15.5	4.8	10.1
$(sp^2)^2(sp^2)^2sp^2\pi$	sp^2	16.3	5.4	10.9
	π	12.7	2.8	7.7

[a] Reference 32.

This review starts with a short guide to names and synonyms. In section II, properties of the S–S bond are discussed, and the present experimental knowledge of molecular variety is summarized. Sections III, IV, and V deal with the composition of the solid, liquid, and gas phase, while section VI discusses phenomena in solutions of nonpolar and ionic solvents. The latter includes a short discussion of positive and negative elemental ions. The thermal and spectral data and the sparse kinetic data will be integrated into the discussion of individual allotropes.

B. Nomenclature

There are many reasons for the confusing multitude of names and nomenclatures which are in use. Several allotropes were discovered at a time when the molecular structure and the nature of chemical bonding were not yet understood. As a matter of fact, the preparation and many properties of polymeric sulfur, α-, β-, and γ-sulfur, were known before it was proven that sulfur is an element. Periodic attempts by various authors to systematize the nomenclature have failed, as they often lead to further confusion. The third modification of Muthmann, for example, is the second monoclinic modification of Korinth, and is also widely called γ-sulfur.

There are so many types of sulfur allotropes that a systematic nomenclature yields long and complicated names. Thus, the choice is between clumsy or ambiguous names, and trivial names will likely remain in use. Table I indicates the names chosen for this review and lists some of the most common synonyms encountered in the references. In case of doubt, the least ambiguous of the most widely accepted name is used.

Greek letters will be used as sparingly as possible. However, α, β, and γ remain the best accepted designations for the three fully identified solid allotropes of cyclooctasulfur. In contrast, ρ and ε for identifying cyclohexasulfur are unnecessary, as only one allotrope exists. The letters π and φ refer to a different class of compounds. These letters are used as comprehensive terms for identifying well-known, but poorly characterized mixtures: π refers to all components, other than cyclooctasulfur, in the sulfur melt; φ-sulfur is a fibrous solid allotrope, obtained by quenching liquid polymeric sulfur.

II. The Sulfur Bond

A. Electronic Structure

The sulfur atom has the same number of valence electrons as oxygen. Thus, sulfur atoms S_2 and S_3 have physical and chemical properties analogous to those of oxygen and ozone. S_2 has a ground state of $^3\Sigma_g^-$. Its excited electronic energy levels[29] correspond to those of O_2. S_3 has a well-known uv spectrum, and probably has a bent structure, analogous to its isovalent molecules[30] O_3, SO_2, and S_2O. Accordingly, S_3, thiozone, most likely has ground state $^1\Sigma$. However, S_8 and not S_2 is the stable STP form of sulfur. Thus, the chemistry of the two elements differs because sulfur has a pronounced tendency for catenation. The most frequently quoted explanation is based on the electron structure of the atom. Sulfur has low-lying unoccupied 3d orbitals,[31] and it is widely believed that the 4s and 3d orbitals of sulfur participate in bonding in a manner similar to the participation of 2s and 2p orbitals in carbon.

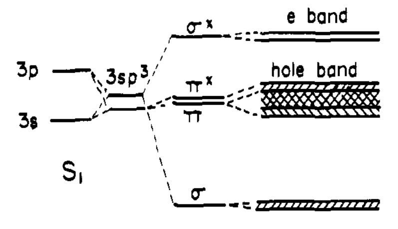

Figure 1. Electronic structure of S_8, and α-sulfur, derived from the energy levels of the free atoms.[31] Both the narrow electron band and the hole band contribute to the electric conductivity (after Gibbons[40]).

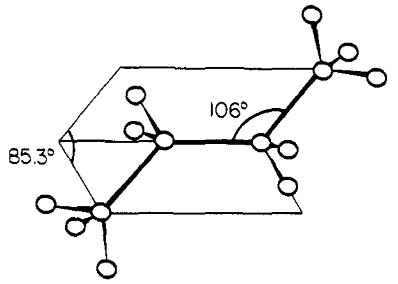

Figure 2. S–S–S–S bond structure. The unrestrained bond angle[146] is 106°, and the torsion angle is 85.3°. Data for various allotropes are listed in Table XI.

A discussion of the wave-mechanical calculations of various configurations and the ionization states of the sulfur atom is given by Cruickshank.[32] The ionization potentials, electron affinities, and Mulliken's electronegativity for various orbitals of atomic sulfur are given in Table II. Considerations regarding the atomic wave functions,[33] radial functions from self-consistent field calculations, and orbital energies (the d-orbital energies are only about 10% of the p-orbital energies[32]) do not justify the belief in strong d-orbital participation[34] in S–S bonds. An ab initio calculation of S_8 arrives at the same conclusion.[35] Recent calculations by Miller and Cusachs[36] on cyclo-S_8, cyclo-S_6, cyclo-S_4, and catena-S_6 ions confirmed that the contribution of d orbitals to the ground-state energies of divalent sulfur compounds[37] is negligible, but they observed that in computations of energy levels of excited states the inclusion of d orbitals yields different energies, and that values calculated with d orbitals fit the observed spectra better than those without d orbitals. The same observation was made by Spitzer and Meyer[38] for an entire series of sulfur rings and chains, and ions. The importance of d orbitals increases drastically in the presence of a ligand field, as was shown by Craig and Zauli[39] for SF_6. A bond model for S_8 in the gas phase and the solid deduced from atomic orbitals has been given by Gibbons[40] and is shown in Figure 1. Clark[41] has described bonding in sulfur chains by a one-electron model and obtained energy levels compatible with those of Palma.[42] Müller and Heegn[43] developed a three-dimensional electron gas model which yields good relative bond energies for sulfur rings of various sizes. The charge distribution in some 100 elemental sulfur molecules and ions has been calculated with a Hückel model by Meyer, Peter, and Spitzer.[38]

B. Bond Geometry

The observed geometry of the divalent S–S–S bond is shown in Figure 2. The sulfur helix of S_∞ yields probably the best values for an undisturbed bond geometry. This "free"

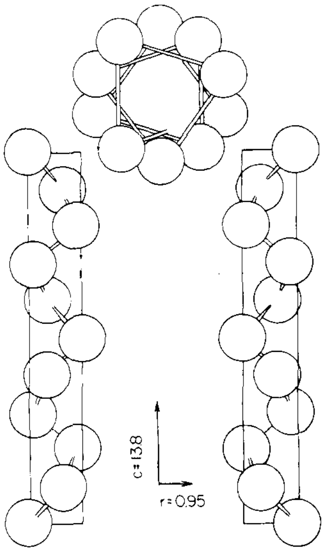

Figure 3. Structure of the sulfur helix. The molecular unit contains three atoms in three turns. The helix radius is 0.95 Å, the molecular unit axis, c = 13.8 Å. In the solid, left- and right-handed helices combine in various ways to form the different structures of polymeric sulfur. Figure 2 (top) is a view along the c axis.

bond is characterized by a torsion angle of 85.3°, a bond angle of 106°, and a bond distance of 2.066 Å. In Figure 2, sp^3 hybrid orbitals[40] are indicated at the terminal atoms, to suggest the direction of further bonds. Bergson[44] and others have proposed that the S-S dihedral angle is determined by repulsion between lone electron pairs on adjacent atoms. The significance of different bond distances has been discussed by Foss.[45] A list of S-S bond distances is given in Table III. The short S-S bond[29] in S_2 is probably due to π bonding. Partial π bonding accounts for all bonds shorter than 2.06 Å. Pauling[46] assumed a single bond value of 2.08 Å, using the S_8 ring as the basis for determining free bonds. His choice proved to be restrictive, as will be discussed below. The unstrained bond distance[47,49] is probably about 2.06 Å. Lindquist[48] correlated the S-S bond distance to the ratio of s/p hybridization. Torsion around the bond is restricted. Semlyen[49] estimated an activation energy of $\Delta E = 6$ kcal/mol for the transition from cis (+−) to trans (++) conformations. Figure 3 shows the left- and right-handed helices of fibrous sulfur, which result from continued +− configurations. A view along the c axis shows the staggering of atoms. Table IV indicates the conformations observed for some other sulfur compounds. Some species can exist in two different conformations, depending on the nature of the terminal group or the cation with which the sulfur chain shares the solid phase. The observed bond data are listed in Table VI.

C. Molecular Variety

There has been much controversy whether sulfur molecules in the various phases exist as rings, chains, or both. Rings can only form if the chain ends can come within bonding distance.[49] The necessary configurations are known to exist[49] for molecules with six or more atoms. In S_4 and S_5 considerable distortion of the normal divalent sulfur bond must occur before a ring can be formed. Table V lists some chain configurations, and the distance between terminal atoms for some short chains. The values are based on a model by Semlyen,[49] and are based on Pauling's[46] bond assumptions of a bond angle supplement of 74°, an internal rotational angle of 90°, and a bond distance of 2.06 Å. The values are good enough for a qualitative comparison. Experimental ionization patterns[50] and thermodynamic considerations[51] as well as theoretical calculations[43] indicate that all molecules, S_n, $6 < n < 12$, including S_7, S_9, and S_{10}, which suffer from unfavorable distances and contain inequivalent atoms, exist as rings in all phases.

TABLE III. Representative S–S Bond Distances

Molecule		S–S bond length, Å	Ref
S_2		1.887	29
S_2F_2		1.89	*a*
$S_2O_3^{2-}$		2.00	*b*
Diphenyl disulfide		2.03	*c*
α-Cystine		2.03	*d*
Me_2S_2		2.038	*e*
$S_3(CF_3)_2$		2.065	*f*
$S_3(Me)_2$		2.04	*g*
S_8O		2.04–2.20	106b
S_8^{+2}		2.04	105
α-Cystine hydrochloride		2.05	*h*
S_{12}		2.053	137
H_2S_2		2.055	*i*
S_6		2.057	7
S_8		2.060	7
S_∞		2.066	145
$S_nO_6^{2-}$	$n = 3$	2.15	*j*
	$n = 4$	2.02	*k*
	$n = 5$	2.04; 2.12	*l*
	$n = 6$	2.04; 2.10	*m*
$S_2O_6^{2-}$		2.15	*n*
$S_2O_5^{2-}$		2.209	*o*
$S_2O_4^{2-}$		2.389	*p*
S_4N_4		2.58	*q*

[a] R. L. Kuczkowski, *J. Am. Chem. Soc.*, **86**, 3617 (1964). [b] L. Csordas, *Acta Chim. (Budapest)*, **62**, 371 (1969). [c] J. D. Lee and M. W. R. Bryant, *Acta Crystallogr., Sect. B*, **25**, 2094 (1969). [d] B. M. Oughton and P. M. Harrison, *Acta Crystallogr.*, **12**, 396 (1959). [e] D. Sutter, H. Dreizler, and H. D. Rudolph, *Z. Naturforsch. A*, **20**, 1676 (1965). [f] H. J. M. Bowen, *Trans. Faraday Soc.*, **50**, 1 (1954). [g] J. Donohue and V. Schomaker, *J. Chem. Phys.*, **16**, 92 (1948). [h] L. K. Steinrauf, J. Peterson, and L. H. Jensen, *J. Am. Chem. Soc.*, **80**, 3835 (1958). [i] M. Winnewisser and J. Haase, *Z. Naturforsch. A*, **23**, 56 (1968). [j] W. H. Zachariasen, *Z. Kristallogr.*, **89**, 529 (1934). [k] O. Foss, S. Furberg, and H. Zacharisen, *Acta Chem. Scand.*, **8**, 459 (1954). [l] O. Foss and O. Tjomsland, *ibid.*, **10**, 288 (1956). [m] O. Foss and K. Johnson, *ibid.*, **19**, 2207 (1965). [n] E. Stanley, *Acta Crystallogr.*, **9**, 897 (1956). [o] I. Lindqvist and M. Mörtsell, *ibid.*, **10**, 406 (1957). [p] J. D. Dunitz, *ibid.*, **9**, 579 (1956). [q] B. D. Sharma and J. Donohue, *ibid.*, **16**, 891 (1963).

TABLE IV. Conformations of Catena Sulfur Compounds

Conformation[a]	Compound
+ +	Di-2-iodoethyl trisulfide
	Dibenzenesulfonyl trisulfide
	Di-*p*-toluenesulfonyl trisulfide
	Dimethanesulfonyl trisulfide
	Ammonium telluropentathionate
+ −	Cyanogen trisulfide
	Triclinic barium pentathionate dihydrate
	Barium pentathionate hydrate acetonate
	Orthorhombic barium pentathionate dihydrate
+ + +	Cesium hexasulfide
	trans-Dichlorodienylcobalt(III) hexathionate monohydrate
+ − +	Potassium barium hexathionate

[a] The sign corresponds to the sign of the internal rotational angle: + + and − − corresponds to trans; + − to cis. See ref 22 and 49.

Obviously, the larger the chain, the greater is the probability that some of the configurations allow strain-free ring closure. However, neither thermodynamic nor kinetic stability of the rings increases with size. Experiments show that S_8, S_{12}, and S_6 are the most stable molecules, in that order,[52] probably because of symmetry considerations and because of non-

TABLE V. Chain Conformations Favoring Ring Formation[a]

No. of atoms in chain	Distance between terminal atoms, Å	Chain conformations
5	3.59	+ − +
6	2.06	+ − + −
7	1.01	+ − + − +
	3.68	+ + − + −
8	1.56	+ − + − + −
	2.94	+ + − + − +
9	2.43	+ + − + − + −
	3.26	+ − + − + − +
	3.71	+ + + − + − +
10	1.07	+ + − + − + − −
	3.24	+ − + − + − − +
	3.42	+ − + − − + + −
	3.70	+ − + + − − + −
	3.72	+ + − + − − + +
	3.75	+ + + − + − + −
11	2.01	+ + − + − + − − +
	2.23	+ − + + − − + − +
	2.27	+ + − + − − + + −
	2.54	+ + + − + − + − −
	2.59	+ + − − + − + + −
	2.63	+ + − − + + − − +
12	0.20	+ − + − − + + − + −
	0.53	+ + − + − − + + − +
	0.66	+ + − − + − + + − −
	0.91	+ + − − + + − − + +
	1.57	+ − + − − − − + − +
20		+ + + − − + + + − − + + + − − + + +

[a] See ref 49.

neighbor interaction[53] and atoms across the ring. The structure of S_8 and S_{12} is shown in Figure 4. Experimental bond data of these molecules are well established, and listed in Table XI. S_6 has a chair structure, as is seen in Figure 5. The crown-shaped S_8 is the thermodynamic stable form of sulfur at STP, and was used by Pauling and his predecessors as the basis for determining "free" S–S–S dimensions. This procedure constituted the best possible approach at that time and was very successful, even though bonding in S_8 differs from that in other rings, as the crown structure allows for considerable cross-ring interaction[53] between nonbonded atoms. The existence of the amazingly stable S_{12} ring[54] confirms that Pauling's assumptions about the S–S bond were correct, even though his unnecessarily restrictive assumptions about S–S–S bond conformations led him to forbid its existence.

Large rings are unstable because they lack higher order bond contributions, are awkward, and have unshielded atoms. Furthermore, the S–S bonds have low-lying triplet states[38b] which make them photosensitive,[55] and the resulting chains undergo quick degradation:[8,56]

$$-S_x- \longrightarrow S_8 + -S_{x-8}-$$

The synthesis of large rings is interrupted by formation of S_8 rings, whenever the chains are long enough. However, Schmidt[9] showed that large rings can be made, that they occur in the melt[54] and that such rings, once they are formed, are far more stable than had been anticipated.

Rings and chains having a given number of atoms have very different electron structure. Sulfur chains, except S_3, are expected to be diradicals,[57,58] while rings have fully paired electrons. Thus, rings correspond to chains with terminal groups, such as, for example, sulfanes $H-S_x-H$. The difference between the ring and chain shows in chemical reactivity, as well as in physical properties, for example, color.

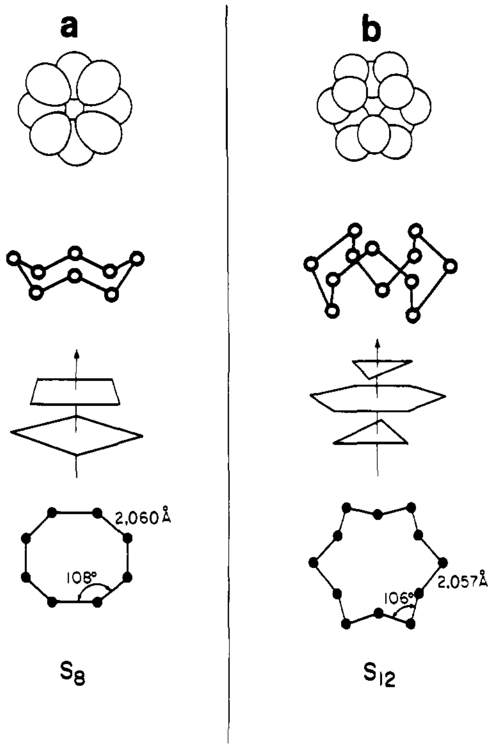

Figure 4. The structures of S_8 and S_{12}.

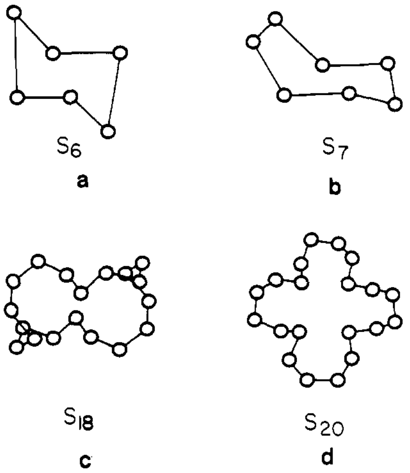

Figure 5. Views of (a) S_6, (b) S_7, (c) S_{18}, and (d) S_{20}. Molecular data are summarized in Table XI, the structures of the solids in Table XIII.

All known rings exhibit yellow hues.[58] The spectra, as far as known, all show an absorption band in the 250–300-nm region. The transition energies[38] are shown in Figure 6. The uv absorption of the corresponding yellow $H-S_x-H$ chains is well established.[59] It lies in the 280-nm region. With increasing chain length, the absorption shifts to the red and converges toward 330 nm. It fits the sequence of electronic transition energies calculated[60] with a one-electron model, as well as those obtained with an extended Hückel calculation.[38] The elemental free-radical chains absorb in the visible. The observed absorption of short chain members and the calculated transitions are also shown in Figure 6.

The calculations[38,58] predict that with increasing chain length the transition energy converges toward 850 nm, i.e., the near-infrared. The convergence of transition energies is an intrinsic property of all homologue series. It has been thoroughly discussed for the alkane series.[61] In the case of free-radical chains of sulfur, it indicates that interaction between terminal atoms, via the chain, becomes negligible. The shift of proton NMR spectra of the sulfanes[62] $H-S_x-H$, of the

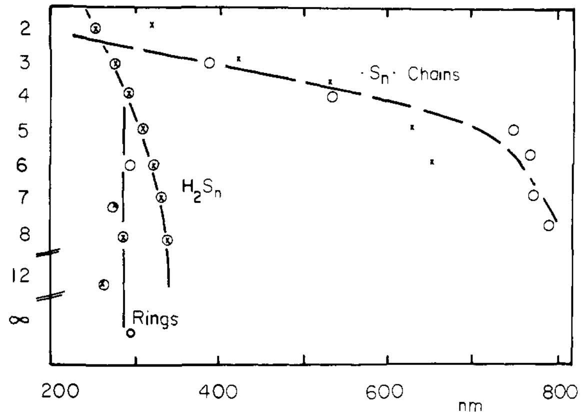

Figure 6. First allowed transition for (a) sulfur chains, (b) sulfur rings, and (c) sulfanes as a function of chain length: (O) observed points, (X) calculated value.

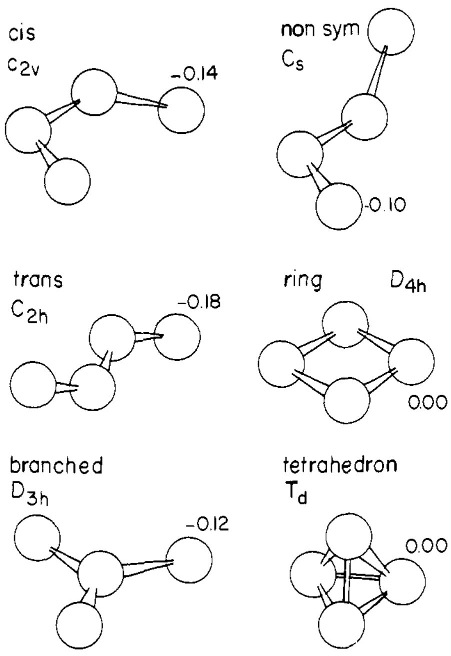

Figure 7. Six isomers of S_4. The numbers on the terminal atoms indicate the electronic charge.

corresponding Raman spectra,[59] and the calculations[38,60] for these compounds, and elemental sulfur chains indicate that approximately eight atoms are sufficient to interrupt intrachain communication between terminal groups. Thus, terminal groups in long chains act as independent functions, and intermediate chain members behave increasingly like members of a large ring. Sulfur chains,[63] absorbing in the visible, are deeply colored, and according to these considerations, $-S_\infty-$ must be black. However, polymeric sulfur is yellow and absorbs in the uv, as is seen in Figure 14b. The puzzling color of polymeric sulfur,[58] and its significance for the elucidation of the structure, will be discussed later.

Another interesting, unsolved structural problem regards the structure of S_4 and S_5. As mentioned, normal bond geometry prevents formation of an unstrained S_4 ring. However, for this molecule, several other structures are feasible. Figure 7 shows six possible isomers of S_4. Extended Hückel calculations,[38] based on spectroscopic atomic parameters,[31] suggest that the ++ conformation and the branched D_{3h} form have comparable stability. All others, including the planar ring, are calculated to be significantly less stable. It will be shown later that experimental evidence is insufficient to determine the structure of S_4, even though thermodynamic[51] and photoionization[50] evidence seems to favor the ring. The question whether sulfur forms branched molecules has been raised periodically, but has always been rejected, largely by analogy with experimental evidence regarding larger molecules. However, the idea of a branched S_4 structure is not as far fetched as it might seem for longer chains, because S_4 is isovalent with SO_3. The calculated electronic charge, indicated on the terminal atoms in all molecules in Figure 7, appears also reasonable. It should be noted that the $S_4{}^{2+}$ ion, observed by Gillespie,[64] has quite a different electron configuration from that of S_4. It probably has a planar ring structure,[65] analogous to that observed for $Se_4{}^{2+}$.

TABLE VI. Summary of Observed Sulfur Species

Atoms per molecule	Ring[a]	Chain[a]	Ion[b] +2	Ion[b] −1	Ion[b] −2
1		g			c
2		g	?	c	c
3		l, g	?	c	c
4	(g)	l, (g)	r		c
5	(s), (g)	l, (g)			c
6	s, (l), g		(r)		c
7	s, (l), g				c
8	s, l, g		r		c
9	s, (l), g				c
10	s, (l), g				c
11	s, (l), g				c
12	s, l, g				c
					c
18	s		r		c
					c
20	s				c
					c
∞	(s), (l)	(s), l			c

[a] Parentheses indicate that the structure is uncertain; s, l, and g indicate solid, liquid, and gas phase. [b] All ions occur in solution; c indicates chain, r indicates rings.

S_5 occurs in the gas phase, and in the liquid. Table V shows that a nonsymmetric ring would be highly stressed. A planar ring would require a quite unnatural bond angle of 75°. Thermodynamic reasoning seems to favor S_5 as a ring[52] in the solid, as a diradical chain in the liquid,[11] and as a ring in the vapor. Maybe a structural elucidation of S_4N^-, which is isoelectronic with S_5, will bring further information.

Table VI lists all species which have been observed. If one considers the polymeric chains, with an average number of atoms of up to 10^6, several million different sulfur molecules exist. According to their properties they can be assigned to one of four groups. All observed rings containing up to 20 atoms can now be isolated as pure solids. Small molecules occur as part of the vapor. Large, polymeric molecules occur both in the solid and liquid phase, while ions are formed only in ionic solution. Each group will be discussed in connection with the phase in which it normally exists.

D. Bond Energy and Spectra

The thermochemical bond strength and the bond dissociation energy have been measured for many sulfur compounds.[54,66,67] However, until recently, little was known about the data for various allotropes.

The average bond energy[67,68] of the S–S bond is about 63 kcal/mol. The dissociation energy[18,69,70] is about 33 kcal/mol. It depends on the position of the S–S bond in the molecule's chain. The bond energies of the gaseous sulfur molecules, believed to be rings, were calculated by Berkowitz[12] from experimental data. Müller[43] used a three-dimensional free electron model to compute bond energies in the corresponding rings and chains. Such calculations do not yet yield reliable absolute values, but their trends are quite reliable

TABLE VII. ν_1 of Ten Sulfur Allotropes

Species	ν_1, cm^{-1}	T, K	Ref
S_2	718 (g)	880	206
S_3	590 (m)	650	199
S_4	668 (m)	20	199, 200
S_4^{2+}	584	300	64, 65
S_x	559 (g)	880	206
S_6	471 (s)	300	91
S_7	481 (s)	300	103
S_8	475 (s)	30	111, 114
S_{12}	459 (s)	200	140
S_∞	456 (l)	400	109
	(s)	300	192

TABLE VIII. Thermal Data for Phase Transitions

Transition	Process or reaction	T, K	ΔH, kcal/g-atom[a]	ΔS, cal/deg·g-atom	Ref
α, β	α-S_8(s) → β-S_8(s)	368.46 ± 0.1	0.096	0.261	119, 128
Sublimation α	α-S_8(s) → cyclo-S_8(g)	368.5	2.979	8.191	
β	β-S_8(s) → cyclo-S_8(g)	368.5	2.883	7.93	172
ϵ	ϵ-S_6(s) → cyclo-S_6(g)	300	4.02	8.38	6
Fusion α	α-S_8(s) → cyclo-S_8(l) + ?[b]	383[c]	0.507		52, 119, 122, 172
β	β-S_8(s) → cyclo-S_8(l) + ?[b]	392.9[c]	0.3842	0.75	173, 174
λ, π	cyclo-S_8(l) → catena-S_8(l)	432	4.1	2.88	71, 193
Polymerization	catena-S_8(l) + cyclo-S_8(l) → catena-S_8(l)	442.8	0.396[d]	0.58	10
Vaporization	S_i(l) → S_i(g)	717.824[e] = 444.674 °C	2.5	3.5	6

[a] 1 g-atom of sulfur = 32.066 g. [b] The composition of the melt is not known. [c] See also Table XIV. [d] See ref 10. [e] Sulfur is a secondary temperature reference point on the International Practical Temperature Scale, ref 201.

and indicate that, except for S_3, rings are indeed more stable than the chains.

The trend in bond energies and dissociation energies for polysulfides with different terminal groups has been reviewed.[59,66] The activation energies for various reactions of the S–S bond are deduced from thermal equilibria.[71] This can be dangerous in the case of sulfur, as traces of impurities can totally alter processes[56] such as bond dissociation, by inducing ionic reactions which proceed far quicker and by a different mechanism than the homolytic scission. Another problem is caused by the photosensitivity[55] of the sulfur bond, which is not yet satisfactorily explained. Since reliable methods for the preparation of pure sulfur allotropes have become available, accurate thermochemical data can be expected within the next few years.

The strength of S–S bonding is reflected in the bond distance, shown in Table III. The Raman and ir frequencies also provide valuable information. Table VII lists the stretching frequency, ν_1, for nine elemental sulfur molecules for which an assignment seems reliable. Except for S_4, for which the assignment is not reliable, and for which a branched structure is possible, the trend follows that expected for a homologue series. The high value of S_7 is clearly due to the bond strain, discussed above. These spectra will be discussed in connection with the individual allotropes. Evaluation of x-ray spectra in terms of S–S bonds has been performed by Whitehead[72] and Narkuts.[73]

III. Solid Sulfur

A. General

The stable STP form of sulfur is orthorhombic α-sulfur consisting of cycloocta-S molecules. At 95.3 °C α-sulfur converts into monoclinic β-sulfur, which melts at 119.6 °C. Other allotropes of cyclooctasulfur can be obtained from solutions. Of these, only monoclinic γ-sulfur is well characterized. Other well-established solid allotropes containing cyclohexa-S, cyclododeca-S, and other sulfur rings have been prepared by reaction of sulfur compounds. Another class of allotropes, made by decomposition of sulfur compounds in aqueous solution or by quenching hot liquid or gaseous sulfur, comprises insoluble and other types of sulfurs. All contain long helices of polymeric sulfur, which is easily prepared, much used commercially, and has well-known bulk properties. However, its structure is still incompletely characterized, as it contains helices mixed with other molecular species. The best identified form of polymeric sulfur is fibrous sulfur, which is identical with one of the many high-pressure allotropes which have been reported.

All these allotropes will be discussed in the following sections which are organized according to the molecular species of which the solid is composed. Thermal data[74] for the conversion of various forms are given in Table VIII. The transition α(s) → β(s) is well established by experiment. The heat of sublimation of cycloocta-S allotropes and of cyclohexa-S has been calculated and seems reliable. The fusion and freezing of sulfur are far more controversial and are separately reviewed in Table VIII and discussed in the section on liquid sulfur, as is ring scission and polymerization.

The specific heat of elemental sulfur has been recently reviewed by Jensen.[74] Some selected values are listed in Table IX. Most are close to those observed by West,[74] except for β-sulfur, for which new data have recently become available.[75]

The thermal conductivity of sulfur[76] decreases from 11 W/m·deg at 4.2 K to 0.29 W/m·deg at 0 °C. At 100 °C it is 0.15 W/m·deg. Sulfur ranks with mica and wood among the best thermal insulators. Recent data have been reviewed by Mogilevskii.[77] Mechanical properties of solid allotropes have been reviewed by Dale.[78]

Standard reference sources list different values for the vapor pressure of sulfur. Some critically selected[74] values are listed in Table X. The high-temperature and high-pressure data will be discussed in the section on sulfur vapor.

B. Allotropes of Cyclic Molecules

Rings of the formula S_n, $6 < n < 24$, are expected to occur in equilibrium with chains in liquid sulfur near the melting point, as part of the fraction called π-sulfur. The smaller rings have been found in a mass spectrometer in the vapor.[12] These pure solid allotropes are not very stable, as some contain very strained bonds.

During the last 10 years, Schmidt[9] and his group obtained seven new metastable allotropes by coupling two compounds with the correct combined number of sulfur atoms and the

TABLE IX. Specific Heat of Elemental Sulfur (cal/g-atom)[a]

T, °K	Sulfur species			
	α-S(s)	β-S(s)[b]	Liquid	Vapor
10	0.103	0.163		
15	0.348	0.412		
20	0.608	0.666		
25	0.868	0.906		
40	1.465	1.490		
50	1.795	1.808		
60	2.089	2.101		
100	3.090	3.077		
150	3.990	4.072		
200	4.650	4.817		
298.15	5.430	5.551		5.659
368.54	5.778	5.913	7.579[c]	
388.36		6.053	7.579	5.569
400			7.712	
420			8.190	
433			11.930	
440			10.800	
460			9.925	
717.75			7.694	5.252
1000				5.137

[a] Reference 74. [b] Reference 75. [c] Reference 176 gives 7.423.

TABLE X. Vapor Pressure of Elemental Sulfur

P, Torr	T,[a] °C	P, atm	T,[b] °C
10^{-5}	39.0	1	444.61
10^{-4}	58.8	2	495
10^{-3}	81.1	5	574
10^{-2}	106.9	10	644
10^{-1}	141	20	721
1	186	40	800
10	244.9	50	833
100	328	100	936
760	444.61	200	1035

[a] See West and Menzies.[74] [b] Rounded average values; see Baker[202] and Rau.[96,203]

appropriate, reactive terminal group. S_{12}, for example,[80] is best prepared from reaction of a sulfane[81] with n sulfur atoms, and a chlorosulfane with 12 − n atoms:[79]

$$H_2S_n + S_{(12-n)}Cl_2 \rightarrow S_{12} + 2HCl$$

With this reaction, S_6, S_{10}, S_{12}, S_{18}, and S_{20} can be prepared. The molecules S_7, S_9, S_{10}, and S_{11} are best prepared by

$$(C_5H_5)_2TiS_5 + S_xCl_2 \rightarrow S_{x+5} + (C_5H_5)_2TiCl_2$$

The titanium dicyclopentadienyl pentasulfide was synthesized by Köpf,[82] using procedures analogous to those employed by Hoffmann,[83] who in 1903 prepared $(NH_4)_2PtS_{15}$, which is now known to contain three S_5 chains forming six-membered rings with the central platinum ion.[84] A similar compound of molybdenum[85] contains four sulfur atoms in a five-membered ring: $(C_5H_5)_2MoS_4$.

1. S_5, *Cyclopentasulfur*

Pure S_5 has not yet been synthesized, but Schmidt[52] proposed the following synthesis of cyclopenta-S:

$$(C_5H_5)_2MoS_4 + SCl_2 \rightarrow S_5 + (C_5H_5)_2MoCl_2$$

Schmidt reports that this allotrope is liquid and polymerizes in daylight. It has been explained above that S_5 is expected to be very unstable, because of its unfavorable bond geometry.

TABLE XI. Structural Parameters of Sulfur Molecules

Molecule	Bond length, Å	Bond angle, deg	Torsion angle, deg	Ref
S_2	1.889			29
S_6	2.057	102	74.5	7, 102
S_8	2.060	108.0 ± 0.7	98.3	7
S_{12}	2.053	106.5 ± 1.4	86.1	137
S_{18}	2.059	106.3	84.4	141
S_{20}	2.047	106.5	83.0	142
S_∞	2.066	106.0	85.3	146
$S_8{}^{2+}$ ion	2.04	102 (93)		105
S_8O	2.04; 2.20	106		106

The strain in cyclopenta-S becomes evident from the separation of 3.59 Å between the terminal atoms[47] in the curled chain (Table V). Semiempirical calculations[38] indicate that the chain isomer would be thermodynamically most stable. The photoionization energy[50] of S_5 is 8.60 eV.

2. S_6, *Cyclohexasulfur*

Cyclohexasulfur was first prepared by Engel[86] by the reaction of concentrated hydrochloric acid with a saturated solution of thiosulfate at 0 °C. Aten[87] identified the rhombohedral crystals and proposed their presence in liquid sulfur. Kellas[88] believed that S_6 formed the liquid constituent responsible for polymerization. However, most chemists ignored the existence of cyclohexa-S, until Frondel and Whitfield[89] determined the unit cell, Donnay[7] established that the lattice is rhombohedral, and Donohue[90,117b] proved the structure. The molecule has the chair form, shown in Figure 5a. The bond length and bond angle are comparable to those of S_8, but the torsion angle is smaller than that of any other known allotrope, Table XI:

$$\text{S–S bond length } (d) = 2.057 \pm 0.018 \text{ Å}$$

$$\text{S–S–S bond angle} = 102.2 \pm 1.6°$$

$$\text{S–S–S–S torsion angle} = 74.5 \pm 2.5°$$

The ir and Raman spectrum of S_6 has been recorded by Berkowitz, Chupka, and Bromels[91] and Nimon.[92] The frequency and their assignment are listed in Table XII. Cyvin[93] reported mean amplitudes at 0 and 300 K, and a normal coordinate analysis. The uv spectrum has been published by Bartlett[94] and Oommen.[63]

S_6 occurs in the equilibrium liquid,[95] and in equilibrium vapor,[12] where it is believed to occur as a ring. The thermodynamic properties[96] have been calculated with a semiempirical theory by Miller and Cusachs,[36] and by Spitzer,[38] who also calculated transition energies and charge distribution for the catenahexa-S. S_6 reacts 10^4 times faster with nucleophilic agents[98] than S_8. In sunlight S_6 decomposes[97] forming S_8, and some S_{12}.

The best method to prepare S_6 was discovered by Wilhelm.[79,99] Dilute solutions of dichlorodisulfane and tetrasulfane in ether are combined to form cyclohexa-S in 87% yield:

$$H_2S_4 + S_2Cl_2 \rightarrow S_6 + 2HCl$$

The orange-red solid can be purified by recrystallization from toluene or CS_2. The solubility[100] has been measured in CS_2 and benzene. The rhombohedral crystals have a density of 2.209 g/cm³. This is the highest density of any sulfur form. Obviously, the 18 molecules of S_6 are very efficiently packed[7] in the unit cell, which has the space group $R\bar{3}$-$C_{3i}{}^2$. The lattice constants are a = 10.818 Å, c = 4.280 Å, and c/a = 0.3956,

TABLE XII. Observed Infrared and Raman Frequencies of Four Sulfur Allotropes (cm^{-1})

			S_8 (30 K)		
S_4^{2+} (planar)	S_6 (8 fundamentals)	S_7 (15 fundamentals)	(11 fundamentals)	Designation[a]	S_{12} (20 fundamentals)
A_{1g} $\nu_1 = 548$	A_{1g} $\nu_1 = 471$ $\nu_2 = 262$	$\nu_1 = 481$ $\nu_2 = 236$	$\nu_1 = 475$ $\nu_2 = 218$	a_1 R	$\nu_1 = 459$
	A_{1u} $\nu_3 = 390$	$\nu_3 = 397$	$\nu_3 = 411$	b_1 I	
	A_{2u} $\nu_4 = 313$	$\nu_4 = 274$	$\nu_4 = 243$	b_2 Ir	
B_{1g} $\nu_2 = 530$	E_u $\nu_5 = 463$ $\nu_6 = 180$	$\nu_5 = 516$ $\nu_6 = 180$	$\nu_5 = 471$ $\nu_6 = 191$	e_1 Ir	$\nu_5 = 465$
E_u $\nu_3 = 460$	E_g $\nu_7 = 448$ $\nu_8 = 202$	$\nu_8 = 145$	$\nu_7 = 475$ $\nu_8 = 152$	e_2 R	$\nu_7 = 425$ $\nu_8 = 266$
B_{2g} $\nu_4 = 330$			$\nu_9 = 86$		$\nu_9 = 62$
		$\nu_{10} = 356$ $\nu_{11} = 274$	$\nu_{10} = 437$ $\nu_{11} = 248$	e_3 R	
Ref 64, 65	Ref 91–93	Ref 103	Ref 107–115, 121		Ref 140

[a] R = Raman active, I = inactive, and Ir = infrared active.

TABLE XIII. Structure of Solid Allotropes

Molecule	Space group	Unit cell[a]	*a*	*b*	*c*	β, deg	Color	Density, gm/cm^3	Mp or dec, °C	Ref
S_6	$R\bar{3}\text{-}C_{3i}^2$	3–18	10.818	$c/a = 0.3956$	4.280		Orange-red	2.209	50–60	90
S_7	?	16–112	21.77	20.97	6.09		Yellow	2.090	39	102
$S_8\text{-}\alpha$	$Fddd\text{-}D_{2h}^{24}$	16–128	10.4646	12.8660	24.4860		Yellow	2.069	94 (112)	116–118
$S_8\text{-}\beta$	$P2_1/a\text{-}C_{2h}^5$	6–48	10.778	10.844	10.924	95.80	Yellow	1.94	133	126
$S_8\text{-}\gamma$	$P2/c\text{-}C_{2h}^4$	4–32	8.442	13.025	9.356	124° 98′	Light yellow	2.19	~20	131, 132
S_{12}	$Pnnm\text{-}D_{2h}^{12}$	2–24	4.730	9.104	14.574		Pale yellow	2.036	148	137
S_{18}	$P2_12_12_1\text{-}D_2^4$	4–72	21.152	11.441	7.581		Lemon yellow	2.090	128	141
S_{20}	$Pbcn\text{-}D_{2h}^{14}$	4–80	18.580	13.181	8.600		Pale yellow	2.016	124–125	142
S_∞	$Ccm2_1\text{-}C_{2v}^{12}$	160[b]	13.8	4 × 8.10	9.25		Yellow	2.01	104	146, 149

[a] First number is the number of molecules in the unit cell; second number is the number of atoms. [b] Ten atoms for three turns.

The structure of all solid allotropes is summarized in Table XIII. The crystals decompose[9,52] at 50 °C, but under high vacuum, for example, in a mass spectrometer,[12] cyclohexa-S molecules vaporize without dissociation. The photoionization energy[50] of S_6 is 10.2 eV.

3. S_7, *Cycloheptasulfur*

This allotrope is formed by the reaction

$$(C_5H_5)_2TiS_5 + S_2Cl_2 \rightarrow S_7 + (C_5H_5)_2TiCl_2$$

The S_7 molecule has the structure shown in Figure 5b. The identity was confirmed by Žahorszky.[101] Not all sulfur atoms are equivalent. The x-ray structure[102] and the ir spectrum[103] confirm this fact. The frequencies of the ir spectrum in solution, and the Raman spectrum of the solid in solutions, are listed in Table XII. Fifteen fundamentals are expected.

The light yellow needles have a density of d = 2.090 g/cm^3. The lattice constants are[102] a = 21.77 Å, b = 20.97 Å, and c = 6.09 Å.

The space group of this allotrope, which decomposes[9] at 39 °C, is not yet known. Sixteen molecules, i.e., 122 atoms, occupy the unit cell.

Semiempirical Hückel calculations[38] for S_7 chains, but not for rings, are available. The photoionization energy[50] is 8.67 eV.

4. *Allotropes of Cyclooctasulfur*

Cycloocta-S has the crown shape shown in Figure 4a. The symmetry is D_{4d} or D_{4h}. The structure is well established:[7]

S–S bond length (d) = 2.060 ± 0.003 Å

S–S–S bond angle = 108.0 ± 0.7°

S–S–S–S torsion angle = 98.3 ± 2.1°

The molecule occurs in the solid, liquid, and gas phase. The S_8 is the most stable configuration at STP. The stability is probably due to cross-ring resonance. Baur[104] suggested that a chair configuration might exist in liquid sulfur. S_8^{2+} has such a chair configuration.[105] In S_4N_4 diagonal sulfur atoms lie in planes above and below the nitrogen atoms,[8] while $S_4(CH_2)_4$ has the S_8 crown structure. A similar structure[106] has been found by Steudel for S_8O, by Cooper for mixed S_nSe_{8-n} rings, and by Weiss for S_7TeCl_2.

Above 150 °C substantial ring scission is observed. The bond dissociation energy[67–69] is estimated to be about 33 kcal/mol. The molecule is sensitive to visible light.[55] The photoionization energy[50] is 9.04 eV. It is not certain whether this is due to the absorption edge[63] at 280 nm, or whether S_8 has a weak triplet absorption in the green. The electronic energy levels have been computed and discussed by Palma,[42] Clark,[41] Miller,[36] and Spitzer.[38] Gibbons[40] discussed the energy levels of S_8 in the solid phase. The other properties of S_8 are well reviewed,[7] except for recent Raman work. Since the review of Strauss,[107] Ward,[108] Ozin,[109] Anderson,[110] Gautier,[111] and Zallen[112] have studied S_8 in solution and in single crystals. They confirmed the assignment of the 11 modes by Scott.[113] The Raman spectrum of $^{34}S_8$ has been measured by von Deuster.[114] A normal coordinate[115] analysis has been performed by Cyvin, and mean square amplitudes[115] have been recalculated by Venkateswarlu. Raman and ir spectral data are summarized in Table XII.

Cycloocta-S can crystallize in several different lattices; the structure of three solid allotropes is now well established.

a. Orthorhombic α-Sulfur

α-Sulfur is the STP form of cycloocta-S. Abrahams[116] has reported very accurate structure parameters.[7] Caron and Donohue[117] established the stacking of molecules, and Pawley and Rinaldi[118] confirmed the structure, and measured the intermolecular distances. The molecular packing is complex.[117] Figure 8a shows a projection perpendicular to the mean plane of half of the molecules. This figure shows the "crankshaft" structure[117] of this allotrope, which is still erroneously assumed by many to contain coaxially stacked rings. The lattice constants are a = 10.4646 Å, b = 12.8660 Å,

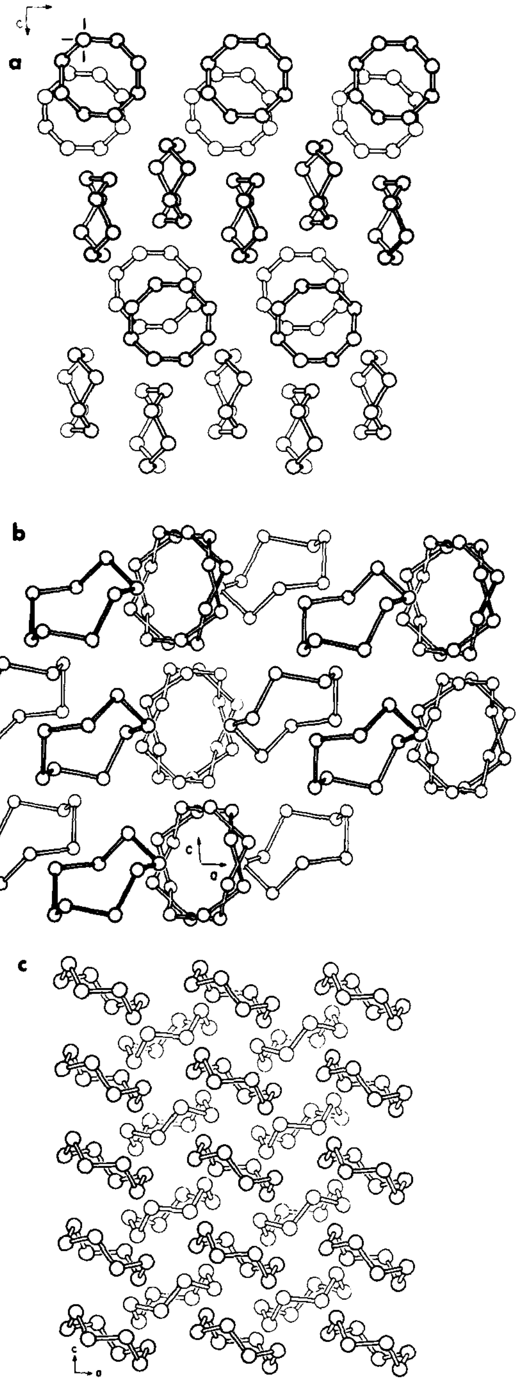

Figure 8. The structure of the solid allotropes of cyclooctasulfur: (a) the "crankshaft" structure of orthorhombic α-sulfur, (b) monoclinic β-sulfur, and (c) the "sheared penny roll" structure of monoclinic γ-sulfur. All views are perpendicular to the *c* axis (after Donohue, ref 15).

TABLE XIV. Melting Point of Allotropes

Allotrope	Mp, °C	Remarks	Ref
α-S	112.8	Single crystal	122
	115.11	Microcrystal	119
β-S	114.6	"Natural"	172
	119.6[a]	"Ideal" and obsd	122, 174 173
	120.4	Microcrystal	119
	133	"Ideal" calcd	52
γ-S	106.8	Classic	5, 6
	108	Optical, DTA	128
	108.6	Microcrystal	119
δ-S	106.0	Microcrystal	119
ω-S	77; 90; 160	Optical, TDA, DTA	128
	104		122
S_∞	75	Optical	128
	104	Classic	5
S_6	(50–)	Decomposition	52.86
S_7	(39–)	Decomposition	52, 82
S_{12}	148	Decomposition	52, 135–137
S_{18}	128	Decomposition	141
S_{20}	124	Decomposition	141

[a] Thermodynamic melting point.

and *c* = 24.4860 Å. The space group is *Fddd*-$D_{2h}{}^{24}$, the unit cell contains 16 molecules, i.e., 128 atoms, and the density is 2.069 g/cm^3.

The crystal growth of α-sulfur has been carefully studied by Thackray[119] and Hampton.[120] Almost perfect single crystals with only very few dislocations can be grown from CS_2; however, such crystals contain traces of CS_2, which has an ir frequency at 658 cm^{-1} which has long been mistaken for a fundamental[121] of S_8. Single crystals of α-sulfur do not easily convert to monoclinic sulfur. Instead, they melt[122] at 112 °C (Table XIV). Ir and Raman spectra of α-sulfur have recently been recorded by Ward,[108] Ozin,[109] Anderson,[110] and von Deuster.[114] These data are summarized in Table XII. Gautier[111] observed crystals at 30 K, and reports a large number of lattice frequencies which are well resolved at the low temperature. Ward[108] published crystal splitting effects. The electronic spectrum of solid S_8 has been discussed by Spitzer[38] and Gibbons.[40] The latter concludes that electric conductivity of α-S is due to two contributions: (a) to hole mobility, which has a value of about 10 cm^2/V·s, and exhibits a negative temperature coefficient, and (b) to electron transport in the electronic band (Figure 1), which is narrow enough for strong vibrational interaction. This contributes approximately 10^{-4} cm^2/V·s to the conductivity. Gibbons gives a site jump probability of 10^9/s, which would indicate that electrons are located on an individual molecule for several vibrations, i.e., that ions can be formed. The self-diffusion rate in α crystals was measured by Hampton and Sherwood.[120] The electric conductivity was measured by Spear and Adams,[123a] Fittipaldi,[123b] and Kuramoto and Watanabe.[124] The thermal conductivity[76] of α-sulfur is 11 W/m·deg at 4.2 K, 0.29 W/m·deg at 0 °C, and 0.15 at 95 °C. The specific heat of α-sulfur is summarized in Table IX; the heat of transition in Table VIII.

b. Monoclinic β-Sulfur

The structure of β-sulfur was determined by Trillat and Forestier,[125] Burwell,[126] and Sands.[127] The space group is *P*2$_1$/*a*-$C_{2h}{}^5$. Six S_8 molecules, i.e., 48 atoms, occupy the unit cell. A view of the lattice along the *b* axis is shown in Figure 8b. The lattice constants are *a* = 10.778 Å, *b* = 10.844 Å, *c* = 10.924 Å, and β = 95.8°.

β-Sulfur forms at 94.4 °C from α-sulfur.[119] It melts at 119.6 °C. A thermal analysis has been conducted by Miller[128] and by Currell.[122] Erämetsä[129] described formation from the melt; Thackray[119] the melting of the solid. Thermal data for transitions are in Table VIII. The density[7] is 1.94 g/cm^3, i.e., about 12% smaller than that of α-sulfur.

There has been some controversy about a phase transition at 101 °C, but this effect was caused by evaporation of water traces. Recently new C_p values have been reported by Montgomery,[75] who reports an anomaly at 186 K. The ir spectrum of β-monoclinic sulfur has been described by Strauss.[107]

c. γ-Monoclinic Sulfur

The structure of γ-sulfur, first described by Muthmann[130] in 1890, has been determined by Watanabe,[131] 1974, who confirmed the "sheared penny roll" stacking, proposed by de Haan[132] (Figure 8c). This allotrope can be obtained from solutions of cycloocta-S, and from its melt, but the best way to prepare the light yellow γ needles, which slowly decompose at room temperature, is to treat cuprous ethyl xanthate with pyridine.[131] γ-Sulfur crystallizes from the brown decomposition product in large needles. The lattice constants are a = 8.442 Å, b = 13.025 Å, c = 9.356 Å, and β = 124° 98′.

The space group is *P2/c*. Some confusion about the structure has been caused by different choices of axes. The conversion of coordinates has been reviewed by Donohue.[7] Four S_8 molecules occupy one unit cell. The density of this allotrope is 2.19 g/cm^3, i.e., higher than α- or β-sulfur.

d. Other Allotropes of Cyclooctasulfur

During the last 100 years about 24 allotropes containing cyclo-S_8 have been described.[6] Some of these are listed in Table I. It is doubtful whether any structures other than α-, β-, and γ-sulfur are reasonably stable. Instead, most of the other Greek letter allotropes are probably mixtures of α-sulfur, β-sulfur, or γ-sulfur, or constitute merely unusual crystal forms. As little progress has been made[7] in developing reliable preparation methods, no new information has become available since the last review.[6] Thus, we can omit discussion of the confusing list of species, and refer for details to earlier reviews.[6,15]

5. S_9, Cycloenneasulfur

Schmidt and Wilhelm[133] prepared deep yellow needles of cyclo-S_9 by the reaction

$$(C_5H_5)_2TiS_5 + S_4Cl_2 \rightarrow (C_5H_5)_2TiCl_2 + S_9$$

The structure of this compound has not yet been published. Thermodynamic considerations[51,52] indicate that this ring molecule also occurs in the vapor. The photoionization energy[50] of S_9 is not published.

6. S_{10}, Cyclodecasulfur

Schmidt and Wilhelm[99] prepared yellow-green solids containing S_{10} rings by the reaction of chlorosulfane with sulfanes. S_{10} is separated from S_6 by recrystallization, as their solubilities differ substantially.[100] A far better yield of 35% can be obtained if the following reaction[81] is conducted at −78 °C:

$$(C_5H_5)_2TiS_5 + 2SO_2Cl_2 \rightarrow S_{10} + 2SO_2 + (C_5H_5)_2TiCl_2$$

The structure has not yet been published, and the mass spectrum[101a] indicated limited stability. The solid must be stored at −40 °C.

7. S_{11}, Cycloundecasulfur

Schmidt and Wilhelm[134] prepared cyclo-S_{11} by the reaction

$$(C_5H_5)_2TiS_5 + S_6Cl_2 \rightarrow S_{11} + (C_5H_5)_2TiCl_2$$

Details of the properties and structure have not yet been published.

8. S_{12}, Cyclododecasulfur

In 1966 Schmidt and Wilhelm[52,133] prepared S_{12} by the reaction of sulfanes and chlorosulfane of proper chain length:

$$2H_2S_4 + 2S_2Cl_2 \rightarrow S_{12} + 4\ HCl$$

$$H_2S_8 + S_4Cl_2 \rightarrow S_{12} + 2HCl$$

TABLE XV. Preparation Methods for Metastable Allotropes

Species	Reagents	Ref
S_5	$(C_5H_5)_2MoS_4 + SCl_2$	82
S_6	(a) $HS_2O_3^- + HCl$	86
	(b) $S_2Cl_2 + H_2S_4$	74, 99
S_7	$(C_5H_5)_2TiS_5 + S_2Cl_2$	82, 85
γ-S_8	$CuSSCOC_2H_5$ + pyridine	131
S_9	$(C_5H_5)_2TiS_5 + S_4Cl_2$	133, 134
S_{10}	(a) $H_2S_6 + S_4Cl_2$	79
	(b) $(C_5H_5)_2TiS_5 + SO_2Cl_2$	138
S_{11}	$(C_5H_5)_2TiS_5 + S_6Cl_2$	138
S_{12}	$H_2S_8 + S_4Cl_2$	135, 136
S_{18}	$H_2S_8 + S_{10}Cl_2$	141
S_{20}	$H_2S_{10} + S_{10}Cl_2$	141

The first reaction[135] yields 3% S_{12}; the second,[136] discovered later, has a yield of 18%. The reaction is conducted in a dilute solution of ether, and the reagents are slowly and simultaneously added. In this way, the reagents have time to react, by forming an intermediate chain

$$H\text{–}S\text{- - -}S_x\text{–}S\text{–}Cl$$

and can complete ring closure before reaction with further reagents occurs. The principle of this synthesis is as beautiful as it is simple. Schmidt and Wilhelm have since prepared eight other new rings[9] with similar methods. A summary of their preparation methods is given in Table XV.

The S_{12} molecule has the structure[137] shown in Figure 4b in D_{3d}, but in the solid it is slightly distorted to C_{2h}. The bond properties are:

S–S bond length (d) = 2.053 ± 0.007 Å

S–S–S bond angle = 106.5 ± 1.4°

S–S–S–S torsion angle = 86.1 ± 5.5°

These values are very similar to those for S_8 and fibrous S_∞, i.e., the unperturbed bond value. As discussed above, this fits Pauling's[46] prediction for the bond value of sulfur species, even though he did not properly analyze all possible conformations of S_{12}, and rejected this molecule from the list of metastable allotropes. However, experiments show that S_{12} is more stable than S_6. It is formed in liquid sulfur,[52] and forms as a decomposition product of S_6 in toluene upon irradiation with light.[9] The solubility of S_{12} in CS_2 and benzene has been discussed by Schmidt.[138] The mass spectrum was studied by Buchler.[139] Solid S_{12} melts at 148 °C. The lattice constants were determined by Hellner and Kutoglu:[137] a = 4.730 Å, b = 9.104 Å, and c = 14.7574 Å.

The space group is *Pnmm*-$D_{2h}{}^{12}$. The unit cell contains two molecules, i.e., 24 atoms. This allotrope has a density of 2.036 g/cm^3. Mixed crystals of S_nSe_{12-n} have a very similar structure. The Raman and ir spectrum was studied by Steudel,[140] who tentatively assigned 6 of the 20 fundamentals.

9. S_{18}, Cyclooctadecasulfur

S_{18} has been prepared from sulfane and chlorosulfane mixtures[141] of the average formula

$$H_2S_8 + S_{10}Cl_2 \rightarrow S_{18} + 2HCl$$

The starting materials cannot be made in pure form, but are synthesized from shorter sulfanes to prevent formation of the more stable S_{12}, and other allotropes. Figure 5 shows a projection of the cyclo-S_{18} molecule. This lemon colored allotrope forms in a mixture with cyclo-S_{20}, and must be separated by recrystallization. The solubility of S_{18} in CS_2 is 240 mg/100 ml at 20 °C. This unexpectedly stable allotrope melts at 128 °C, and can be stored in the dark for several days, without a noticeable change in the x-ray diffraction pattern. The bond parameters[142,143] are:

S–S bond length (d) = 2.059 Å

S–S–S bond angle = 106.3°

S–S–S–S torsion angle = 84.4°

The bond properties are intermediate to those of S_6 and S_8, and similar to those of fibrous sulfur helices, given in Table XI. The lattice constants[142] are a = 21.152 Å, b = 11.441 Å, and c = 7.581 Å.

Four molecules, i.e., 72 atoms, form a unit cell. The space group is $P2_12_12_1$ and the density is 2.090 g/cm³.

10. S_{20}, Cycloicosasulfur

Schmidt[141,143] prepared S_{20} by combination of carefully prepared intermediates

$$H_2S_{10} + S_{10}Cl_2 \rightarrow S_{20} + 2HCl$$

S_{20} melts at 124 °C, but already decomposes in solution at 35 °C. The pale yellow crystals have a density of d = 2.016 g/cm³. The structure of the molecule, Figure 5, provides for four atoms each in a plane. The bond values[142] are:

S–S bond length (d) = 2.047 Å

S–S–S bond angle = 106.5°

S–S–S–S torsion angle = 83°

similar to those of S_{12}, S_{18}, and fibrous sulfur. The lattice parameters are a = 18.580 Å, b = 13.181 Å, and c = 8.600 Å. Four molecules, with 80 atoms, form a unit cell.

C. Allotropes of Polymeric Sulfur

All of the allotropes described below contain polycatenasulfur. The polycatena molecule forms long helices.[7,144,145] Figure 3 shows a section of a left- and a right-handed helix. Three turns of the helix contain 10 atoms. The bond characteristics[7,146] are:

S–S bond length (d) = 2.066 Å

S–S–S bond angle = 106°

S–S–S–S torsion angle = 85.3°

These values are very close to those in S_{20} and S_{12}, and lie between those of S_8 and S_6. It is believed that they represent the unperturbed values of the S–S bond.

Solid polycatenasulfur comes in many forms.[6,7,10,145] It is present in rubbery sulfur, plasic (χ) sulfur, laminar sulfur, fibrous (ψ, ϕ), η, μ, and insoluble ω, supersublimation, white, and crystex.[6,7,10] All of these forms are metastable mixtures of allotropes containing more or less well-defined concentrations of helices, cyclo-S_8, and other forms, depending on how they are made. Their composition changes with time. Unless impurities are present, formation of S_8 sets in and conversion to α-S will occur within less than 1 month. They are prepared by precipitation of sulfur in solution, or by quenching of hot liquid sulfur. In some allotropes, the helices can be purified by extraction of the nonpolymeric fraction with CS_2 or other solvents.

Donohue[7] summarized the structural information on the various forms in which the helices are stacked or curled. The best defined forms are *fibrous sulfur*, in which helices are mainly parallel because of stretching during their solidification, and *laminar sulfur* in which helices are at least partly criss-crossed in a "cross-grained" or a "plywood" like structure.

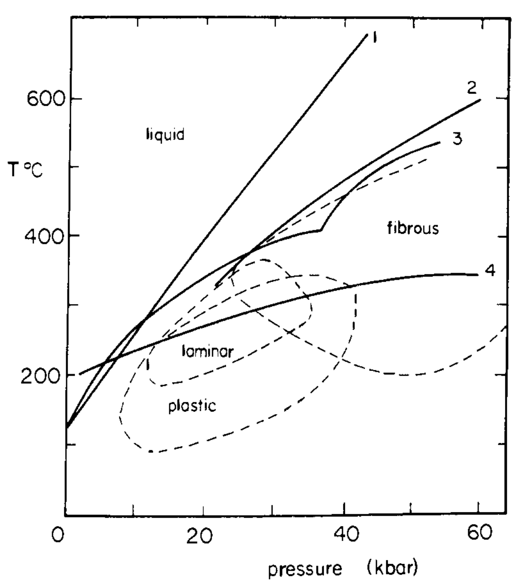

Figure 9. Melting curve of sulfur, and structure of allotropes obtained by quenching: (1) Deaton[153] and Vezzoli,[154] (2) Susse[155] and Sklar,[156] (3) Ward and Deaton[157] and Pankov,[158] and (4) Bäák.[159] The zone from which laminar,[148] fibrous,[149] and plastic[156] allotropes have been quenched is also indicated.

1. Fibrous Sulfur

The x-ray diffraction of freshly drawn fibrous sulfur[147] was first analyzed by Trillat and Forestier in 1931, and by Meyer and Go in 1934. The data by Donohue,[148] Tuinstra,[145] and Geller[146] indicate that the unit cell contains 160 atoms. The space group is $Ccm2_1$-$C_{2v}{}^{12}$. The structural parameters[146] are a = 13.8 Å, b = 4 × 8.10 Å, c = 9.25 Å, and β = 85.3°.

Geller's analysis was conducted on diffraction patterns obtained with samples prepared at 27 kbars. The density of fibrous sulfur is d = 2.01 g/cm³. Lind and Geller[146] believe that their preparation of phase II yields single crystals of φ-sulfur. The phase II structure has been indexed by Roof.[149] The thermal expansion coefficient[150] of φ-sulfur is 19 × 10^{-6} cm/deg along the pitch, 94 × 10^{-6} cm/deg along the a axis, and 72 × 10^{-6} cm/deg along the b axis. Thermal transition, polarization, dilatometry, and other properties have been reported by Miller.[128]

2. Laminar Sulfur

Laminar sulfur first described by Das,[152] seems to be identical with Geller's phase I, obtained at 250–300 °C and 20 kbars (Figure 9). Its structure has been discussed by Donohue.[7] The characterization seems still incomplete; it is very similar to, or possibly identical with, insoluble ω-sulfur and the "second fibrous" sulfur of Tuinstra.[145]

D. High-Pressure Allotropes

Various sulfur allotropes can be obtained by heating sulfur under pressure. Figure 9 shows some of the high pressure effects observed. Deaton[153] obtained a melting curve which is similar to that of Vezzoli.[154] Susse[155] obtained a curve similar to that of Sklar.[156] Ward and Deaton[157] published another melting curve which matches that of Paukov.[158] Bäák's[159] melting curve is also shown in Figure 9, but his cubic phase is not indicated, as it has not yet been confirmed. However, Figure 9 shows the p, T zones from which laminar sulfur[148] and fibrous sulfur[149] have been quenched. The plastic sulfur zone of Sklar[156] agrees well with Geller's observations. Tonkov[161] measured the molar volume of liquid sulfur under pressure, Bröllos and Schneider[162] report the optical properties of sulfur under pressure, and Kuballa and

Schneider[163] report a differential thermal analysis of sulfur under pressure. Block and Piermarini's experiments[164] explain the divergent observations reported for pressures above 24 kbars and temperatures above 250 °C. They waited at this point for 3 days without observing equilibrium, and explain this effect by slow kinetics and the poor thermal conductivity.[76] No wonder that authors using different equipment and different *p*, *T* cycling techniques observe dozens of different phases! The best established high-pressure forms are phase I and phase II of Geller.[146] In contrast, metallic sulfur has not been reproduced.[160] It is likely that some of the 12 phases of Vezzoli[154] contain interesting new structures.

E. Low-Temperature Solids

Cyclo-S_7, -S_9, and -S_{10} must be stored below room temperature.[9,52] At −78 °C and below quickly quenched hot liquid sulfur or hot sulfur vapor contains a variety of colored metastable solids.[63,165] Ir and uv spectra have shown that these solids contain S_3, S_4, and other allotropes. In the next section it will be shown that these quenched phases have been repeatedly used to determine the composition of hot sulfur, and the π fraction. However, great experimental care must be taken if a significant fraction of the high temperature species is to be trapped, because these particles recombine quickly and because sulfur is such a poor thermal conductor[76] that heat exchange is slow. Most molecules formed in trapped or quenched solids are intermediates,[166] i.e., recombination products. The properties of these are discussed in the next two sections together with those of the starting material. The absorption spectra of various molecules in frozen low-temperature solution or rare gas matrices are indicated in Figure 14. S_2 can be produced in rare gas matrices from elemental sulfur vapor trapped at 20 K, or by photolysis[167] of S_2Cl_2 in matrices. S_3 is best prepared from the vapor, by combination of atoms with S_2, or by gentle photolysis of S_3Cl_2 in frozen solution. S_4 can be prepared from S_4Cl_2, or by recombination of S_2 in matrices. S_5 has been deposited in mixtures from vapor, and S_6 and S_8 can be studied in frozen solution. Polymeric sulfur can be quenched as a thin film. Slowly quenched polymeric sulfur is yellow. Polymer quickly quenched to 76 K is red, because it contains small molecules which recombine at −100 °C.[165] The properties and reaction of the species will be discussed in the section on liquid sulfur and sulfur vapor, i.e., in the phase in which they are stable.

IV. Liquid Sulfur

The appearance and the molecular composition of liquid sulfur differ in three distinct temperature ranges. These regions and the effect of high pressure on liquid sulfur will be discussed separately.

A. The Melt below 150 °C

At least 19 different melting points of sulfur have been published. Table XIV gives a selection of values for the melting points of β-sulfur, which constitutes the stable solid at the melting point, and for other allotropes. The freezing point of sulfur is influenced by the *p*, *T* history of the melt, and by impurities. As high-purity sulfur was not readily available[168] until 1942, most old data are unreliable; i.e., the freezing points are too low.

Small droplets of sulfur can be supercooled. LaMer[169] kept particles with a diameter of 0.2 μ liquid at 25 °C for up to 20 days. Hamada[170] observed nucleation of droplets at −70 to −120 °C under a microscope, and determined a crystallization rate of 1.16 $cm^{-3} \cdot s^{-1}$ at −50 °C. Bolotov[171] and others have observed formation of various types of spherulites during crystallization of molten sulfur. The best present value for the melting point of pure β-sulfur is 119.6 °C, but Thackray[119] observed melting of microcrystals at 120.4 °C, while Schmidt[9,52] indicates that the ideal melting point might be as high as 133 °C. The freezing point of an equilibrated melt is 114.6 °C. This point has been called "natural" melting point.[172] The best value of the heat of melting seems to be the one observed by Pacor[173] and Feher,[174] ΔH_m = 384.2 ± 1.9 cal/g-atom at 119.6 °C, while the higher values of up to 414.8 ± 2.4 cal/g-atom are valid at 114 °C in an impure mixture. The specific heat[174] of the liquid at 120 °C is 7.02 cal/g-atom·deg. Feher also measured the expansion coefficient,[175] the electric conductivity,[176] and the viscosity of the melt, as did Bacon and Fanelli[168] and Doi.[177]

TABLE XVI. Freezing Point Depression

Equilibrated at *T*, °C	$T_\lambda - T_f$, °C		Av no. of atoms/ring
	Calcd	Obsd	
120	4.6		13.8
130	5.7	4,9	14.6
140	7.1	5.9	15.7
150	9.1	7.6	17.6

[a] See ref 11, 174, 179, 180, and 187.

Gernez[172] reported in 1876 that the melting point and the freezing point of sulfur differed. He recognized that this effect was not fully due to supercooling, or to impurities, but to a chemical effect which could be influenced by annealing the liquid at various temperatures. Aten[178] proposed in 1913 that the freezing temperature was caused by autodissociation of sulfur, forming a new species, π-sulfur, the concentration of which determined the freezing point depression. Krebs[95] argued in 1953 in favor of the existence of small rings in liquid sulfur, and determined the concentration of π-sulfur in liquid sulfur by quickly quenching it, extracting the solid with CS_2, and isolating π-sulfur, which precipitates from the extract upon cooling to −78 °C. The problem with this fraction is that it changes its composition for several days. Furthermore, it is questionable whether quenching of an insulator such as sulfur and extraction of the solid preserve the composition of the liquid. Most physical chemists familiar with Pauling's[46] paper tended to distrust explanations based on rings other than S_8 or S_6, until Schmidt[9,52] proved that at least seven of these can be prepared, are metastable, and that, for example, S_{12} can be found in all solidified melts. In 1967 Krebs published another very careful study[95] on π-sulfur which he extracted with a mixture of CS_2–methanol. In these solvents, S_6 has a distribution coefficient of 0.13, while the coefficient for S_8 is 0.11. After 700 distribution steps, π-sulfur could be separated into three fractions, one having a molecular weight of about S_6, a middle fraction containing S_8, and an average composition of about $S_{9.2}$, and a heavy fraction in which he suspected S_n rings, with $20 < n < 33$. Wiewiorowski[179] analyzed the freezing point depression and computed the concentration of cycloocta-S, and determined for this molecule a bond dissociation energy of 32 kcal/mol. This value agrees well with that of 32.8 kcal/mol obtained by Tobolsky[10] by analysis of the polymerization at higher temperature. Table XVI shows the freezing point depression observed, and the average number of atoms per ring calculated by Semlyen[180] with the help of a polymer model.

Obviously, the equilibrium composition of the sulfur melt is not yet established. The "natural" thermodynamic melting point is difficult to determine because of slow kinetics. It is now assumed to be 119.6 °C. At this point, solid monoclinic β-sulfur is in equilibrium with a liquid mixture of unknown composition. Higher "ideal" melting points can be observed because of the slow kinetics of the cyclooctasulfur ring dissociation. The "ideal" melting point for the transition of solid

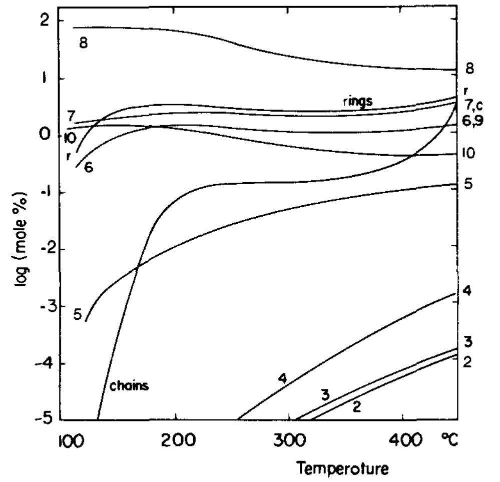

Figure 10. Composition of liquid sulfur I. Estimated mole fraction of liquid sulfur components of small species, large rings (r), and chains (n), computed from ref 11.

monoclinic β-sulfur to pure liquid cyclooctasulfur is not yet established. The fact that the p, T history reproducibly influences the freezing point indicates not only slow kinetics but also that cooling of the various hot sulfurs proceeds via different reaction paths and leads to different metastable mixtures of different metastable species, probably mostly rings.

The temperature dependence of the equilibrium composition of liquid sulfur computed by Harris[11,181] from various observed and estimated thermodynamic data is shown in Figure 10.

Baur[104] observed an unusual molar polarization effect and proposed a cyclo-S_8 with a chair configuration as a further component of the liquid. It is now certain that liquid sulfur contains rings other than S_8. Whether, and how much, catena-S_8 or other catena-S_x the melt contains, is not yet established. However, calculations by Miller,[36] and Cusachs,[36] and Spitzer[38] show that the acid–base character of rings and chains, first discussed by Wiewiorowski,[179] is sufficient to cause formation of cyclo-S_n–catena-S_x–cyclo-S_n charge-transfer complexes. Such complexes have been invoked to explain the small concentration of free spins in liquid sulfur at 150 °C. This observation is discussed in detail by Koningsberger.[181]

The melting point of sulfur is also pressure dependent.[153-160] Four different melting curves are shown in Figure 9. The different slopes are probably partly due to different purity of the samples. However, the curves also depend on the p, T history because of slow kinetics.[164]

B. Polymerization at T_λ = 159.4 °C

Around 159.4 °C almost all properties of liquid sulfur suffer a discontinuity. Figure 11 shows, for example, the density change.[182] Points close to the transition were observed after 12 h of equilibration. The values were interpreted as due to a logarithmic singularity, a cooperative phenomenon, which is very rare.[182] The velocity of sound,[183] polarizability,[183] compressibility,[162] molar polarization,[103] the electric conductivity,[176,183,184] the surface tension,[185] and many other properties have been measured in the same temperature region. However, the most striking effect of this temperature, which is often called λ temperature, is the sudden change in viscosity.

Eötvös[88] and Kellas[88] long ago described the well-known sudden gelling of the liquid, as did Schenk. Hammick[5] and Schenk[5] determined the weight percent of polymer.[186] Bacon and Fanelli[168] demonstrated the influence of impurities on the viscosity, and showed how sulfur can be purified.

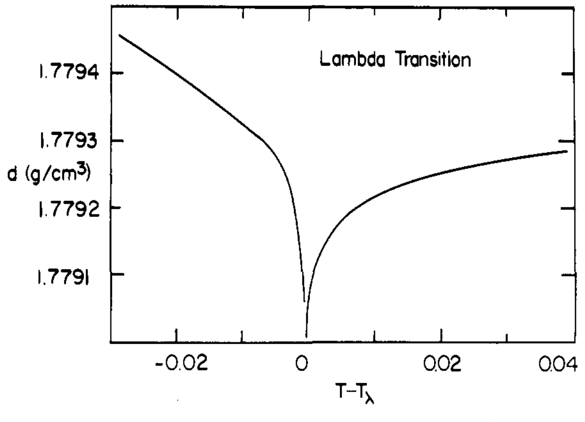

Figure 11. Density of liquid sulfur at 159 °C (after Patel[182]).

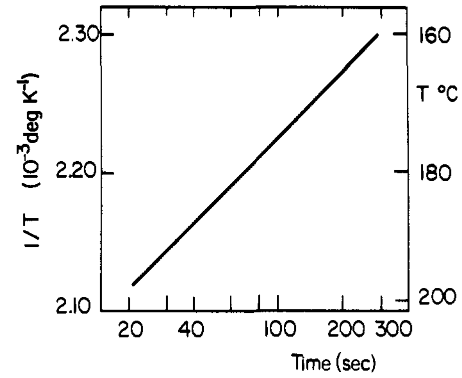

Figure 12. Temperature dependence of polymerization rate of liquid sulfur, based on 12 observation points (after Klement[191]).

Schenk[187] discussed the viscosity again, as did Doi.[177] Eyring[188] and Tobolsky and Eisenberg[71] developed a polymerization theory which quantitatively explains the viscosity change. It is based on two steps:

$$\text{cyclo-}S_8 \leftrightarrows \text{catena-}S_8 \qquad \text{(I)}$$

$$\text{catena-}S_8 + \text{cyclo-}S_8 \rightarrow \text{catena-}S_{8\times 2} \qquad \text{(II)}$$

This theory has been extensively discussed and thoroughly reviewed. Various small modifications adapted to this theory allow for rings other than S_8, and make possible the explanation of other phenomena.[181,182,189,190]

The thermodynamic properties of the polymerization have been extensively researched. The values of ΔH and S (Table VIII) were determined by Tobolsky.[10,71] West and Feher[174] measured the specific heat (Table IX), and Klement,[191] Kuballa,[163] and Ward[192] conducted a differential thermal analysis. Ward[191,192] and Ozin[109] used laser Raman spectroscopy to study the polymerization, which is characterized by intensity changes of bands at 456, 416, and 273 cm^{-1}. Eisenberg[189] discussed the mechanism of the polymerization, comparing a chain-end interchange mechanism with bond interchange, and concluded that bond interchange is important in viscous sulfur. The kinetics of equilibration have been investigated by Klement.[193] He determined rates at 15 temperatures, and found the correlation shown in Figure 12.

Wigand[194] observed as early as 1909 that the polymerization equilibrium is photosensitive. The influence of impurities on the degree of polymerization was measured by Feher[174] for Cl_2, Koningsberger[181] for I_2, Wiewiorowski[195] for CS_2, Rubero[196] for H_2S, and Ward[192] for As. Six percent of the latter causes sulfur to polymerize at the melting point. Schmidt[52] showed that 2% S_6 lowers the polymerization temperature by 10° for over 15 min, while $(SCH_2)_9$, added at 200 °C, reduces the average chain length greatly.

The effect of pressure on polymerization was reported by

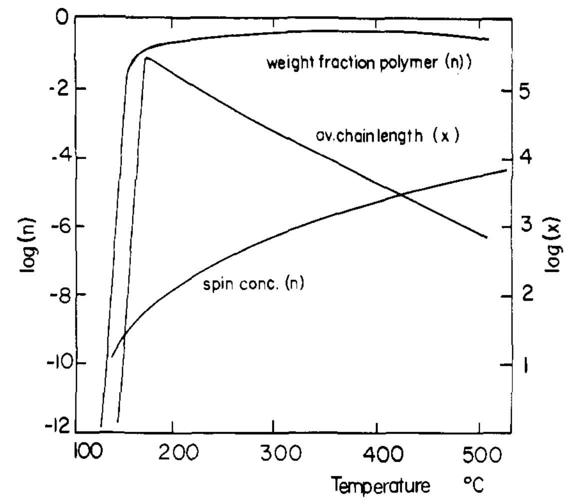

Figure 13. Composition of liquid sulfur II. The weight fraction of the polymer was computed from data of ref 11 and 186. The average chain length is from ref 10, and the free spin concentration from ref 181.

Doi.[177] Bröllos[162] used the visible absorption edge of liquid sulfur to study the same effect.

The ESR spectrum of liquid sulfur was first observed by Gardner and Fraenkel.[197] They found a signal, but it was far weaker than anticipated. It was first suggested that this was due to line broadening in the hot liquid, but paramagnetic susceptibility measurements by Poulis and Massen[183] gave similarly small free spin concentrations. Koningsberger[181] completed a thorough study of the ESR spectra of pure sulfur, and selenium, and of sulfur doped with I_2. He obtained the free spin concentrations shown in Figure 13. Koningsberger correlated the spin concentration with the polymer concentration, which can be computed from the weight fraction[71,183] of the polymer P and the average chain length, and reported a similar temperature dependence. Figure 10 shows, however, that the free spin concentration is also almost identical with the concentration of S_5, as computed by Harris[11] from various thermodynamic considerations. It is not clear whether the spectrum is due to polymer,[181] S_5, or charge-transfer complexes,[195] but this question does not raise doubts regarding the validity of the polymerization theory; it merely raises the question as to what small species are present in the liquid at the polymerization temperature, and in what concentration. So far, only the uv and visible spectra[58,63] suggest an answer. At the melting point, liquid sulfur is pale yellow. The corresponding absorption spectrum is shown in Figure 14a. The spectrum of S_8 in an organic glass[63] at 76 K, indicated in the same figure, explains the absorption edge. At 250 °C, sulfur is still yellow, but the absorption is now due to superposition of the spectrum of S_8 with that of plastic sulfur.

Liquid polymeric sulfur is dark yellow[63] and has an absorption edge at 350 nm. Solid polymeric sulfur, obtained by quenching of a thin film of liquid sulfur at 200 °C in liquid nitrogen, remains yellow, while cyclo-S_8 turns snow white, and has the spectrum indicated in Figure 14b. Thus, polymeric sulfur is not dark red, as is erroneously believed by many who know that boiling sulfur is deep red or who have seen impure liquid sulfur turn dark because of organic impurities. The origin of the red color in the hot liquid will be explained in the next section; but the absence of deep dark color in solid and liquid polymeric sulfur at 160 and 200 °C remains a puzzle, because the free-radical chains, according to all known theories,[58,61] should be deeply colored. Several possible explanations have been proposed. One is that 10^{-5} mol of organic impurity is sufficient to scavenge polymeric chains by conversion to sulfanes.[58] Another explanation revives the model of long intertwined rings. However, so far Wiewiorowski's charge complex theory[36,195] explains the situation best. Sulfur is known to form charge transfer complexes with iodoform,[198] and possibly with iodine; calculations[38] indicate that S_8–S_x–S_8 should be stable.[38]

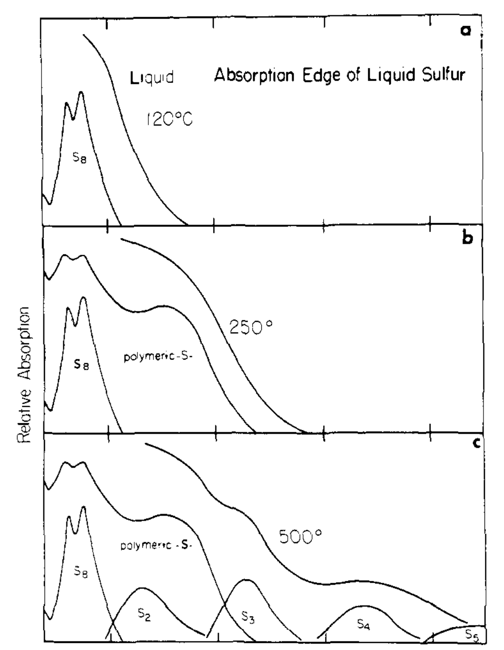

Figure 14. Visible absorption edge of liquid sulfur at (a) 120, (b) 250, and (c) 500 °C. The absorption of individual components was obtained for S_8 at −70 °C in EDTA, for polymeric sulfur at −196 °C, as a thick film; S_3, S_4, and S_5 in EDTA at −196 °C; and S_2 at −253 °C, in a rare gas matrix (after ref 58 and 63).

C. Liquid Sulfur above 250 °C

At high temperature, the viscosity of liquid sulfur decreases rapidly, and the color turns first red, then brown, and almost black. Simultaneously, it becomes extremely reactive. Thus, in all except the most pure sulfur (99.999+%), the color effect is obscured by irreversible darkening due to reaction of organic impurities. Pure boiling sulfur[63] has the same color as the equilibrium vapor.[63] The absorption edge of Figure 14c corresponds to the spectrum obtained on hot thin liquid films, quenched in liquid nitrogen. Such films retain the color of the liquid.[63] The shoulder in the absorption curve coincides with the spectra of S_3, S_4, and S_5. The spectra of these species[199,200] are known from the gas phase, or from low temperature matrices, in which they can be isolated. Very little else is known about hot liquid sulfur, except that it is very reactive toward almost every chemical. This is explained by the presence of S_3, thiozone, and other small molecules.

The boiling point[201] of sulfur, believed to be 293 °C by Davy, and 440 °C by Dumas, is 444.64 °C. This transition is no longer a primary, but a secondary temperature reference point, according to IUPAC.[201] The critical point[202,203] of sulfur is at 1040 °C and 200 atm. The critical properties, Table XVII, indicate that liquid sulfur, as well as the vapor, consists essentially of S_2, S_3, and S_4 with very little S_5, S_6, S_7, and S_8. Figure 15 shows that thermodynamic considerations indicate that just below the critical point, liquid sulfur has a smaller average molecular weight than the vapor.[96,203] It remains to be seen whether experiments will confirm this. However, the composition of the vapor[12,50,51,96] (Figure 17) and of the liquid[11] (Figure 10) extrapolate smoothly to the critical data (Figure 15).

The recent discovery of small molecules in hot liquid sulfur

TABLE XVII. Critical Data

Quantity	Value	Ref
T_c	1313 K = 1040 °C	5 96
p_c	179.7 atm 200 atm	203 202
V_c	158 cm^3/mol	
d_c	0.563 g/cm^3	
ν_c	2.8 atoms/molecule	

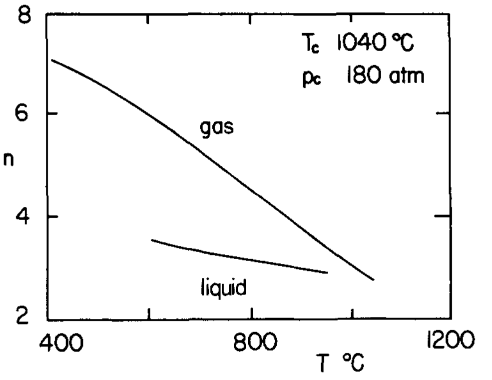

Figure 15. Average number of atoms per molecule in vapor and liquid at the critical point (after Rau[203]).

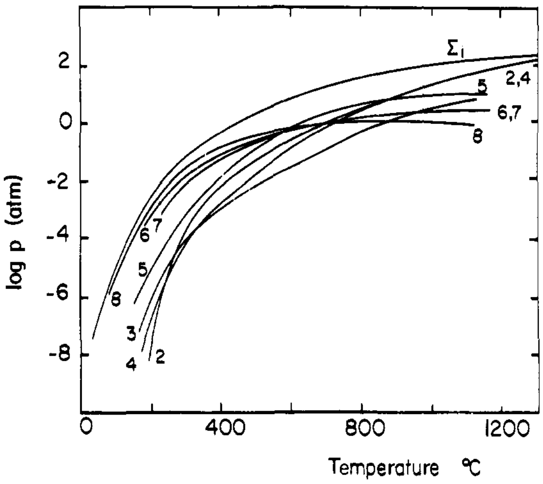

Figure 16. Equilibrium pressure of sulfur; the total pressure curve Σ_i was constructed from data in ref 96, 201–203. The partial pressures of S_n, $2 < n < 8$, were estimated from data of ref 12 and 51.

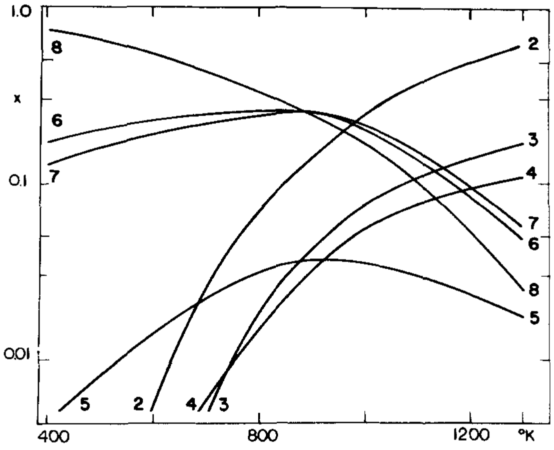

Figure 17. Mole fraction of S_n, $2 < n < 8$, in a saturated vapor, between 120 and 1000 °C, estimated from data in ref 12, 51, 63, and 201–203.

casts light on a formerly unknown phase, which surely must display interesting chemical properties.

V. Sulfur Vapor

A. General

The vapor pressure of sulfur from room temperature to 2300 K was first measured by Bilz and Meyer.[15] Some points of the vapor pressure curve (Figure 16) are listed in Table X. Recently published high-pressure values[202,203] agree well. The critical temperatures reported by Baker and Rau[203] are within 1 K, i.e., 0.1%; however, Baker's critical pressure is 200 atm, i.e., 20% larger than that reported by Rau (Table XVIII). Specific heat and other thermal data for the vapor have been summarized for JANEF by Jensen[74] and others.

Preuner and Schupp[204] concluded that equilibrium vapor consists of S_8, S_6, and S_2. Braune and Steinbacher[205] studied the vapor pressure and the uv spectrum and concluded correctly that an absorption at 510 nm was due to S_4. They also observed the spectrum now known to be due to S_3, but assigned it erroneously to another transition of S_4. The 100-year-old controversy about the vapor composition was finally settled when Berkowitz[12,50,51] showed that vapor contains all molecules S_n, $2 < n < 10$, including all odd-numbered species. Buchler[139] even detected S_{12} in the vapor. The fact that photoionization yields only one ionization value[50] supports earlier thermodynamic reasoning[12] that all vapor species occur as rings.

The vapor pressure depends upon the phase with which it is in contact. LaMer produced[169] airosols with particle diameter of 0.2 μ at 25 to 75 °C which are stable for several days and have five times equilibrium vapor pressure.

Berkowitz[12] has shown by mass spectroscopy that vapor in equilibrium with rhombohedral cyclohexa-S contains S_6. The preferential vaporization of sulfur species has since been used by Berkowitz[50] and Drowart.[51] The latter used Rickert's electrolytic cell:

$$\mathrm{Pt,Ag|AgI|Ag_2S|Pt}$$

to overcome problems in identifying the molecular ionization pattern in a mass spectrometer. Thus, it became possible to unravel the molecular composition of equilibrium vapor over a large temperature range. At low temperature, S_8 accounts for over 90% of the vapor, while S_6 and S_7 make up the rest; and the vapor is green due to the uv absorption[63] of the terminally excited ground state[41,42] of S_8 and of the other molecules. Upon heating, the concentration of S_8 in equilibrium vapor steadily decreases, and the vapor consists increasingly of the small species. Above 1000 K, S_2 is the most abundant species. At the critical point,[202,203] the vapor contains mainly S_2, S_3, and S_4 (Figure 15). The composition in the intermediate temperature range is shown in Figure 17. The S_5, S_6, and S_7 concentration of each goes through a maximum at about 1000 K. According to Rau,[203] S_5 never accounts for more than about 3% of the total vapor pressure, while Baker[202] estimates a maximum of 18% at about the same temperature.

The relative concentration of small species increases in unsaturated pressure. Spectral studies[206,207] indicate that at 800 K and 100 Torr, S_2 accounts for over 80% of all vapor species. At 1000 K and 1 Torr, the corresponding value is 99%. This vapor is violet,[204] due to the $B \leftarrow X$ absorption of S_2. The color of this vapor was already studied by Gernez[172] in 1876. S_3 and S_4 in concentrations[63,199] of about 10% are obtained at about 10 Torr and 800 K. This vapor is cherry red.[63] Sulfur atoms are not present in equilibrium vapor below the critical point.[202] They can be prepared as transient species by photolysis.[208-212] The thermodynamic properties of the various sulfur species are given in Table XIX. The cor-

TABLE XVIII. Thermodynamic Data of Gaseous Sulfur[a]

Molecule	Equilibrium	ΔH°_f, kcal/mol	S°, cal/mol·deg	B(S–S), kcal/mol Obsd[b]	Calcd[c]
S_2	$2S(s) \rightleftarrows S_2(g)$	31.20	54.40		
S_3	$2S_3(g) \rightleftarrows 3S_2(g)$	33.81	64.39	55.8	48.7
S_4	$S_4(g) \rightleftarrows 2S_2(g)$	34.84	74.22	57.8	58.6
S_5	$2S_5(g) \rightleftarrows 5S_2(g)$	26.14	73.74	60.0	58.3
S_6	$\frac{3}{4}S_8(g) \rightleftarrows S_6(g)$	24.36	84.60	61.8	62.8
S_7	$\frac{7}{8}S_8(g) \rightleftarrows S_7(g)$	27.17	97.41	62.2	63.6
S_8	$S_8(g) \rightleftarrows 4S_2(g)$	24.32	102.76	63.0	60.1

[a] Standard state: 1 atm, 298.15 K; see ref 12, 96, and 51. [b] Reference 12. [c] Reference 43.

TABLE XIX. Heat Capacities C_p of Gaseous Sulfur Molecules[a]

	A	B	C	C_p, cal/deg·mol 300 K	1000 K
S_2	8.54	0.28	−0.79	0.8	1.8
S_3	12.854	1.04	−1.554	1.3	1.9
S_4	19.092	0.783	−2.820	1.4	1.9
S_5	25.558	0.253	−3.771	1.5	1.9
S_6	31.580	0.120	−4.400	1.6	1.9
S_7	37.038	0.613	−4.723	1.6	1.9
S_8	42.670	0.860	−5.110	1.7	1.9
α-S_8(s)[b]	5.268	6.121	−0.816	5.4	
β-S_8(s)[b]				5.6	

[a] See ref 203. [b] See also Table IX.

TABLE XX. Dissociation Energy of S_2

$D^\circ_0(S_2)$, kcal/mol	Method	Ref	Year
100.69 ± 0.01	Uv spectroscopy[a]	224	1969
101.0 ± 0.2	Photoionization	12	1969
≤101.0 ± 0.8	Photoionization	223	1968
101.7 ± 2.9	Knudsen-torsion effusion	222	1968
101.0 ± 2.5	Thermochemistry	51, 221	1966
97 ± 5	Mass spectrometric	221	1964

[a] 100.69 kcal/mol corresponds to the predissociation at 35 590 cm^{-1}.

responding specific heats have been calculated by Rau,[96] who makes available a computer program which allows computation of vapor pressures.

If hot sulfur vapor is rapidly quenched to 76 K, or below, colored solids can be obtained,[165] which contain a mixture of various vapor components, together with recombination products which are formed during condensation. It is possible to trap individual vapor species by diluting the vapor with an inert gas. This matrix method[166] has been used to trap S_2, S_3, S_4, S_6, and S_8. Photolysis of chlorosulfanes[63] and other sulfur compounds in glasses and matrices has made possible selective preparation of solutions containing S atoms, and chains of S_n, $2 < n < 7$. Upon warming, all these systems yield polymeric sulfur, and eventually S_8.

B. Individual Species

Sulfur atoms are not present in equilibrium pressure below the critical point.[202] Sulfur atoms can be produced as an electric discharge, and by photolysis. Gunning and Strausz[208] have perfected gas-phase preparative methods, using COS. The electronic energy levels[31] of atomic sulfur are well known. Photolysis produces atoms in the ^3P ground state, as well as in the excited state ^1D. At short wavelengths the ^1S level is also obtained in good yield.[211] Excited atoms carry 26 kcal/mol excess energy and have a sufficient lifetime to enter chemical reactions. Strausz and Gunning[208] have explored extensively the chemistry of sulfur atoms with organic molecules. Some inorganic reactions have been studied by Donovan.[213] With themselves, the atoms form S_2, and eventually S_8. The ESR spectrum[214] of two ^3P sublevels has been studied by Brown in a gas stream containing about 10^{13} atoms/cm^3. Thermodynamic properties[215] of the atom, such as specific heat, heat of formation, and entropy have been recently reviewed.

S_2 constitutes nearly 45% of the equilibrium vapor[202,203] at 1040 °C, the critical point. At 1000 K and 1 Torr, and lower pressures, S_2 is almost 99% pure. S_2 can also be obtained in discharges,[216] or by photolysis[63] of S_2Cl_2 and similar compounds in the gas phase, in organic glass, or in matrices. The formation of S_2 via recombination of atoms has been discussed by Oldershaw.[217] Many reactions yield a significant fraction of S_2 in the first electronic excited state $^1\Delta$.[218]

S_2 is the most stable of the small sulfur molecules. Its ground state[29] is $^3\Sigma_g^-$, as is that of O_2. However, the triplet levels exhibit a far larger splitting[29,207] than O_2. Recently, the ESR spectrum[219] of S_2 has yielded accurate ground-state data. The ground-state frequency, observed by Raman spectroscopy,[206] is 718 cm^{-1}. The existence of S_2 has long been recognized. Seventeen of its electronic energy levels are known,[29,207] far more than for O_2. The violet color is due to the lowest allowed transition B $^3\Sigma_u \leftarrow$ X $^3\Sigma_g^-$ which has a transition energy of 31 689 cm^{-1}. The corresponding B → X emission is observed whenever sulfur compounds are burnt in a reducing flame. This emission, for which the transition strength is well determined, is widely used for quantitative determination[220] of sulfur compounds, separated by gas chromatography. The properties of electronic energy levels have been reviewed by Barrow,[29,207] who has made most of the original observations.

There has been an extended controversy about the dissociation energy of S_2. It can now be considered solved, as thermochemical considerations,[221] Knudsen-torsion effusion measurements,[222] mass spectroscopy,[51,223] and photoionization, listed in Table XX, all agree on the "higher" of the possible values. The predissociation[29,224] in the uv spectrum yields the most accurate value; 35 590 cm^{-1} = 101.8 ± 0.01 kcal/mol. A recent value for photoionization[51] is 9.36 eV, and confirms the earlier value of 9.9 ± 0.6 eV obtained by electron impact. The photoelectron spectrum[50] of S_2 corresponds, as expected, to that of O_2 and Te_2.

Several studies have been conducted on S_2 in rare gas matrices.[200,225] S_2 is produced by trapping vapor, a discharge, or photolysis. The absorption spectrum shows a simple progression with $\nu_n' \leftarrow \nu_0''$, as kT is insufficient at 20 K to yield vibrationally excited ground state atoms. The emission spectrum and a Raman band at 720 cm^{-1} have also been reported. An ir band[165] at 668 cm^{-1} is observed and is now assigned[200] to S_4. Its uv spectrum can be observed when S_2 containing matrices are annealed.

The S_2^- ion will be discussed in the section on ionic solutions.

S_3 was called thiozone by Erdmann,[226] 1908, who assumed that it exists in liquid sulfur. L d'Or published the uv spectrum of S_3 in 1909, but Rosen[29] assigned it to S_2. Braune[205] assigned it to S_4, and most physical chemists rejected the existence of S_3 until 1964, when Berkowitz[12] found it in the mass spectrometer. It has since been proven that S_3 occurs in sulfur vapor[199] and in liquid sulfur.[63] At the critical point, thermodynamic measurement indicates that 6% S_3 is present.[202,203]

The best conditions[63] for observing S_3 in sulfur vapor are found at 10 Torr and 440 °C, when it makes up about 10–20% of the vapor, and gives it its characteristic deep, cherry red color. The first allowed electronic transition[199] shows extensive rotational structure. The origin is at 23 465 cm^{-1}, as vibrational shifts of 34 bands of $^{32}S_3$ show. The bands indicate a ground-state stretching frequency of $\nu_1 = 590\ cm^{-1}$, and $\nu_1' = 420\ cm^{-1}$ for the first excited state. The transition energy is amazingly close to that calculated from a Hückel model,[38] using sulfur atom parameters. S_3 is not only isovalent with O_3, but also with SO_2 and S_2O, and has accordingly a bent structure, a ground state of $^1\Sigma$, and carries on the terminal atom a charge of -0.078. The calculations[38] give a bond distance of 1.98 Å, and assume a bond angle of 120°.

Uv spectra show that S_3 can be prepared in matrices and glasses[199] by careful photolysis of S_3Cl_2, and other similar compounds. Ir frequencies of 585, 490, and 310 cm^{-1} found in discharges[227] of SO_2 and Raman[227] frequencies at 662 and 583 cm^{-1} of recombination products of S_2O have been recently attributed to S_3.

The experimental photoionization[50] of S_3 is 9.68 ± 0.03 eV. Two ions of S_3 are known. The S_3^- ion, which can be easily recognized by its pale blue color, will be discussed in the section on ions. S_3^{2-}, the trisulfide ion, forms in aqueous solutions.

S_4 occurs in liquid[199-203] and gaseous sulfur. Its continuous absorption at 530 nm has been repeatedly reported.[204,205] It occurs together with S_3. Its vapor spectra can be best recorded at 450 °C and 20 Torr, where it is assumed to account for about 20% of the vapor.[63] At the critical point, it forms between 24 and 40% of all species.[201,202] Bonding considerations suggest that S_4 can occur as a ring,[50] as a chain,[38] and as a branched molecule,[38] as shown in Figure 7. Semiempirical Hückel calculations[38] indicate that the trans chain and the branched molecule have similar stability, and that both are far more stable than the pyramid, the planar ring, or any other form, including the ring. It is quite possible that the branched SO_3-type structure, with a charge of -0.12 on the terminal atoms, can exist, at least at low temperature.

S_4 is found in matrices[63,200] by careful photolysis of tetrasulfide, or, much easier, by recombination[200] of S_2. Ir bands at 688, 483, 320, and 270 cm^{-1} have been assigned to it. Raman bands in trapped discharges[227] through SO_2 have also been assigned to S_4.

The photoionization[50] of S_4 has not been published yet. The electron impact method[12] yielded a value of 10.4 eV.

Three ions of S_4 have been reported: S_4^{2+} is assumed to be planar,[65] like Se_4^{2+}. S_4^- supposedly forms in salt melts, while S_4^{2-}, the stable tetrasulfide ion, occurs in aqueous solution, at a high pH, as a chain.

S_5 has rarely been studied or discussed, even though it occurs in the vapor,[12] the liquid,[63] in matrices,[63] and possibly even as a solid.[52] Thermodynamic considerations suggest that it is a ring.[12,50,51] Calculations[38] favor the chain, as do stereochemical considerations. If the S–S–S–S bond geometry is to be preserved, even the most favorable unstrained S_5 chain conformation would leave the terminals 3.5 Å apart[49] (Table V), while for all observed rings, values of about 2 Å are computed. Except for its weak absorption,[63] its vapor pressure,[201,202] which accounts for about 13% at the critical pressure, and its photoionization energy[50] of 8.60 eV, very little is known about S_5. It is isoelectronic with S_4N^- which is fairly well known.[228] It should be pointed out that in liquid sulfur, S_5 might be the most abundant of all small paramagnetic species.[11] If so, the striking similarity between the S_5 concentration computed by Harris[11] (Figure 10) and the concentration of free species observed by Koningsberger[181] (Figure 13) might not be accidental.

S_6, S_7, S_8, S_9, S_{10}, and S_{12} have all been found in the vapor.[12,139] It is likely that they exist as rings.[12,50] The same rings are very likely present in the π fraction of liquid sulfur,[95,178,179] which causes the curious melting phenomena of sulfur. However, all these molecules also exist as pure solids at room temperature, where they can be much more easily studied. Thus, they are discussed in section IIIB, with solid allotropes. In the liquid and perhaps also in the vapor, S_n, $6 < n < 12$, can also occur as chains, at least as transient equilibrium species. These should be easily recognizable by the deep color which they must exhibit.[63]

VI. Solutions

In *nonpolar liquids*, cyclooctasulfur and other rings dissolve at room temperature without decomposition. Representative solubility values of frequently used solvents are indicated in Table XXI. Distribution factors for S_6 and S_8 in eight solvent mixtures can be found in ref 95 and 230. Binary systems including sulfur have been studied and reviewed by Wiewiorowski.[14] Systems including liquid sulfur and aromatic hydrocarbons have been reviewed by Scott.[13] Recently, fugacities[231] of similar systems have been measured, however, it should be noted that above 130 °C thermal dissociation of the ring by homolytic scission induces free-radical reactions,[6] usually hydrogen abstraction. Thus, many of the reported systems suffer slow chemical reaction, recognizable by the color change.

Wiewiorowski[232] has demonstrated that liquid sulfur itself makes an excellent solvent, and lends itself to ir studies of reaction. With H_2S sulfur forms a reactive system,[195,233] as it does with iodine,[181] chlorine,[174] arsenic,[192] and at higher temperatures with CS_2.[234] At room temperature, light converts S_8 into insoluble photosulfur, which partly redissolves.[55,235]

In *ionic solutions*, elemental sulfur suffers nucleophilic or electrophilic attack and forms deeply colored solutions, first described by Geitner,[236] which contain molecular ions, usually chains.

Molecular Ions. Three classes of molecular ions are known. The *polysulfides* are doubly charged negative ions that are quite stable in aqueous solutions at high pH, and as solid salts. Singly charged *negative ions* form in salt melts at high temperature, and doubly charged *cations* are observed in so-called "super acids".

The *polysulfides* are formed by chain scission, which is followed by rapid chain degradation or by polymerization yielding chains S_n with $1 < n < 20$ atoms. The molecular bond characteristics of polysulfides are:

$$S\text{–}S = 2.048\ \text{Å}$$

$$S\text{–}S\text{–}S = 107°\ 53'$$

$$S\text{–}S\text{–}S\text{–}S = 90°$$

These compounds are pale yellow, and equilibrate rapidly with each other, yielding mixtures[237,238] with well-established compositions.[62,235,239] Feher[81] prepared the free sulfanes

TABLE XXI. Solubility of Sulfur

Solvent	Solubility (wt %) g of S/100 g solvent	*T*, °C	Ref
H_2S	0.14	−60	233
	0.005	0	
	1.3	80	
SO_2	0.0078	25	234
	0.039	60	
	0.46	140	
CS_2	4	−80	234
	35.5	25	
	55.66	60	
CCl_4	0.148	−24	234
	0.86	25	
	1.94	60	
$CHCl_3$	1.2	60	5, *a*
$CHBr_3$	3.64	5.6	
CHI_3	42	85	
$H_2O–(CH_3)_2SO$ (1:1)	0.003	60	*b*
Ethanol–$(CH_3)_2SO$ (1:1)	0.37	60	*b*
Acetone–$(CH_3)_2SO$ (1:1)	0.45	60	*b*
$NH_3–(CH_3)_2SO$ (1:1)	15	60	*b*
NH_3	38.6	−20	*c*
	21	30	
$(NH_4)_2S$	37	20	*d*
S_2Cl_2	7.3	−9	*a*
	17	21	
	97	110	
Pyridine	10.5	85	27
	19.2	100	
Aniline	46	130	27
Benzene	2.1	25	5, *a*
	17.5	100	
Ethanol	0.066	25.3	
Ethyl ether	0.283	23	27
Acetone	2.7	25	
Hexane	0.25	20	27
	2.8	100	

[a] D. L. Hannick and M. Zvegintzov, *J. Chem. Soc.*, 1785 (1928). [b] T. Kawakami, N. Kubota, and H. Terni, *Technol. Rep. Iwate Univ.*, 77 (1971). [c] A. Keouanton, M. Herlem, and A. Thiebault, *Anal. Lett.*, 6, 171 (1973). [d] S. Bretsznajder and J. Piskorski, *Bull. Acad. Pol. Sci., Cl. 3*, 15, 93 (1967).

H_2S_n, observed the spectra[59] of individual, pure sulfanes, and calculated their uv spectra[60] with a one-electron model. A semiempirical Hückel calculation[38] gives very similar transition energies. Figure 6 shows that with increasing chain length the transition energy converges at 320 nm. Recently, the structure of some alkaline earth di- and trisulfides has been determined. The S–S bond distance[240] varies between 2.050 Å for SrS_3 and 2.124 Å for BaS_2.

The *singly charged ions*, S_2^-, S_3^- and S_4^-, have been observed when elemental sulfur or certain sulfur compounds are dissolved in the KCl–LiCl melt,[241,242] in liquid KCNS,[243] and in dimethylformamide.[244,245] They also occur in minerals.[246] The color of various ultramarines is explained by the presence of such ions, but also by neutral sulfur species.[246]

The green S_2^- ion absorbs[241] at 400 nm, and has a Raman[242] active stretching frequency, which lies between 592 cm^{-1} in NaI and 612 cm^{-1} in KBr, depending on the solvents. From this an S–S bond distance of about 2.00 Å can be estimated.[47]

Blue S_3^- absorbs at 610–620 nm. It has Raman[242] frequencies at 523 cm^{-1} and an ir absorption at 580 cm^{-1}. Its bond distance has been estimated[47] to be 1.95 Å. The ESR spectrum has been observed.[247] The molecule has C_{2v} symmetry, and a bond angle smaller than 120°. The omnipresence of this ion,[248] i.e., its superior stability in the ionic media, is not yet satisfactorily understood. S_3^- is isoelectronic with O_3^- and SO_2^-, both of which have been reported.[249,250]

Gillespie identified *cations of sulfur* in oleum and in super acids.[64] The cations are parts of complex ions: $S_8^{2+}(AsF_6)_2$. S_8^{2+} is known best.[105] Its structure is well established. The S_8 ring is converted into a chair structure, and the bond distances are 2.04 Å, i.e., somewhat shorter[7] than in S_8. Likewise, nonbonding S–S distances are closer than in S_8. The structure of S_8^{2+} is intermediate[106] to that of S_4N_4. Wilkinson[251] studied the ESR spectrum of S_8^+.

The S_4^{2+} ion is quite well established.[65] In analogy[64] to the Se_4^{2+} ion, it is expected to be a planar ring. The Raman frequency[252] has been measured and assigned to the following modes:

$\nu_1 = 584\ \mathrm{cm}^{-1}$ A_{ig} $\nu_3 = 460\ \mathrm{cm}^{-1}$ E_u

$\nu_2 = 530\ \mathrm{cm}^{-1}$ B_{ig} $\nu_4 = 330\ \mathrm{cm}^{-1}$ B_{ug}

TABLE XXII. Molecular Composition of Sulfur Phases and Reaction Products

Reagents		Allotrope	
Phase	Molecular species	Well-established	Inconclusive or mixture
Solid sulfur	(a) Stable (STP): Cyclo-S_8 as α-S_8 (b) Metastable:	S_ψ (Geller II)	Laminar, ω, orange, metallic, Vezzoli, Geller, Baäk
Solid sulfur	Cyclo-S_n[a] Catena-S_i, $16 < i < 10^5$ Charge transfer complex cyclo-S_n—catena-S_i—cyclo-S_n	S_ψ	
Liquid sulfur	Cyclo-S_n, $6 < n < 24$ (?) Catena-S_i, $3 < i < 10^5$	α, β, S_{12} ψ $(=\mu)$	π, ι, ν, ψ
Sulfur vapor	Cyclo-S_n, $6 < n < 12$ Catena-S_i, $2 < i < 5$	α, S_∞	Crystex, ω, red, ξ, secondary fibrous, green, blue, black (Schenk) violet, green, purple
Solution, containing cyclo-S_8	Cyclo-S_8	α, β, γ	$\omega_{1,2}(\epsilon)$, ψ, μ, ξ, η, o, χ, φ, κ, §, θ, τ,
Solution, containing sulfur compounds	Cyclo-S_5, S_6, S_7, S_8, S_9, S_{10}, S_{12}, S_{18}, S_{20}, S_∞, γ	S_6, S_7, S_8, S_9, S_{10}, S_{11}, S_{12}, S_{18}, S_∞, γ	δ, ν, ω, $\pi_1 - \pi_2$, red (E, F, G), orange (I, K, L, M)

[a] n = 6, 7, 8, 9, 10, 11, 12, 18, 20.

They have also been identified by ESR[252] and circular dichroism.[65]

A third species, Gillespie's S_{16}^{2+} is also formed in super acids, but its identity and properties are still incompletely demonstrated.[64]

VII. Conclusion

In the last 10 years much has been learned about the molecular structure of elemental sulfur. It is now known that many different types of rings are sufficiently metastable to exist at room temperature for several days. It is known that at high temperature, the equilibrium composition allows for a variety of rings and chains to exist in comparable concentration, and it is known that at the boiling point and above, the vapor as well as the liquid contains small species with three, four, and five atoms.

Now that many of these species can be isolated in pure form, it should become possible to study the relative reactivity of different allotropes. Such knowledge would make possible selective reactions, which would open simpler and cheaper paths to synthesize sulfur compounds, such as polysulfides, and other industrially important and useful compounds. So far, very little is known about the reactivity of different pure allotropes. Bartlett[94] and Davis[98] have reported the kinetics of S_6 with triphenylphosphine chloride. Knippschild[253] discovered that S_6 reacts with many nucleophilics about 10^4 times faster than does S_8. The quick reaction of S_6 with HI, which reacts only very slowly with S_8, has been reported by Schmidt.[254] The mechanism of these reactions is not yet conclusively established, but the degradation of S–S chains,[56] as it occurs, for example, in the reaction of sulfur with the sulfite ion, and the formation of chains,[255] has been plausibly explained.[25] The work of Norris and his group[256] has shown that radioactive marking with ^{35}S can greatly help with the unraveling of reaction paths and the determination of the kinetics.

The reaction of sulfur with various organic compounds has been recently reviewed by Juraszyk.[257] Such reactions are very sensitive to traces of acids and bases.[25] Reactions of sulfur with sulfide have been studied by Oae[258] and his group, and many others.[21] The reactions of liquid sulfur have been investigated by Langer and Hyne.[259] Above 180 °C liquid sulfur reacts with aromatic and other hydrocarbons, and their halogen derivatives.[5] This reaction is due to the small sulfur species[63] formed at this temperature. These reactions explain the irreversible darkening of all but the purest molten sulfur. The reaction of high temperature species has only been superficially explored.[260] However, the reaction of atoms is now well established, due to the work of Gunning and Strausz.[208]

Table XXII presents, in conclusion, a summary of those sulfur allotropes which have been most widely described. A study of the pure allotropes which would yield better bond data and better models for the formation and reaction of S–S bonds would be most valuable.

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