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ELEMENTAL SULFUR

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ELEMENTAL SULFUR

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ELEMENTAL SULFUR

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I. Introduction

A. General Background

During the last ten years 12 new elemental sulfur rings have been synthesized, the structure of the third solid cycloocta sulfur allotrope has been determined, and much has been learnt 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 H. 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 were produced in the U.S. In contrast, and despite the excellent process of C. F. 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 ten 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 were consumed last year, and a comparable amount was released into the atmosphere.

This review is primarily concerned with progress during the last ten 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 A. V. 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 for impurities in sulfur,[27] and traces of sulfur[28] are established. Furthermore, 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.

This review starts with a short guide to names and synonyms. In Section II, properties of the S-S bond is discussed, and the present experimental knowledge of molecular variety is summarized. Section III, IV and V deal with the composition of the solid, liquid and gas phase, while Section VI discusses phenomena in solutions of non-polar 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 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, so 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 names 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 cycloocta-sulfur. In contrast, δ and ε for identifying cyclohexa-sulfur 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 cycloocta-S, in the sulfur melt; φ -sulfur is a fibrous solid allotropes, obtained by quenching liquid polymeric sulfur.

Table I

Guide to Nomenclature

Name	Synonyms	Molecular Species	Designation used in this Review	Section or Reference
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, b) polymeric	Catenapoly-S	Solid or liquid Polymeric-S	III C 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^{1-4}			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

Table : Guide to Nomenclature
Page 2

Name	Synonyms	Molecular Species	Designation used in this review	Section or Reference
χ (chi)	Plastic	Mixture	Polymeric	III C
ψ (psi)	Fibrous	Mixture	Fibrous	III C, D
ω (omega)	Insoluble, white, Das, super-sublimation	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}	Cyclodode a-S		III B
Amorphous	ω, μ	Mixture	Solid, polymeric	III C
Cubic	High pressure cubic plastic, see:		High pressure forms	III D
Fibrous	ψ, , phase II	Catenapoly-S	Fibrous	III C, D
Insoluble	"Crystex", super-sublimated	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 b)Rice, Schenk	? Mixture	Quenched liquid Trapped vapor	III E
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 b) Erämetsä	Mixture Mixture	Trapped vapor Trapped vapor	III E III E
Violet	Rice	Mixture	Trapped vapor	III E
E, F, G	Erametsä's red	Mixture	Allotrope of S_8	6
I, K, L, M	Orange			6

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, 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.

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] radical functions from self consistent field calculations, and orbital energies - the d-orbital energies are only about 10% of the p-orbital energies[32] - indicate that d-orbitals of the free atom do not justify the belief in strong d-orbital participation[34,35] in S-S bonds. Recent calculations by Miller and Cusachs[36] on cyclo-S_8, cyclo-S_6, cyclo-S_4,

Table II

Table II

Orbital Ionization Potential (I_v), Electron Affinity (E_v), and Mulliken's Electronegativity (χ) of Atomic Sulfur (after ref 32)

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

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 liquid 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 Hegen[43] developed a three dimensional electron gas model which yields good relative bond energies for sulfur rings of various sizes.

Figur

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. The free bond is characterized by a torsion angle of 85.3°, a bond angle of 106°, and a bond distance of 2.066 A, as observed in helices. 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

Figu

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 probably accounts for all bonds shorter than 2.06 A. Pauling[46] assumed a single bond value of 2.08 A, using the S_8 ring as the basis for determining free bonds. This is a problematic device, as will be discussed below. The unstrained bond distance[47] is probably about 2.06 A. 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 ΔE = 6 kcal/mole 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 is listed below, in Table VI.

Table III

Fig. 3

Table IV

(do not place Tab VI)

C. Molecular Variety

There has been much controversy whether sulfur molecules in the various phases exist as rings, chains, or both. The most widely recognized prerequisite for ring formation is that a bond configuration e exists which brings the chain ends within bonding distance.[49] This condition is fulfilled for molecules with six or more atoms. In S_4 and S_5 considerable deviations from normal divalent sulfur bond properties are necessary if a ring is to be formed. Table V lists some chain

Table V

Table III

Representative S-S Bond Distances(a)

Molecule	S-S Bond Length (A)
S_2	1.89
S_2F_2	1.89
$S_2O_3^{-2}$	2.00
diphenyl disulfide	2.03
2,2'-biphenyl disulfide	2.03
α-cystine	2.03
Me_2S_2	2.038
$S_3(CF_3)_2$	2.04
$S_3(Me)_2$	2.04
S_8O	2.04-2.20
α-cystine hydrochloride	2.05
S_{12}	2.053
H_2S_2	2.055
S_8	2.060
S_∞	2.066
$S_nO_6^{-2}$	2.11
$S_2O_6^{-2}$	2.15
$S_2O_4^{-2}$	2.39
S_4N_4	2.58

(a) See refs. 22, 29, 66.

Table IV

Conformations of Catena Sulfur Compounds

Conformation*	Compound
++	di-2-iodoethyl trisulfide
	dibenzene sulfonyl trisulfide
	di-p-toluene sulfonyl trisulfide
	dimethane sulfonyl trisulfide
	ammonium telluropentathionate
+-	cyanogen trisulfide
	triclinic barium pentathionate dihydrate
	barium pentathionate hydrate acetonate
	orthorhombic barium pentathionate dihydrate
+++	caesium hexasulfide
	trans-dichloro-dien-cobalt(III) hexathionate monohydrate
+-+	potassium barium hexathionate

*The sign corresponds to the sign of the internal rotational angle: ++ and -- corresponds to trans; +- to cis. See refs. 22 and 49.

Table V

Chain Conformations Favoring Ring Formation

Number of atoms in the chain	Distance between the terminal atoms (A)	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		+++--+++--+++--+++

configurations, and the distance between terminal atoms for some short chains. The values are based on a model by Semlyen,[47] 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 A. 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 unequivalent atoms, exist as rings in all phases.

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 ring 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-neighbor interaction[53] between atoms across the ring. The structure of S_8 and S_{12} is shown in Figure 4. The experimental bond data of these molecules is well established, and listed below in Table XI. S_6 has a chair structure, as is seen in Figure 5. S_8 is the thermodynamic stable form of sulfur at STP, and was used by Pauling and his predecessors as the basis for determining ideal 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, because the crown structure allows for considerable cross-ring interaction[53] between non-bonded atoms. The existence of the amazingly stable S_{12} ring,[54] confirms that Pauling's assumptions about

Fig. 4

Fig. 5

the S-S bond were correct, even though his erroneous 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 are photosensitive,[55] and the resulting chains undergo quick degradation:[8,56]

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

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 $H\text{-}S_x\text{-}H$. The difference between the ring and chain shows in chemical reactivity, as well as in physical properties, for example color. 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 $H\text{-}S_x\text{-}H$ chains is well established.[59] It lies in the 280 nm region. With increasing chain length, the absorption shifts to the red and converge toward 330 nm. It fits the sequence of electronic transition energies calculated[60] with a one-electron model,

Fig. 6

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] $H\text{-}S_x\text{-}H$, of the 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 intra-chain 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 15b below. 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 than S_4. It probably has a planar ring structure,[65] analogous to that observed for Se^{+2}.

Fig. 7

S_5 occurs in the gas phase, and in the liquid. Table V shows that a non-symmetric 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

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

Table VI

Summary of Observed Sulfur Species

Atoms per Molecule	Ring a)	Chain a)	Ion b)		
			+2	-1	-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) ( ) Indicates that the structure is uncertain; s, l, g indicate solid, liquid and gas phase.

b) All ions occur in solution; c indicates chain, r indicates rings.

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/mole. The dissociation energy[18,69,70,[illegible]] is about 33 kcal/mole. The bond energies of the gaseous sulfur molecules, believed to be rings, were calculated by Berkowitz[12] from experimental data. Muller[43] used a three dimensional electron free 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 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 have 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 process,[56] such as bond dissociation, by inducing ionic processes 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]

Table V

Table VII

ν_1 of 10 Sulfur Allotropes

Species	ν_1	(cm^{-1})	Temp. (°K)	Reference
S_2	718	(g)	880	Barrow[206]
S_3	590	(m)	650	Meyer[199]
S_4	668	(m)	20	Meyer[199,200]
S_4^{+2}	584		300	Gillespie[64,65]
S_x	559	(g)	880	Barrow[206]
S_6	471	(s)	300	Berkowitz[91]
S_7	481	(s)	300	Rogstadt[103]
S_8	475	(s)	30	Gautier[111]
S_{12}	459	(s)	200	Steudel[140]
S_∞	456	(l)	400	Ozin[109]
		(s)	300	Ward[192]

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 cycloocta-sulfur 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, which are easily prepared, much used commercially, and have well known bulk properties, but their structure is incompletely characterized, as it contains helices mixed with other molecular species. The best identified form 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. The thermal data[74] for the conversion of various forms is given in Table VIII. The transition $\alpha(s) \rightarrow \beta(s)$ 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.

Table [illegible]

Table VIII

Thermal Data for Phase Transitions

Transition	Process or Reaction	Temperature (^{o}K)	ΔH (kcal/g-atom)[a]	ΔS (cal/deg·g-atom)	Reference
α, β	$\alpha\text{-}S_8(s) \rightarrow \beta\text{-}S_8(s)$	368.46 ± 0.1	0.096	0.261	119,128
Sublimation: α	$\alpha\text{-}S_8(s) \rightarrow \text{cyclo-}S_8(g)$	368.5	2.981	8.17	6
β	$\beta\text{-}S_8(s) \rightarrow \text{cyclo-}S_8(g)$	368.5	2.883	7.93	172
ε	$\varepsilon\text{-}S_6(s) \rightarrow \text{cyclo-}S_6(g)$	300	4.02	8.38	6
Fusion: α	$\alpha\text{-}S_8(s) \rightarrow \text{cyclo-}S_8(l)$	383[b]	0.507		52,119,122,172
β	$\beta\text{-}S_8(s) \rightarrow \text{cyclo-}S_8(l)$	392.9 [b]	0.3842	0.75	173,174
λ, π	$\text{cyclo-}S_8(l) \rightarrow \text{catena-}S_8(l)$	432	4.1[c]	2.88	71,193
Polymerization	$\text{catena-}S_8(l) + \text{cyclo-}S_8(l) \rightarrow \text{catena-}S_8(l)$	442.8	0.396[d]	0.58	10
Vaporization	$S_i(l) \rightarrow S_i(g)$	717.824[e] = 444.674°C	2.5	3.5	6

(a) 1 g-atom of sulfur = 32.066 g; (b) see also Table XIV; (c) $K = (\pi)/(\lambda) = 1.137 \times 10^{4} \exp(-16520/T)$; (d) $K_3 = (\pi)/(\pi\lambda) = 10\ 43 \exp(-1596/T)$; see ref. 10 ; (e) sulfur is a secondary temperature reference point on the International Practical Temperature Scale, ref. 201.

The specific heat values of elemental sulfur listed in Table IX are close to those observed by West,[74] except for β-sulfur,[75] for which some data has recently become available.

Table IX

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

The vapor pressure[74] of sulfur is listed in Table X. The high temperature and high pressure data will be discussed in the section on sulfur vapor.

Table X

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 masspectrometer 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 7 new metastable allotropes by coupling two compounds with the correct combined number of sulfur atoms and the appropriate, reactive terminal group. S_{12}, for example, is best prepared from reaction of a sulfane 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:

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

Table IX

Specific Heat of Elemental Sulfur (Cal/g-atom)[a]

$T(^oK)$	Sulfur Species			
	α-S(s)	β-S(s)	Liquid	Vapor
10	0.103			
15	0.348			
20	0.608			
25	0.868			
40	1.465			
50	1.795			
60		2.091[b]		
100	3.090	3.100		
150	4.000	4.100		
200	4.650	4.798		
298.15	5.430	5.649		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) Ref. 74; b) ref. 75; c) ref. 176 gives a different value.

Table X

Vapor Pressure of Elemental Sulfur

P (Torr)	$T^{a)}$ (^oC)	P (atm)	$T^{b)}$ (^oC)
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) After West and Menzies,[56]

b) rounded average values after Baker, and Rau.[96,202,203]

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: The strain in cyclopenta-S becomes evident from the separation of 3.59 A 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] Donnay[7] and Donohue[90] 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:

Table XI

Table XI

Structural Parameters of Sulfur Molecules

Molecule	Bond length (A)	Bond angle (deg.)	Torsion angle (deg.)	Reference
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	141
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

S-S bond length, d = 2.057 ± 0.018 A

S-S-S bond angle = $102.2 \pm 1.6^{\circ}$

S-S-S-S torsion angle = $74.5 \pm 2.5^{\circ}$

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°K and 300°K, and a normal coordinate analysis. The uv spectrum has been published by Bartlett[94] and Oommen.[63] Table X

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 have been calculated with a semi-empirical theory by Miller and Cusachs,[36] and by Spitzer,[38] who also calculated transition energies and charge distribution for the catenahexa-S. In sunlight S_6 decomposes[97] forming S_8, and some S_{12}. It reacts 10^4 times faster with nucleophilic agents.[98]

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

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

The orange-red solid can be purified by recrystalization 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/cm^3. 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 $R3 - C_{3i}^{2}$. The lattice constants are:

Table XII

Observed Infrared and Raman Frequencies of 4 Sulfur Allotropes (cm^{-1})

S_4^{+2} (planar)		S_6 (8 fundamentals)			S_7 (15 fundamentals)		S_8 (30° K) (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.

a = 10.818 A

b = 4.280 A

c/a = 0.3956

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

3) S_7, Cyclohepta-S. This allotrope is formed by reaction of

$$(C_5H_5)_2TiS_5 + S_2Cl_2 \quad S_7 + (C_5H_5)_2TiCl_2.$$

The S_7 molecule has the structure shown in Figure 5b. The identity was confirmed by Zahorszky.[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 A

b = 20.97 A

c = 6.09 A

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.

Table XIII

Structure of Solid Allotropes

Molecule	Space group	Unit cell[(a)]	a	b	c	β (deg.)	Color	Density gm/cm^3	Melting pt. or decomp.(°C)	Reference
S_6	$R3\text{-}C_{3i}^{2}$	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)	116,117,118
$S_{8\text{-}\beta}$	$P2_1/a\text{-}C_{2h}^{5}$	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	141
S_∞	$Ccm2_1\text{-}C_{2v}^{12}$	160[(b)]	13.8	4x8.10	9.25		yellow	2.01	104	146,149

(a) First number = number of molecules in unit-cell, second number = number of atoms.

(b) 10 atoms for 3 turns.

4) Allotropes of Cycloocta-S_8. 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 A

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 $S_4(CH_2)_2$ has the S_8 crown structure. 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/mole. 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] A normal coordinate analysis has been performed by Cyvin,[114] and mean square amplitudes have been recalculated by Venkateswarlu.[115] The Raman and IR spectral data is 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 this data, 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 coaxually stacked rings. The lattice constants are:

Fig. 8a

a = 10.4646 A

b = 12.8660 A

c = 24.4860 A

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] and Anderson[110]. The data is summarized in Table XII. Gautier[111] observed crystals at 30°K, and reports a large number of lattice requencies 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·sec, and exhibits a negative temperature coefficient, and b) due to electron transport in the electronic band, Figure 1, which he believes is narrow enough for strong vibrational interaction. This contributes approximately 10^{-4} cm^2/V·sec to the conductivity. Gibbons gives a site jump probability of 10^9/sec, which would indicate that electrons are located on an individual molecule for several vibrations, i.e. that ions can be formed. Self diffusion rate in α-crystals was measured by Hampton and Sherwood.[120] The electric conductivity[123] was The thermal conductivity[10] of α-sulfur is 11 Watts/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.

Table XIV

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 $P2_{1/a} - C^5_{2n}$. 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:

Fig. 8'

Table XIV

Melting Point of Allotropes

Allotrope	mp (°C)	Remarks	Reference
α - S	112.8	single crystal	Currell[122]
	115.11	micro crystal	Thackray[119]
β - S	114.6	"natural"	Gernez[172]
	119.6	"ideal" & obsv.	Currell,[122] Feher,[174] Pacor[173]
	120.4	micro crystal	Thackray[119]
	133	"ideal" calc.	Schmidt[52]
γ - S	106.8	classic	Meyer[5,6]
	108	optical, DTA	Miller[128]
	108.6	micro crystal	Thackray[119]
δ - S	106.0	micro crystal	Thackray[119]
ω - S	77;90;160	opt.,TDA,DTA	Miller[128]
	104		Currell[122]
S_∞	75	optical	Miller[128]
	104	classic	Gmelin[5]
S_6	(50 -)	decomposition	Schmidt[52,86]
S_7	(39 -)	"	Schmidt[52,82]
S_{12}	148	"	Schmidt[52,135-137]
S_{18}	128	"	Schmidt[141]
S_{20}	124	"	Schmidt[141]

a = 10.778 A

b = 10.844 A

c = 10.924 A

$\beta = 95.8^{\circ}$

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 controvery about a phase transition at 101°C, but this effect was caused by evaporation of water traces. Recently new Cp 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 ethylxanthate with pyridine.[131] γ-Sulfur crystallizes from the brown decomposition product in large needles. The lattice constants are:

Fig 8c

a = 8.442 A

b = 13.025 A

c = 9.356 A

$\beta = 124^{\circ}\ 98'$

The space group is P2/c. Some confusion about the structure has been caused by difference 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 Cycloocta-sulfur. During the last hundred years about two dozen 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. Thus, we can omit discussion of the confusing list of species, and refer for details to earlier reviews.[6,15]

5) S_9, Cycloennea-S. Schmidt and Wilhelm[133] prepared deep yellow needles of cyclo-S_9 by the reaction of

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

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}, Cyclodeca-S. 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 by the following reactions[81] to be 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 masspectrum[101a] indicated limited stability. The solid must be stored at -40°C.

7) S_{11}, Cycloundeca-S. 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}, Cyclododeca-S. In 1966 Schmidt and Wilhelm[52,132] prepared S_{12} by the reaction of sulfanes and chlorosulfane of proper chain length:

$$H_2S_4 + S_2Cl_2 \rightarrow S_6 + S_{12} + 2HCl$$

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

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 8 other new rings[9] with similar methods. A summary of their preparation methods is given in Table XV.

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:

Table XV

Preparation Methods for Metastable Allotropes

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

S-S bond length, d = 2.053 ± 0.007 A

S-S-S bond angle = $106.5 \pm 1.4^{\circ}$

S-S-S-S torsion angle = $86.1 \pm 5.5^{\circ}$

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] preduction 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 masspectrum 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 A

b = 9.104 A

c = 14.7574 A

The space group is Pnmm-D_{2h}^{12}. The unit cell contains 2 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}, Cyclooctadeca-S. 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 A

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 A

b = 11.441 A

c = 7.581 A

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}, Cycloicosa-S. 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 4 atoms each in a plane. The bond values[142] are:

S-S bond length, d = 2.047 A

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:

$a = 18.580$ A

$b = 13.181$ A

$c = 8.600$ A

Four molecules, with eighty atoms, form a unit cell.

C. Allotropes of Polymeric Sulfur

All of the allotropes described below contain polycatena sulfur. 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 = 2.066A

S-S-S bond angle = 106°

S-S-S-S torsion angle = 85.3°

These values are very close to those in S_{20}, 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 polycatena sulfur comes in many forms.[6,7,10,145] It is present in rubbery sulfur, plastic (χ) sulfur, lamina 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 a 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 non-polymeric 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.

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] Tunistra[145] and Geller[146] indicates that the unit cell contains 160 atoms. The space group is $Ccm2_1 - C_{2v}^{12}$. The structural parameters[146] are:

$a = 13.8$ A

$b = 4 \times 8.10$ A

$c = 9.25$ A

$\beta = 85.3^o$

Geller's analysis was conducted on diffraction patterns obtained with samples prepared at 27 kbar. The density of fibrous sulfur is $d = 2.01$ g/cm^3. 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 ψ-sulfur is 19 x 10^{-6} cm/deg along the pitch, 94 x 10^{-6} cm/deg along the a-axis, and 72 x 10^{-6} cm/deg along the b-axis. Thermal transition, polarization, dilatometry and other properties have been reported by Miller.[128]

2) 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] Baak'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

Figure 9

pressure. Block and Piermarini's experiments[164] explain the divergent observations reported for pressures above 24 kbar, and temperatures above 250°C. They waited at this point for three 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 twelve 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 is indicated in Figure 15. 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 nineteen 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 thermodynamically 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 1949, most old data is unreliable, i.e. the freezing points are too low.

Small droplets of sulfur can be supercooled. LaMer[169] kept particles with a diameter of 0.2μ liquid 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}·sec^{-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] $\Delta H_m = 384.2 \pm 1.9$ cal/g at. at 119.6°C, while the higher values of up to 414.8 ± 2.4 cal/g at. are valid at 114°C in an impure mixture. The specific heat[174] of the liquid at 120°C is 7.02 cal/g at·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]

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 $20<n<33$. Wiewiorwski[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/mole. This value agrees well with that of 32.8 kcal/mole obtained by Tobolsky[10] by analysis of the polymerization at higher temperature. Table XVI shows the freezing point depression observed, and the values calculated, by Semlyen[180] who determined the average number of atoms per ring with the help of a polymer model. The composition of liquid sulfur, computed by Harris[11,181] from various observed and estimated thermodynamic data is shown in Figure 10.

Table XVI

Fig. 10

Baur[103] 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] Cusachs[36] and Spitzer[38] show that the acid-base character of rings and chains, first discussed by Wiewiorowsky,[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.

Table XVI

Freezing Point Depression[a)]

Equilibrated at (T, °C)	$T_\lambda - T_f$ (°C) calculated	observed	Av. no. atoms per ring
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: Feher[174]
Harris[11]
Schenk[187]
Semlyen[180]
Wiewiorowski[179]

However, the curves also depend on the p, T-history, because the composition of the solid phase changes, due to S_8 ring scission followed by formation of helices. This, together with the extremely poor thermal conductivity of sulfur, causes very slow solid-liquid transition. Block and Piermarini[164] waited at 235°C and 30 kbar 3 days for equilibrium. It is not surprising that authors using different equipment observe new compositions.

B. Polymerization at $T_\lambda = 159.4^\circ C$

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 hours 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 onductivity,[176,183-185] and many other properties have been measured in the same temperature region. However, the most striking effect at this temperature, which is often called lambda temperature, is the sudden change in viscosity.

Fig 11

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

$$\text{Cyclo-S}_8 \rightleftarrows \text{Catena-S}_8 \qquad \text{I}$$

$$\text{Catena-S}_8 + \text{Cyclo-S}_8 \rightarrow \text{Catena S}_{8x2} \qquad \text{II}$$

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, and disappearance, as well as appearance, 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.

Fig. 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, Wiewiorowsky[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 showed that 2% S_6 lowers the polymerization temperature by 10° for over 15 minutes, while $(SCH_2)_9$, added at 200°C, reduces the average chain length greatly.

The effect of pressure on polymerization was reported by Doi.[177] Bröllo[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 Franckel.[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 14 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 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 15a. 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

Fig. 13

Fig. 14

Fig. 15

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 15b. 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°C and 200°C remains a puzzle, because the free radical chains, according to all known theory[58,61] should be deeply colored. Several possible explanations have been proposed: One is that 10^{-5} mole 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]

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 15c 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 towards 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 16 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 18, and of the liquid,[11] Figure 14, extrapolate smoothly to the critical data, Figure 16.

Table XVII

Fig 16

The recent discovery of small molecules in hot liquid sulfur cast light on a formerly unknown phase, which surely must display interesting chemical properties.

Table XVII

Critical Data

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

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 17, are listed in Table X. Recently published high pressure values[202,203] agree well. The critical temperature 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 has been summarized for JANEF by Jensen,[74] and others.

Fig 17

Table XVIII

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 hundred year old controvery 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 0.2μ at 25° to 75°C which are stable for several days and have five times equilibrium vapor pressure.

Table XVIII

Thermodynamic Data of Gaseous Sulfur[a]

(Standard state; 1 atm, 298.15K)

Molecule	Equilibrium	ΔH^{o}_{f} (kcal/mole)	S^{o} (cal/mole·deg)	B (S-S) (kcal/mole)	
				observed[12]	calculated[43]
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	$3/4S_8(g) \rightleftarrows S_6(g)$	24.36	84.60	61.8	62.8
S_7	$7/8S_8(g) \rightleftarrows S_7(g)$	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) See refs. 12, 96, 51.

Berkowitz[12] has shown by masspectroscopy 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:

$$\text{Pt, Ag / AgI / Ag}_2\text{S / Pt}$$

to overcome problems in identifying the molecular ionization pattern in a masspectrometer. 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 16. The composition in the intermediate temperature range is shown in Figure 18. The S_5, S_6, and S_7 concentration of each goes through a maximum at about 1000°K. According to Rau,[202] S_5 never accounts for more than about 3% of the total vapor pressure, while Baker[203] estimates a maximum of 18% at about the same temperature.

Fig. 18

The relative concentration of small species increases in unsaturated pressure. Spectral studies[206] 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 corresponding specific heats have been calculated by Rau,[96] who makes available a computer program which allows computation of vapor pressures.

Table XIX

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[208-211] 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. Excited atoms carry 26 kcal/mole excess energy and have a sufficient lifetime to enter

Table XIX

Heat Capacities C_p of Gaseous Sulfur Molecules

(After ref. 203)

	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)[a]	5.268	6.121	-0.816	5.4	-
β-S_8 (s)[a]				5.6	

a) See also Table IX

chemical reactions. Strausz and Gunning[211] have explored extensively the chemistry of sulfur atoms with organic molecules. Some inorganic reactions have been studied by Donovan.[213] With itself, 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.

$\underline{S_2}$ 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 glasses, 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, Table XX. 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 know,[29,207] far more than for O_2. The violet color is due to the lowest allowed transition $B \leftarrow X$. The corresponding $B \rightarrow X$ 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

Table XX

Table XX

Electronic Energy Levels of S_2 (Refs. 29,207)

State	T_0(cm^{-1})	ω_e(cm^{-1})	B_e(cm^{-1})	$D_e \cdot 10^8$ (cm^{-1})	r_e(A)
$^1\Sigma_u^+$, $^1\Delta_u$	~64,000?	-	>0.29	-	<1.9
	~59,900?	-	-	-	-
h $^1\Sigma_u^+$	~59,900?	819.6	>0.29	~14.52	<1.89
D $^3\Pi_u$	58,750	793.9	0.3066	~16.293	(1.854)
C'? $^3\Sigma_u^-$	56,984	-	>0.295	-	<1.89
g $^1\Delta_u$	~56,700	816.4	0.3217	20.0	1.811
C $^3\Sigma_u^-$	55,633.3^a	829.15	0.32196	18.7 22.0	1.810
f $^1\Delta_u$	~41,200	438.32	0.2267	24.5	2.157
e $^1\Pi_g$	~37,000	533.7	~0.25	-	~2.08
B' $^3\Pi_{g,i}$	~36,000	-	0.244	-	2.08
B $^3\Sigma_u^-$	31,689^b	434	0.2244	23.1	2.168
B'' $^3\Pi_u$	$\leq$31,700	-	>0.2029	-	<2.280
A $^3\Sigma_u^+$	~22,550	477	-	-	-
c $^1\Sigma_u^-$	~23,550	533.6	~0.235	-	2.122
A' $^3\Delta_{u,i}$	~21,855	488.6	0.2284	19.96	2.148
b $^1\Sigma_g^+$	~ 8,500	700.8?	-	-	-
a $^1\Delta_g$	~ 4,500	702.35	0.2923	20.4	1.899
X $^3\Sigma_g^-$	0^c	725.668	0.29541	19.58 21.48	1.889

a) λ=-11.61, γ=0.03; b) λ=-4.9, γ=0.05; c) λ=-11.61, γ=0.006.

compounds, separated by gas chromotography. 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] masspectroscopy,[51,223] and photoionization, listed in Table XXI, all agree on the "higher" of the possible values. Table XXI The predissociation[29,224] in the uv spectrum yields the most accurate value; 35,590 cm^{-1} = 101.8 ± 0.01 kcal/mole. 51 A recent value for photoionization[51] is 9.36 eV, and confirms the earlier value of 9.9 eV ± 0.6 obtained by electron impact.

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 $\nu'_n \leftarrow \nu''_o$, as kT is insufficient at 20^oK to yield vibrationally excited ground state atoms. The emission spectrum, and a Raman band at 720 cm^{-1} has 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.

$\underline{S_3}$ was called thiozone by Erdmann,[226] 18 , who assumed that it exists in liquid sulfur. L d'Or published the uv spectrum os 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 masspectrometer. It has since been proven

Table XXI

Dissociation Energy of S_2

$D_0^o(S_2)$ kcal/mol	Method	Reference	Year
100.69 ± 0.01	uv-Spectroscopy[a]	Ricks and Barrow[224]	1969
101.0 ± 0.2	Photoionization	Berkowitz and Chupka[5,12]	1969
$\leq$101.0 ± 0.8	Photoionization	Dibeler and Liston[223]	1968
101.7 ± 2.9	Knudsen-torsion Effusion	Budininkas et al.[222]	1968
101.0 ± 2.5	Thermochemistry	Drowart and Goldfinger[51,221]	1966
97 ± 5	Mass-spectrometric	Colin et al.[221]	1964

a) 100.69 kcal/mole corresponds to the predissociation at 35,590 cm^{-1}.

$\underline{S_4}$ 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. Semi-empirical 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 -.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_2^{+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.

$\underline{S_5}$ 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 3.6 A apart[49] (Table V), while for all observed rings, values of about 2 A 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, and 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 III B, 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]

V. Solutions

A. In non-polar liquids, cycloocta-sulfur and other rings dissolve at room temperature without decomposition. Representative solubility values of frequently used solvents are indicated in Table XXII. Distribution factors for S_6 and S_8 in 8 solvent mixtures can be found in references 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, recognizeable by the color change.

Table XXII

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]

B. 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

Table XXII

Solubility of Sulfur

Solvent	Solubility (weight percent) g S/100 g Solvent	Temp. (^oC)	Reference
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	

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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-S = 2.048 A
S-S-S = $107^{\circ}53'$
S-S-S-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 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.

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,[240-242] 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.

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}. The ESR spectrum has been observed.[247] The molecule has C2v 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 formed cations of sulfur in oleum and in super acids,[64] and for solid salts. 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 A, i.e. somewhat shorter[7] than in S_8. Likewise, non-bonding 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:

$\nu_1 = 584\ cm^{-1}$ Aig
$\nu_2 = 530\ cm^{-1}$ Big
$\nu_3 = 460\ cm^{-1}$ Eu
$\nu_4 = 330\ cm^{-1}$ Bug

They have also been identified by ESR[252] and circular [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 ten years much has been learnt 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 triphenylphosphinechloride. 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] have 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 sufide 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.[211]

Table XXIII presents, in conclusion, a summary of those sulfur allotropes which have been most widely described.

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Table XXIII

Molecular Composition of Sulfur Phases, and Reaction Products

Phase	Reagents	Allotrope	
	Molecular Species	Well-established	Inconclusive or Mixture
Solid Sulfur	a) Stable (STP): Cyclo-S_8 as α-S_8	S_ψ (Geller II)	Laminar, ω, Orange, Metallic, Vezzoli, Geller, Baak
Solid Sulfur	b) Metastable: Cyclo-$S_{n=6,7,8,9,10,11,12,18,20}$ 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} $\psi(=\mu)$	π, ι, ν, ψ,
Sulfur Vapor	Cyclo-S_n, $6<n<12$ Catena S_i, $2<i<5$	α, S_∞	Crystex, ω, Red, ξ, sec. fibrous, Green, Blue, Black (Schenk) Violet, Green, Purple
Solution, containing cyclo-S_8	Cyclo-S_8	α, β, γ	$\omega_{1,2}(\varepsilon)$, 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, π_1-π_2 Red (E;F,G), Orange (I,K,L,M)

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FIGURE CAPTIONS

Fig 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].)

Fig 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 is listed in Table XI.

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

Fig 4 The structure of S_8 and S_{12}.

Fig 5 Views of a) S_6, b) S_7, c) S_{18}, and d) S_{20}. The molecular data is summarized in Table XI, the structure of the solids in Table XIII.

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

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

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

Fig 14 Estimated mole fraction of liquid sulfur components.

Fig 15 Visible absorption edge of liquid sulfur at a) 120°C, b) 250°C, 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 think 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 refs. 58, 63.)

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Fig 18 Mole fraction of S_n, $2<n<8$, in a saturated vapor, between 120 and 1000°C, estimated from data in refs. 12, 51, 63 and 201-203.

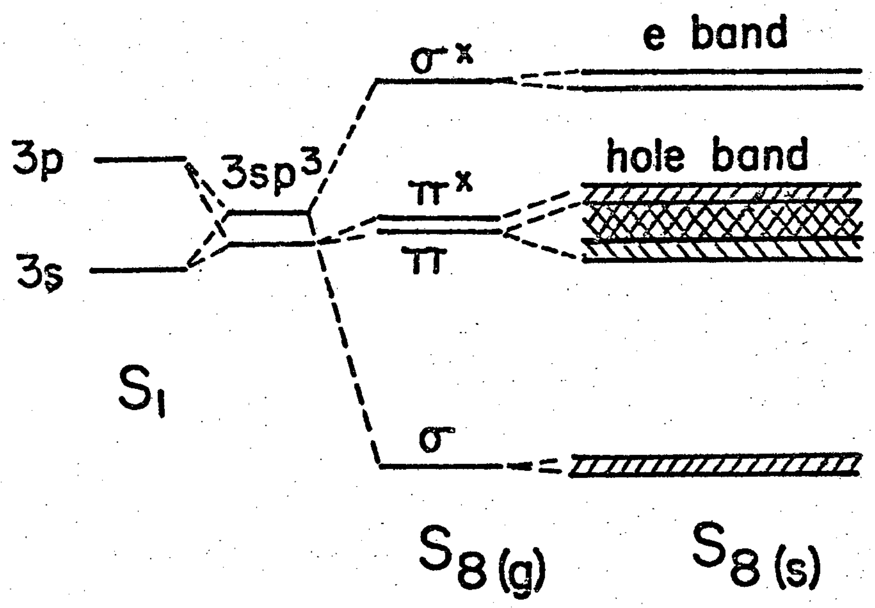


Fig 1 Electronic structure of S_8, and α-sulfur, derived from the energy levels of the free atoms.[31] Both the narrow electron band and the hole band contribute to the electric conductivity. (After Gibbons[40].)

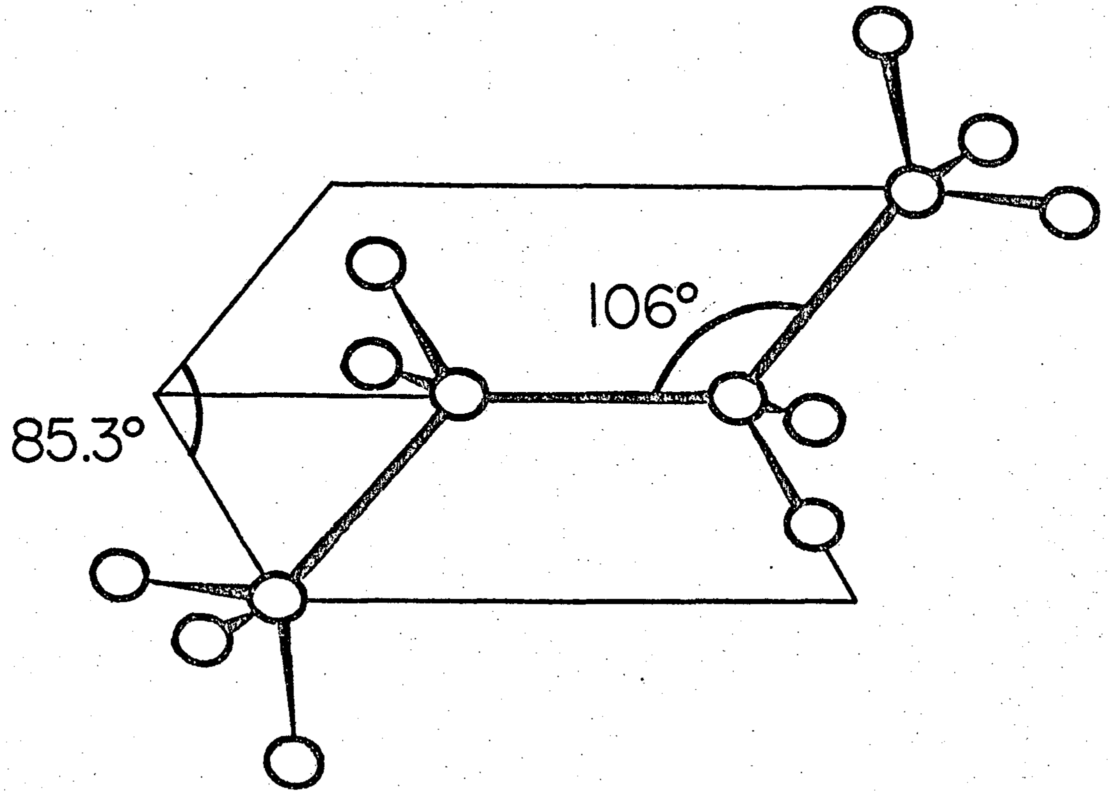
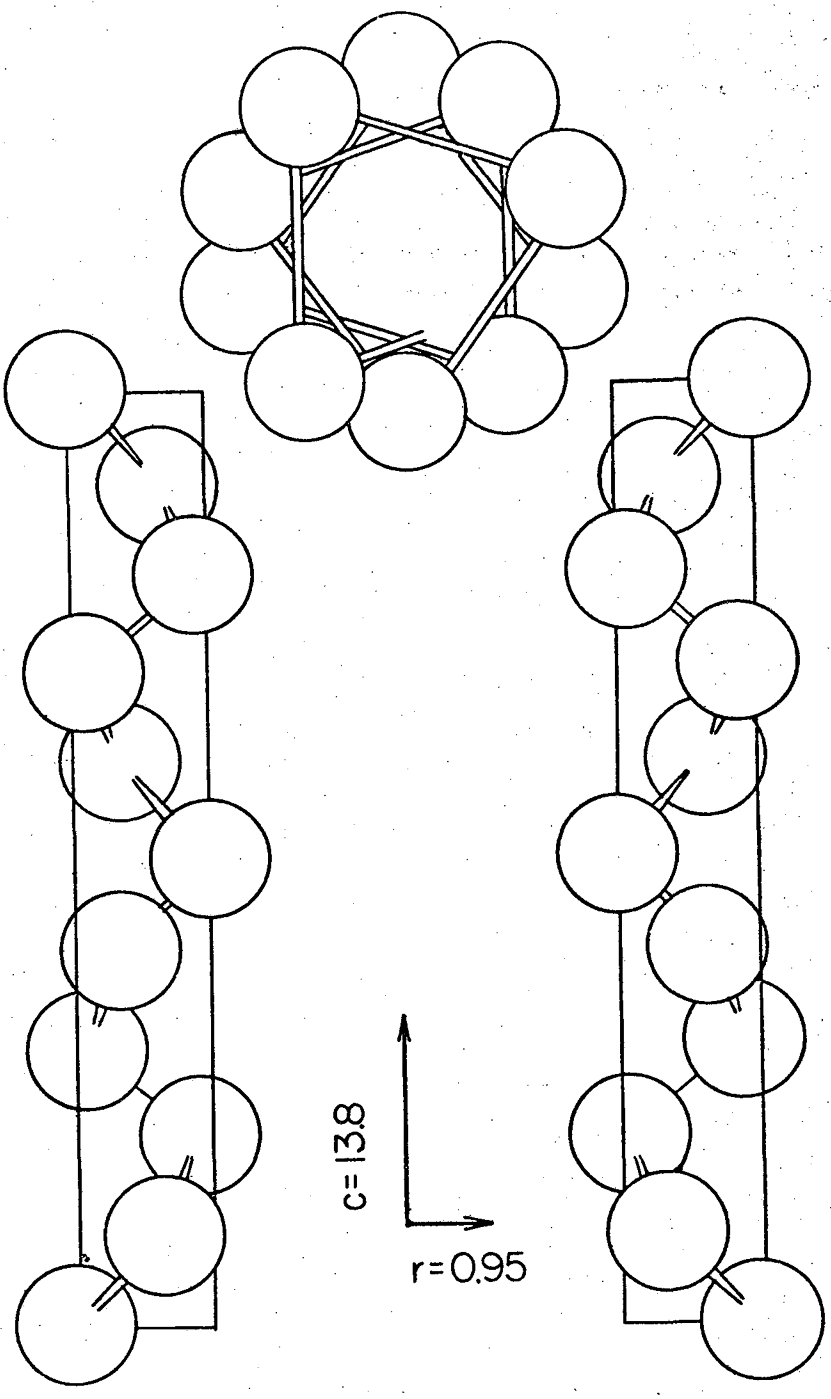


Fig 2 S-S-S-S bond structure. The unrestrained bond angle[146] is 106°, and the torsion angle is 85.3°. Data for various allotropes is listed in Table XI.



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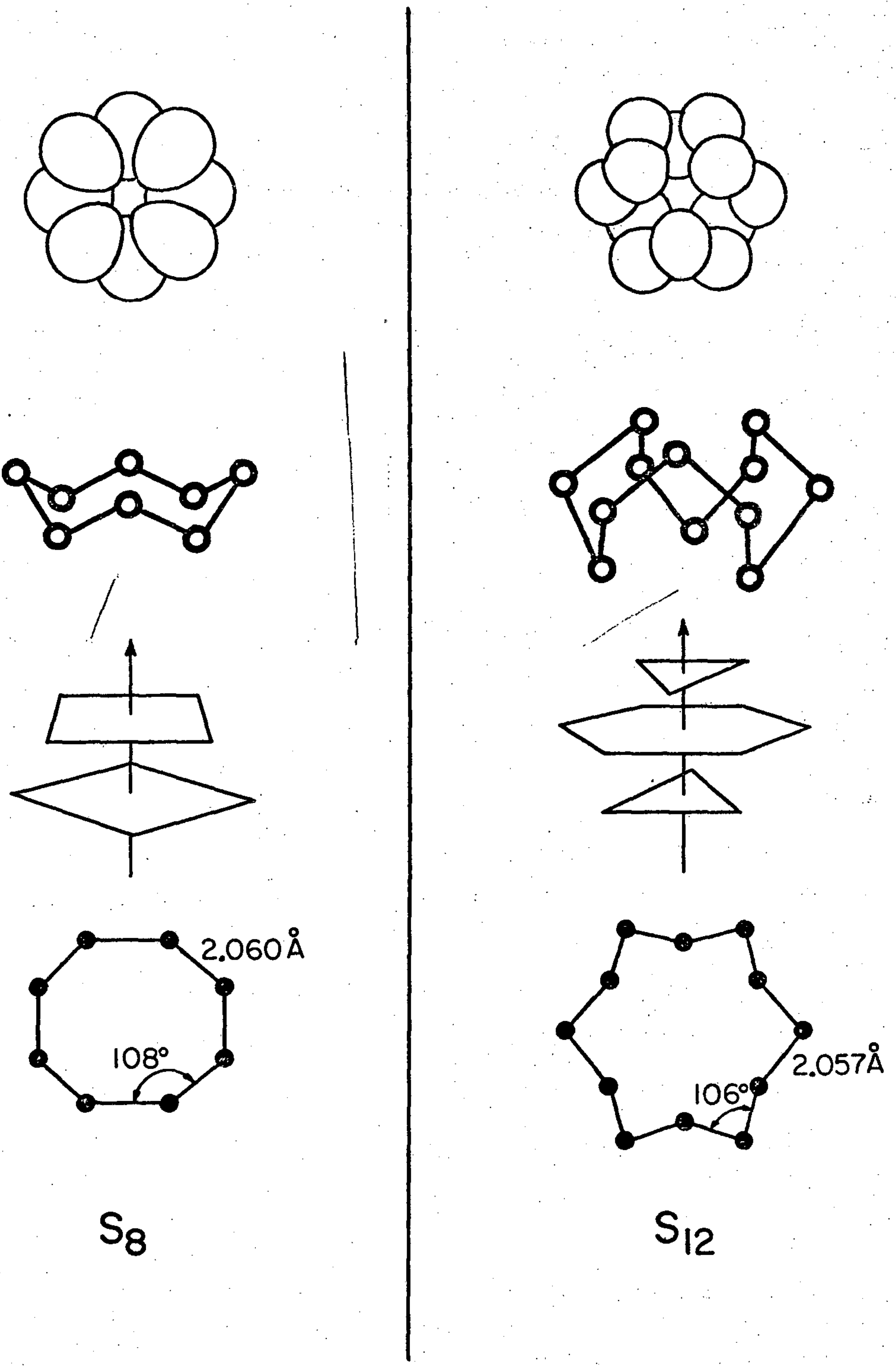

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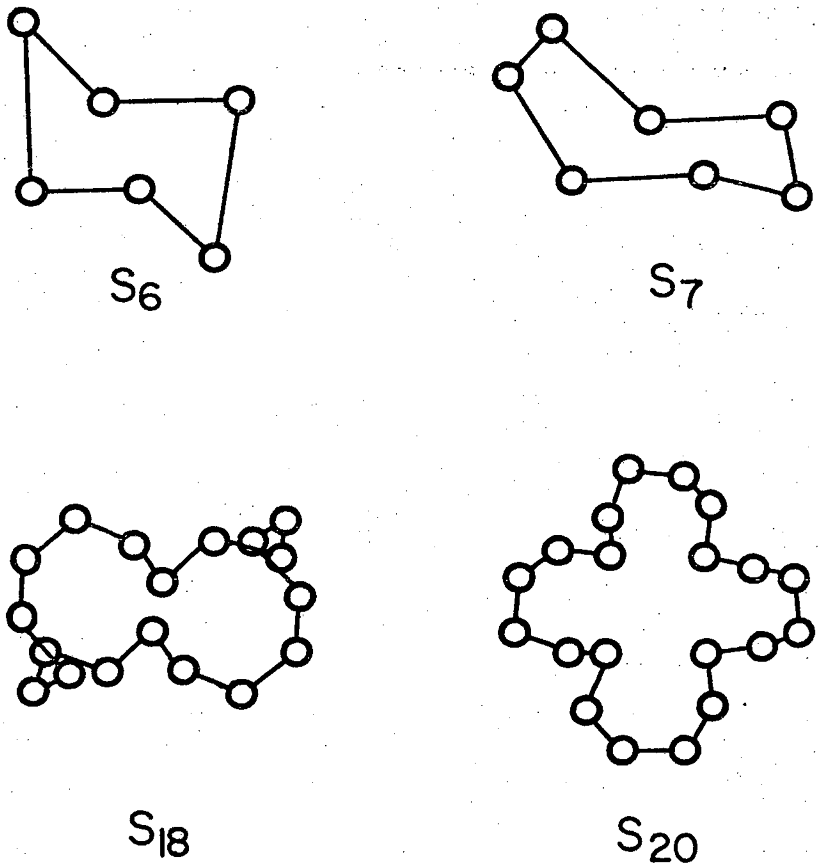

S_6 S_7

S_{18} S_{20}

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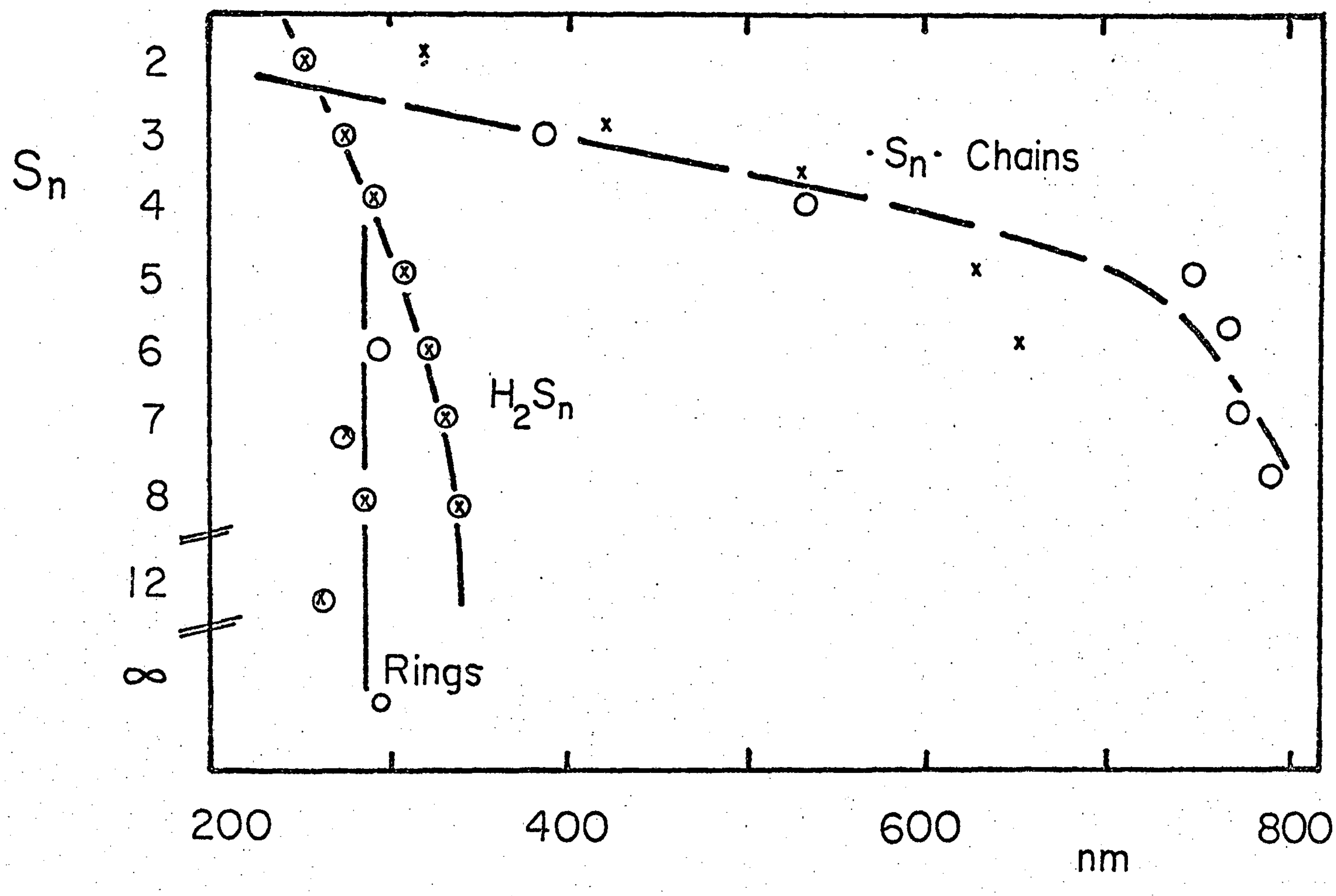

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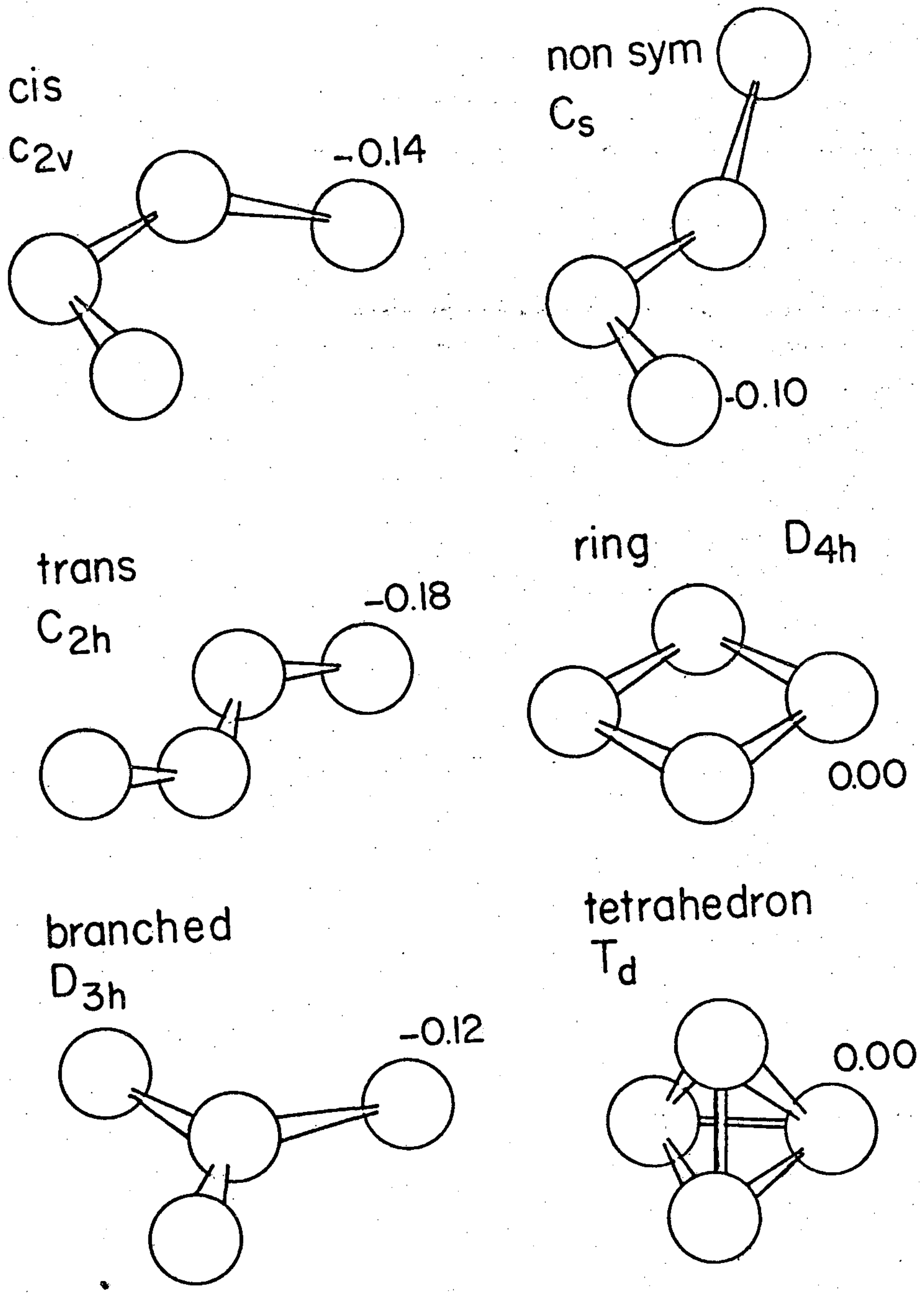

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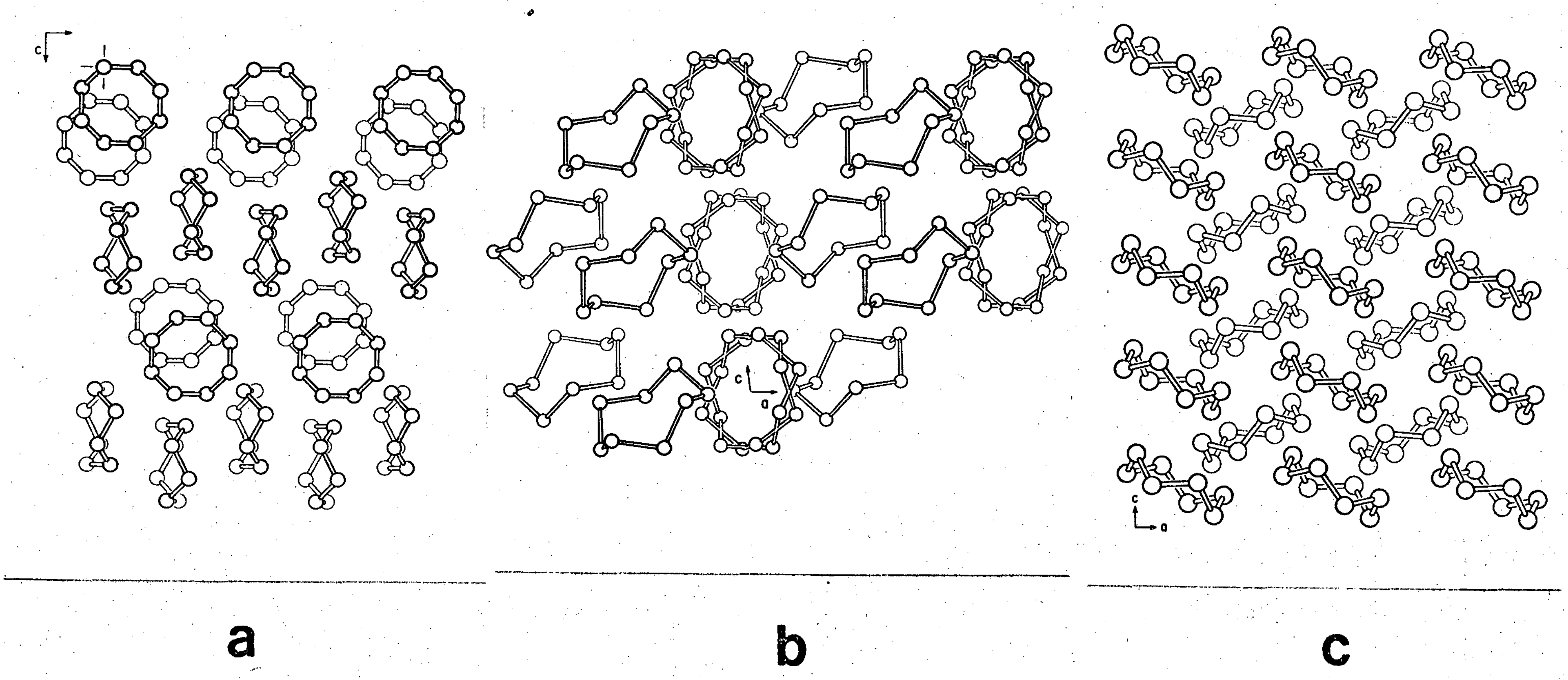

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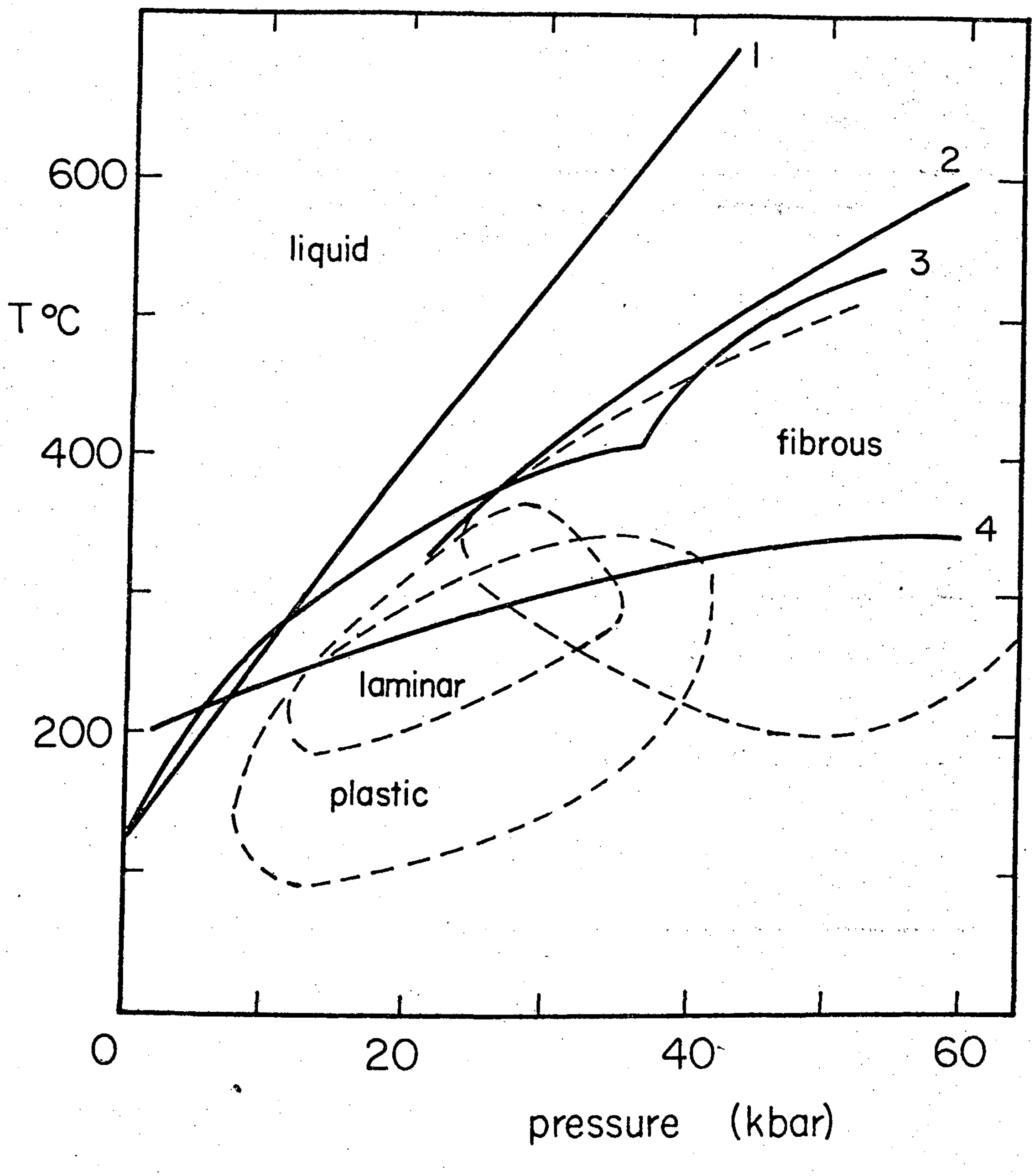

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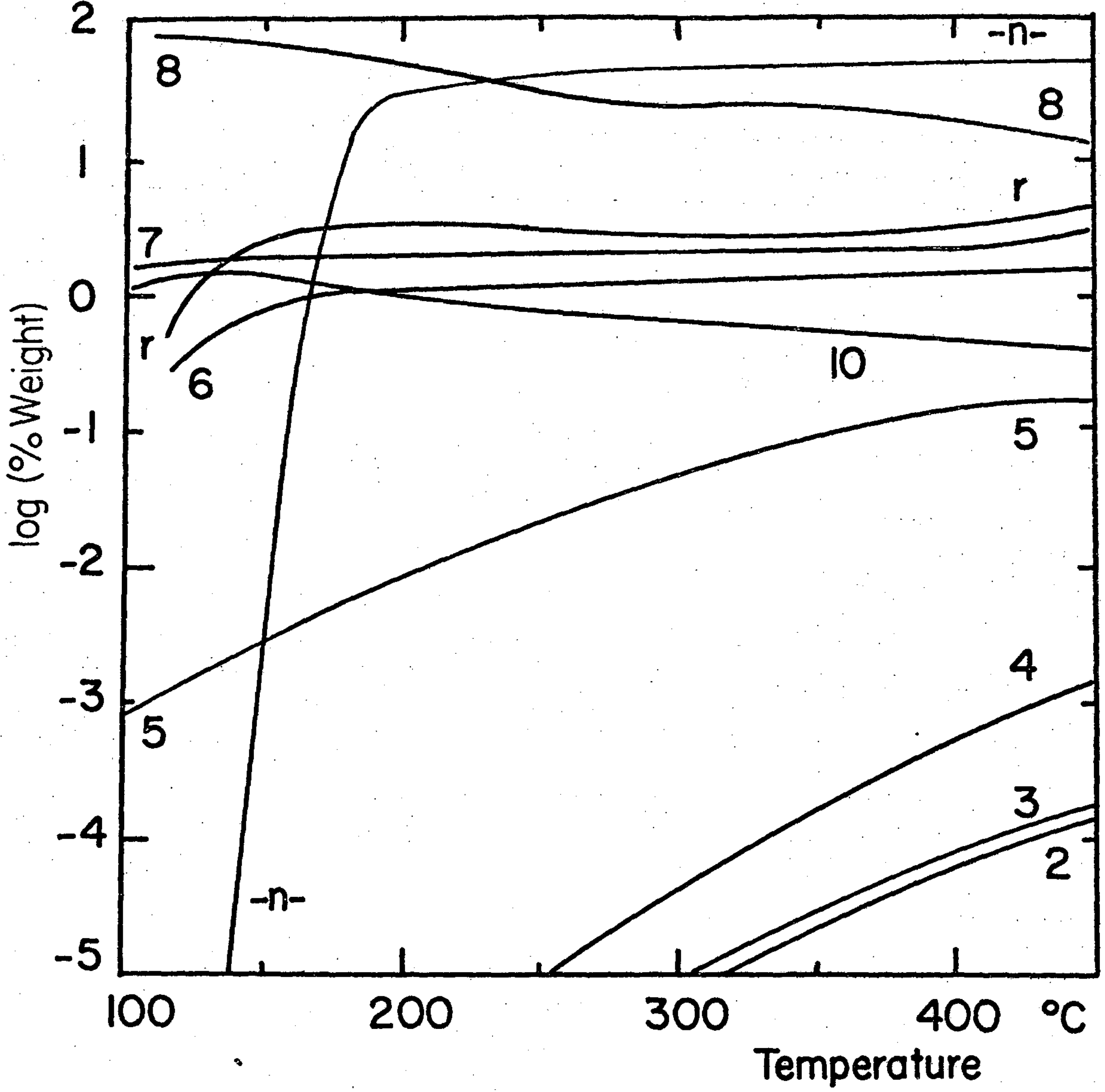

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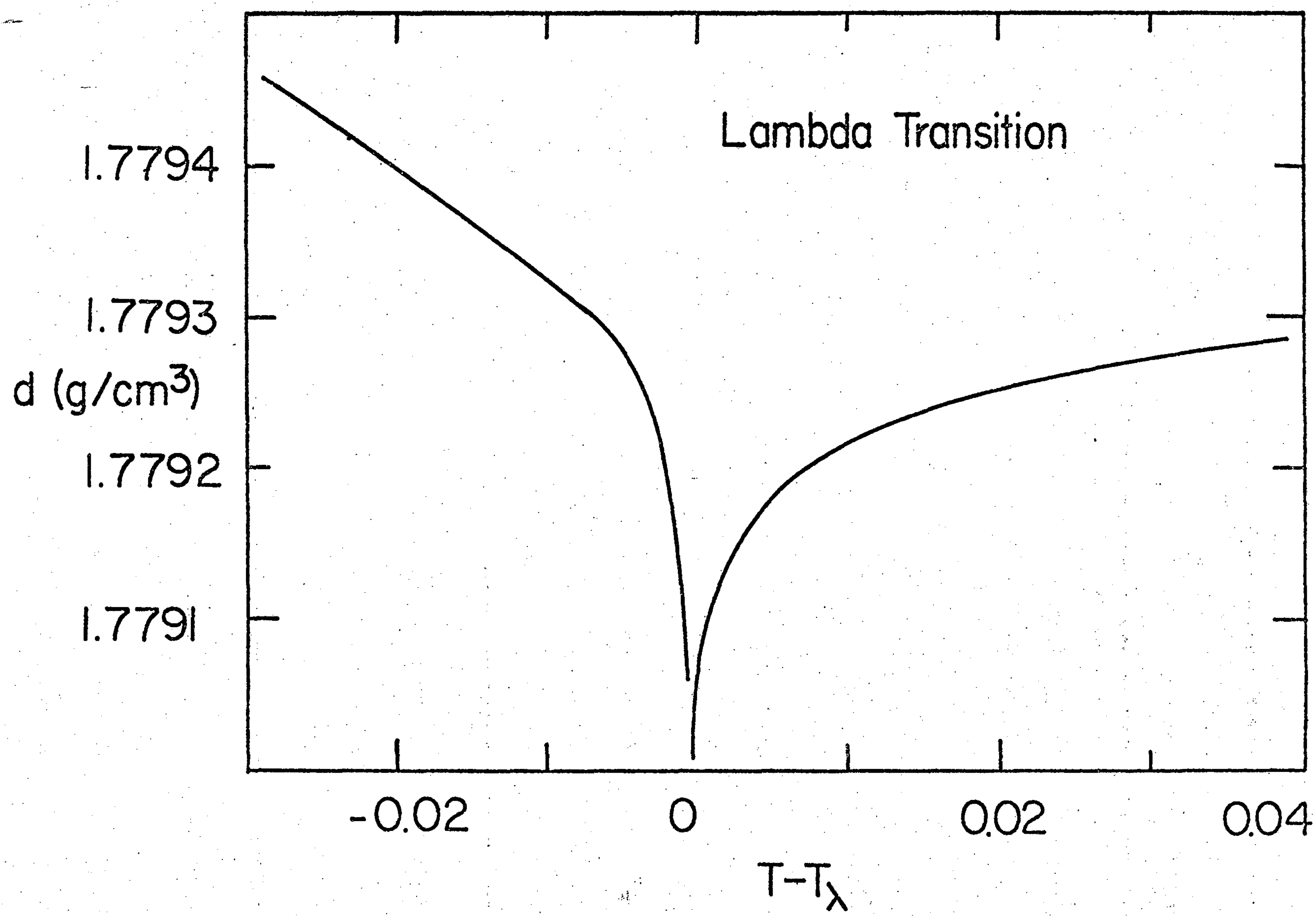

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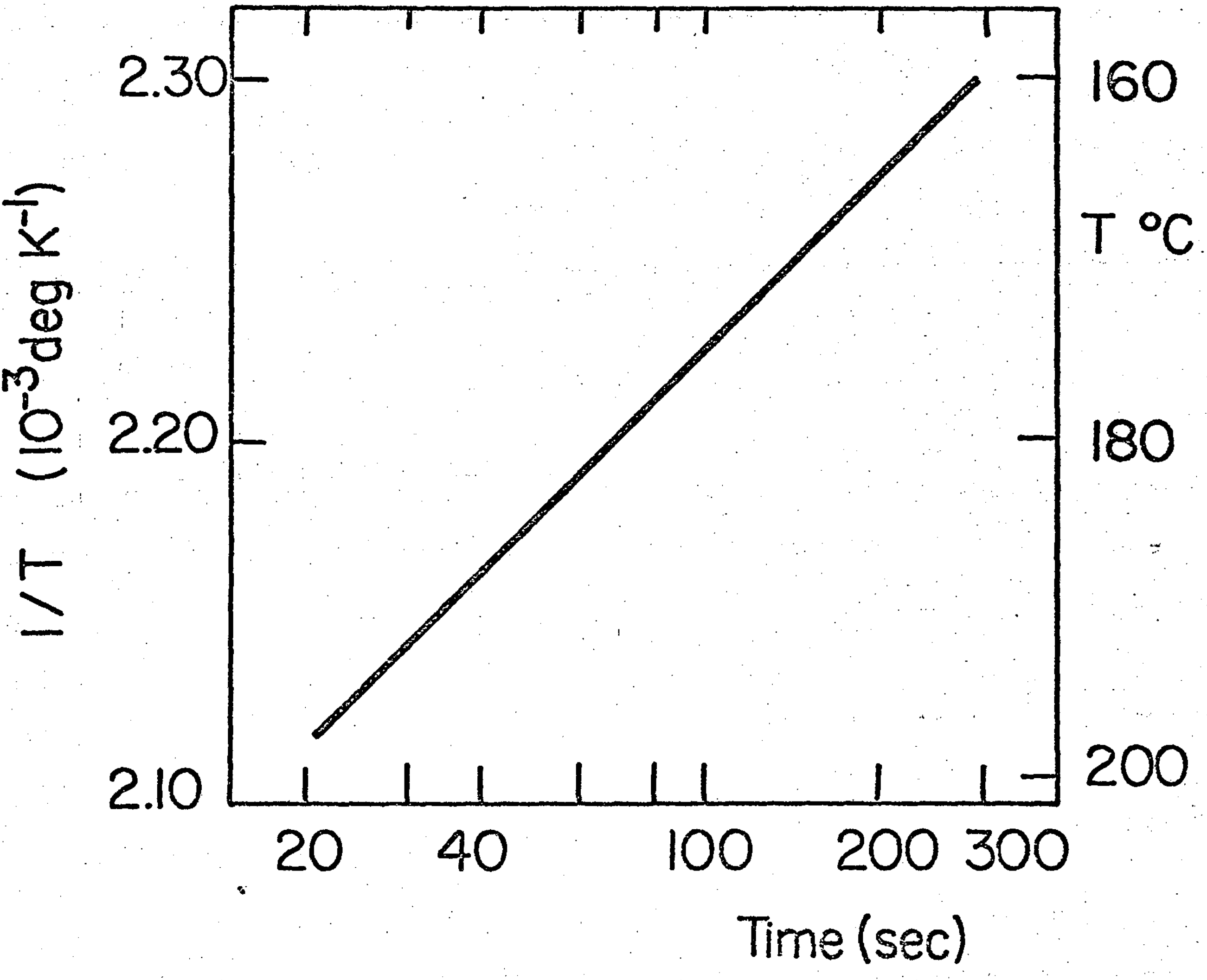

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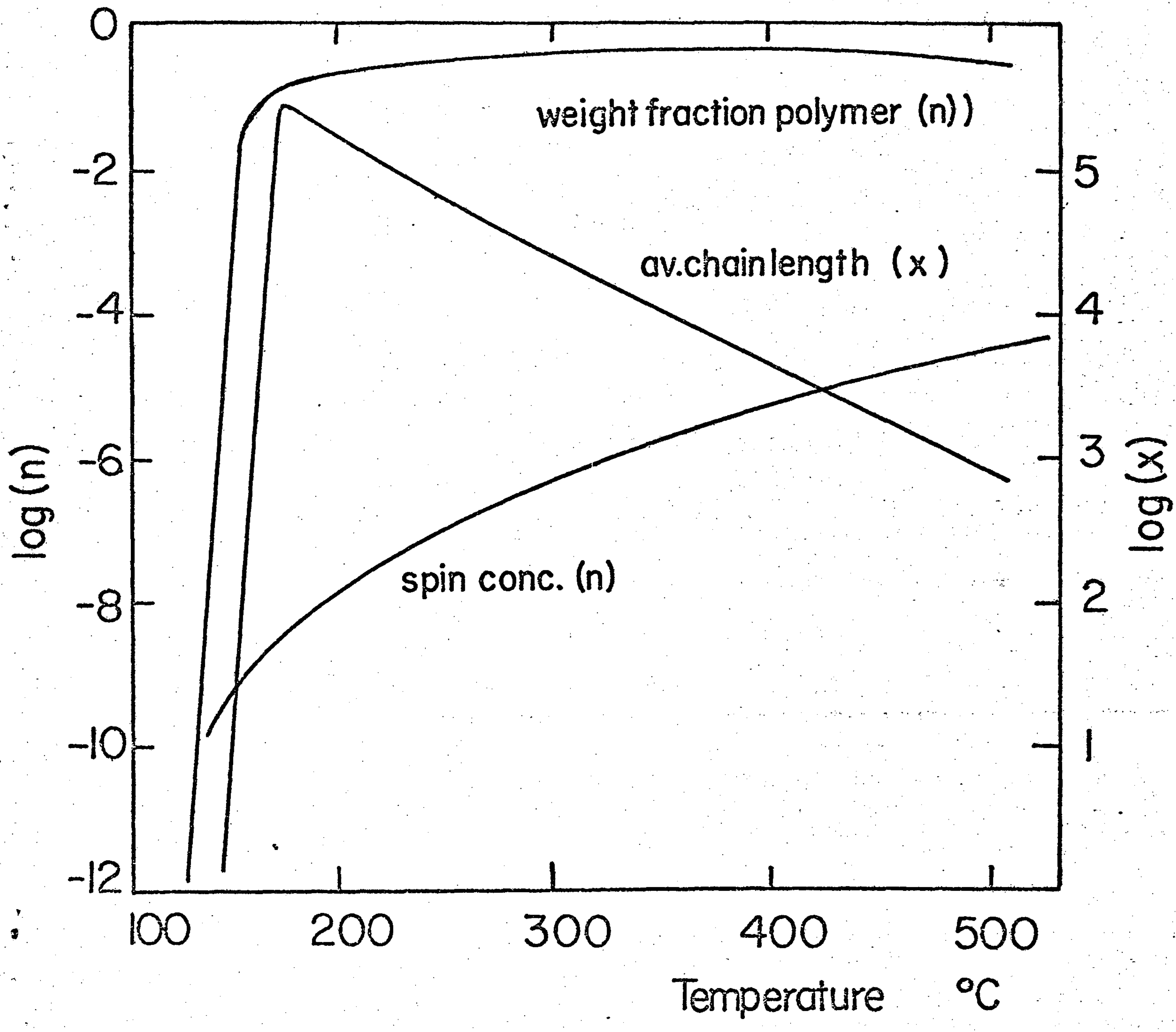

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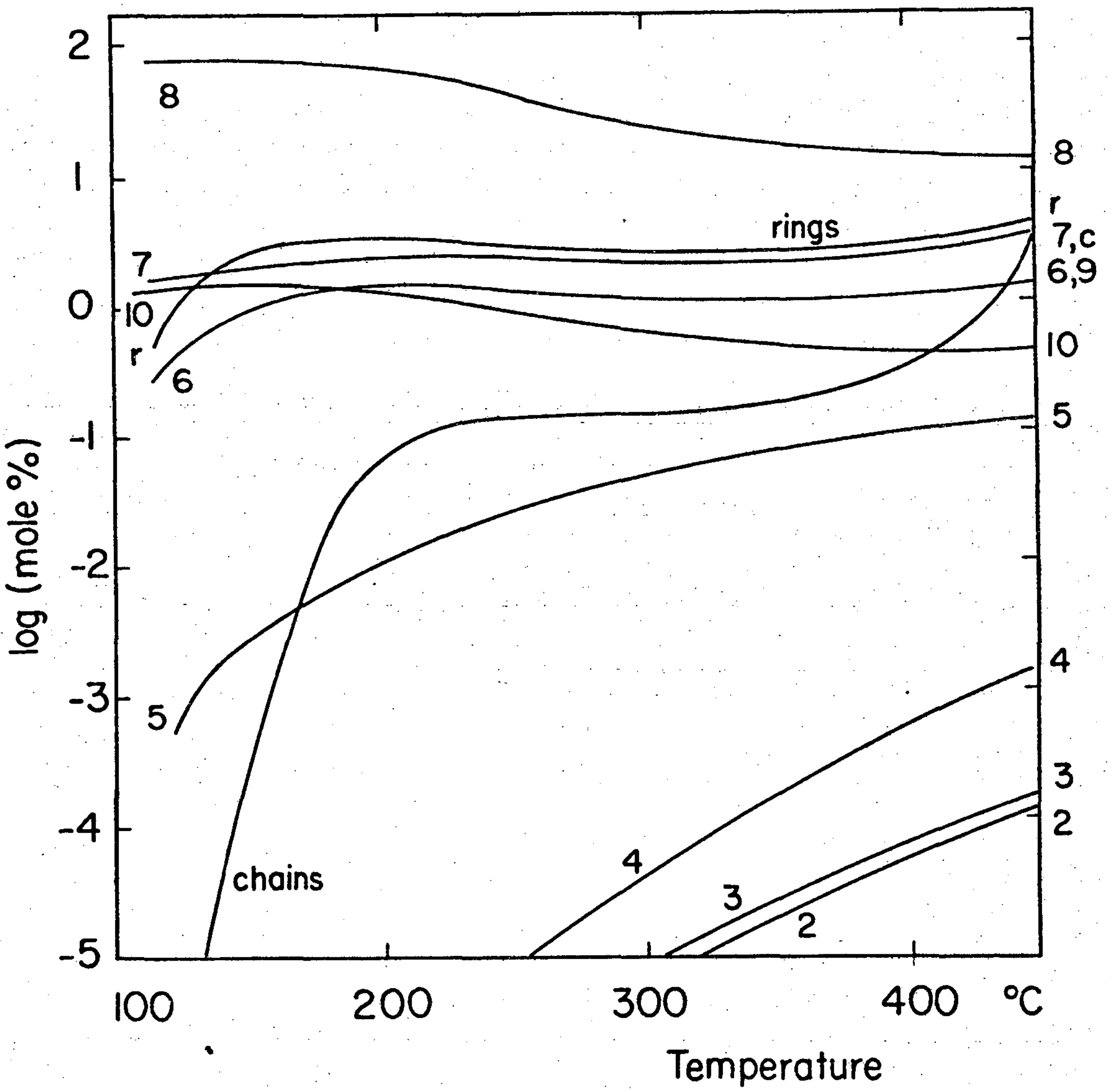

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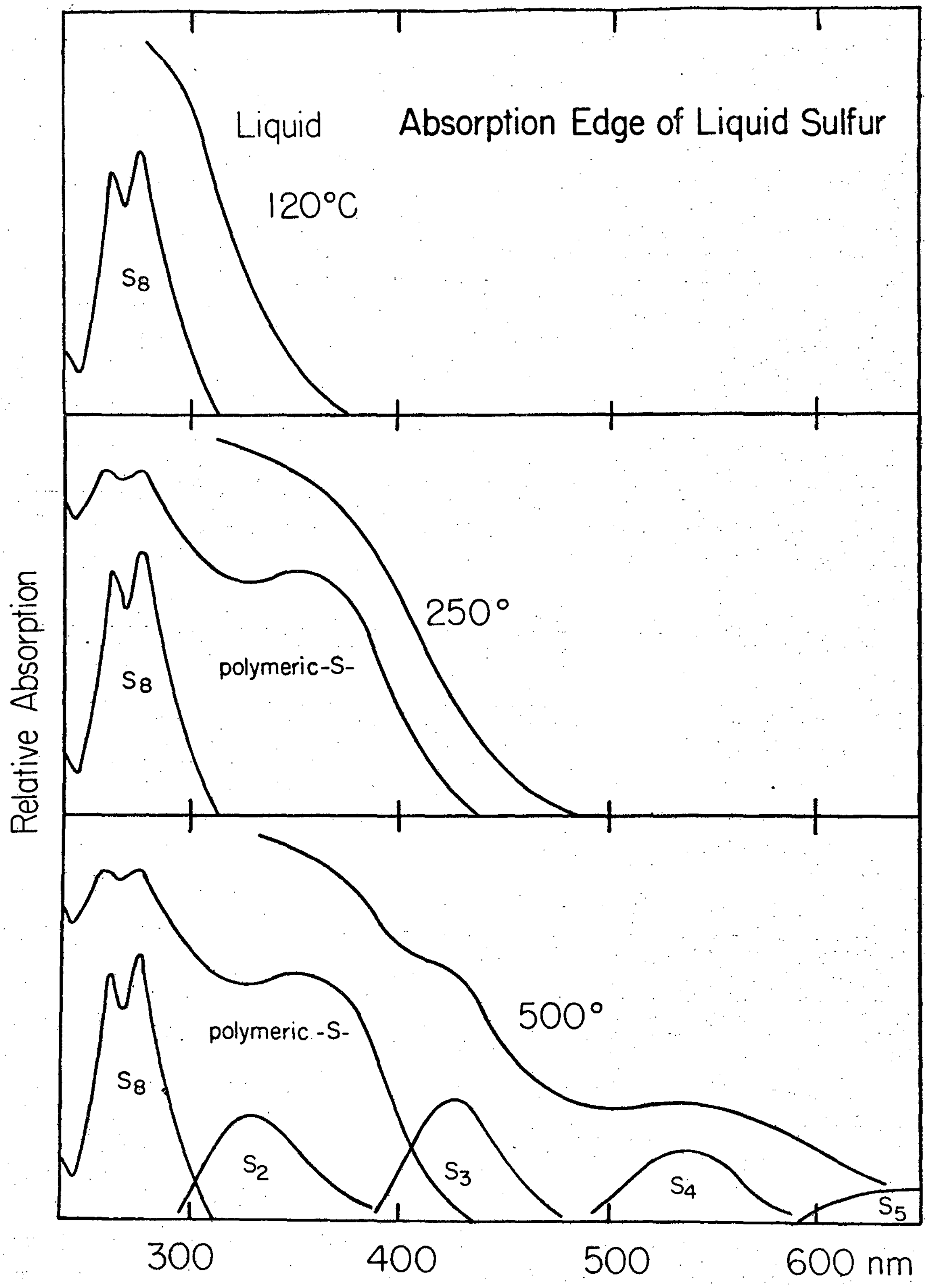

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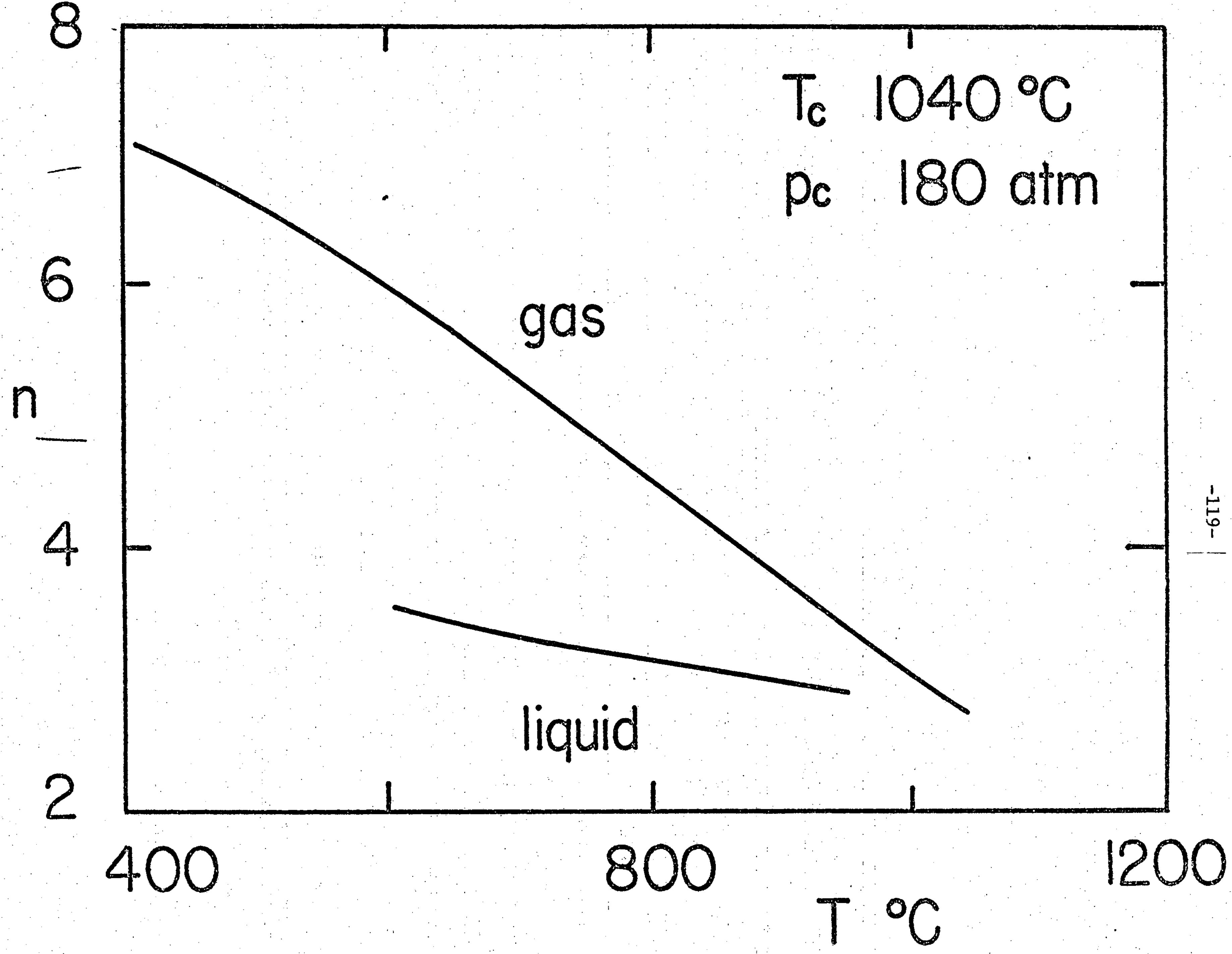

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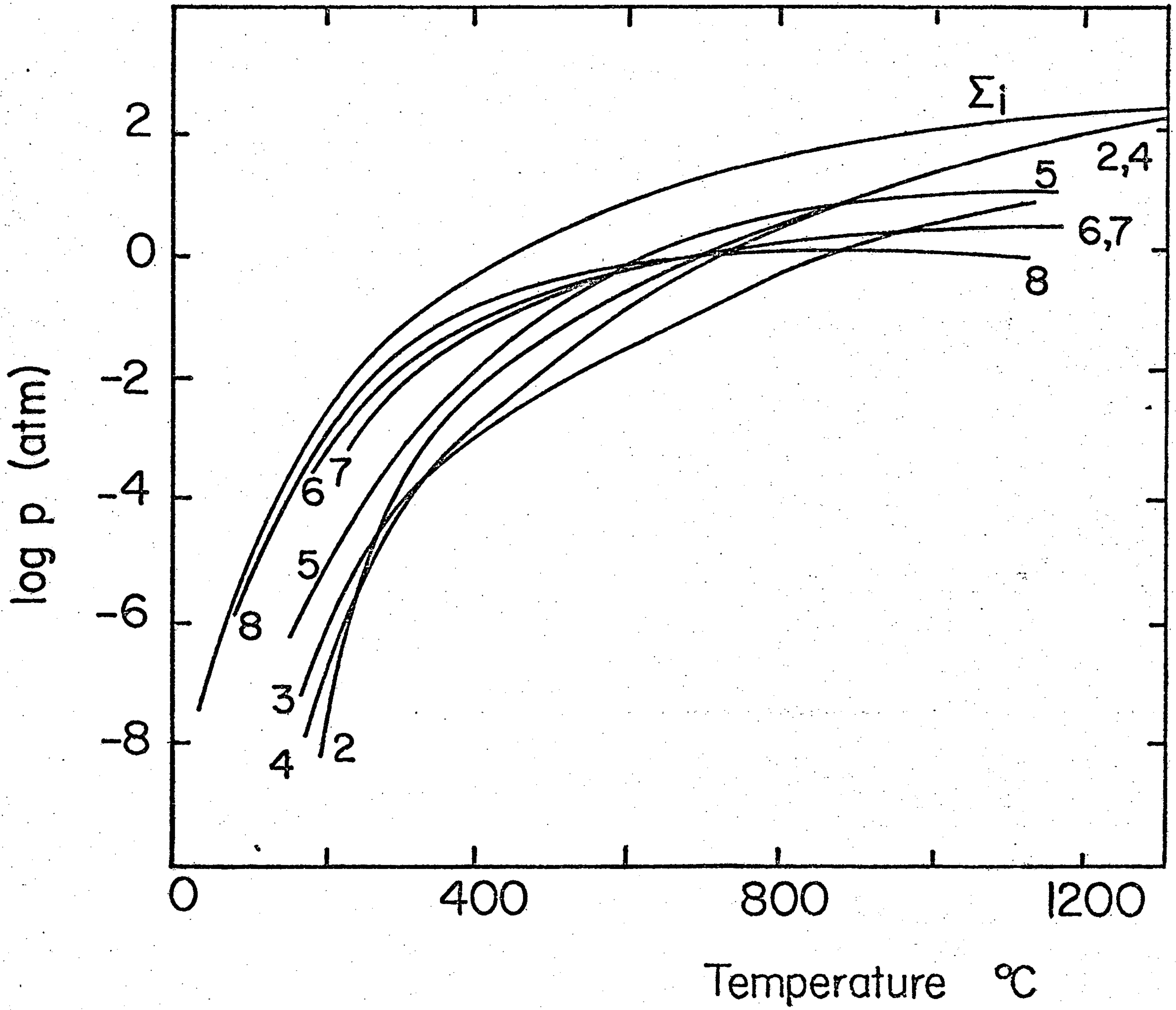

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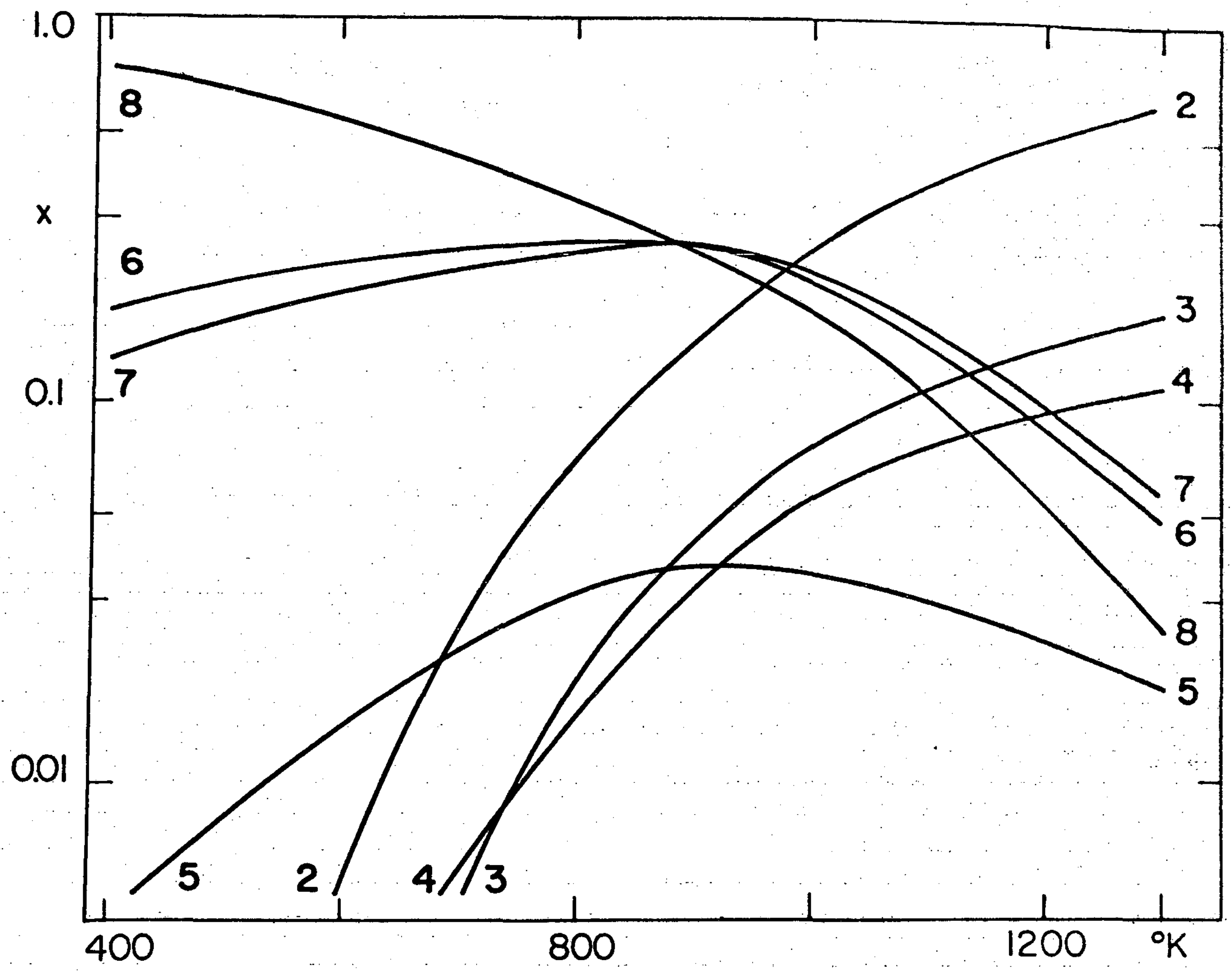

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Table of Tables

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