

		1 H		2 He												3 B										4 C										5 N										6 O										7 F										8 Ne																											
9 Li		10 Be												11 Na										12 Mg										13 Al										14 Si										15 P										16 S										17 Cl										18 Ar									
19 K		20 Ca		21 Sc		22 Ti		23 V		24 Cr		25 Mn		26 Fe		27 Co		28 Ni		29 Cu		30 Zn		31 Ga		32 Ge		33 As		34 Se		35 Br		36 Kr																																																											
37 Rb		38 Sr		39 Y		40 Zr		41 Nb		42 Mo		43 Tc		44 Ru		45 Rh		46 Pd		47 Ag		48 Cd		49 In		50 Sn		51 Sb		52 Te		53 I		54 Xe																																																											
55 Cs		56 Ba		57 La		58 Ce		59 Pr		60 Nd		61 Pm		62 Sm		63 Eu		64 Gd		65 Tb		66 Dy		67 Ho		68 Er		69 Tm		70 Yb		71 Lu																																																													
73 Fr		74 Ra		75 Ac		76 Th		77 Pa		78 U		79 Np		80 Pu		81 Am		82 Cm		83 Bk		84 Cf		85 Es		86 Fm		87 Md		88 No		89 Lr																																																													

15

Sulfur

15.1 The Element

15.1.1 Introduction

Sulfur occurs uncombined in many parts of the world and has therefore been known since pre-historic times. Indeed, sulfur and carbon were the only two non-metallic elements known to the ancients. References to sulfur occur throughout recorded history from the legendary destruction of Sodom and Gomorrah by brimstone⁽¹⁾ to its recent discovery (together with H₂SO₄) as a major component in the atmosphere of the planet Venus. The element was certainly known to the Egyptians as far back as the sixteenth century BC and Homer refers to its use as a fumigant.⁽²⁾ Pliny the Elder⁽³⁾ mentioned the occurrence of sulfur

in volcanic islands and other Mediterranean locations, spoke of its use in religious ceremonies and in the fumigation of houses, described its use by fullers, cotton-bleachers, and match-makers, and indicated fourteen supposed medicinal virtues of the element.

Gunpowder, which revolutionized military tactics in the thirteenth century, was the sole known propellant for ammunition until the mid-nineteenth century when smokeless powders based on guncotton (1846), nitroglycerine (1846), and cordite (1889) were discovered. Gunpowder, an intimate mixture of saltpeter (KNO₃), powdered charcoal and sulfur in the approximate ratios 75:15:10 by weight, was discovered by Chinese alchemists more than 1000 years ago:⁽⁴⁾ The earliest known recipe for explosive gunpowder (as distinct from incendiary mixtures and fireworks) appeared in a Chinese military manual of AD 1044 and its use in a gun (bombard) dates from at least as early as 1128. Arab and European formulae and technology were derived from this. The first use of gunpowder

¹ Genesis 19, 24: "Then the Lord rained upon Sodom and Gomorrah brimstone and fire from the Lord out of heaven." Other biblical references to brimstone are in Deuteronomy 29, 23; Job 18, 15; Psalm 11, 6; Isaiah 30, 33; Ezekiel 38, 22; Revelation 19, 20; etc.

² HOMER, *Odyssey*, Book 22, 481: "Bring me sulfur, old nurse, that cleanses all pollution and bring me fire, that I may purify the house with sulfur."

³ G. PLINY (the Elder), AD 23–79, mentions sulfur in several of the many books of his posthumously published major work, *Naturalis Historia*.

⁴ A. R. BUTLER, *Chem. in Britain*, 1119–21 (1988); and research by Joseph Needham, Cambridge, UK.

Developments in the Chemistry of Sulfur

- Prehistory Sulfur (brimstone) mentioned frequently in the Bible.⁽¹⁾
 ~800 BC Fumigating power of burning S mentioned by Homer.⁽²⁾
 ~ AD 79 Occurrence and many uses of S recorded by G. Pliny.⁽³⁾
 AD 940 Sulfuric acid mentioned by Persian writer Abu Bekr al Rases.
 1044 Earliest known (Chinese) recipe for explosive gunpowder.⁽⁴⁾
 1128 Gunpowder used by Chinese military in a bombard.
 ~1245 Gunpowder "discovered" independently in Europe by Roger Bacon (England) and Berthold Swartz.
 1661 Effects of SO₂ pollution in London dramatically described to Charles II by John Evelyn (p. 698).
 1746 Lead chamber process for H₂SO₄ introduced by John Roebuck (Birmingham, UK); this immediately superseded the cumbersome small-scale glass bell-jar process (p. 708).
 1777 Elemental character of S proposed by A.-L. Lavoisier though even in 1809 experiments (presumably on impure samples) led Humphry Davy to contend that oxygen and hydrogen were also essential constituents of S.
 1781 Sulfur compounds first detected in plants by N. Deyeux (roots of the dock, horse-radish, and cochlearia).
 1809 Sulfur firmly established as an element by J. L. Gay Lussac and L. J. Thenard.
 1813 Sulfur detected in the bile and blood of animals by H. A. Vogel.
 1822 Xanthates (e.g. EtOCSK) discovered by W. C. Zeise who also prepared the first mercaptan (EtSH) in 1834 (see also p. 930).
 1831 Contact process for SO₃/H₂SO₄ patented by P. Philips of Bristol, UK (the original platinum catalyst was subsequently replaced by ones based on V₂O₅).
 1835 S₄N₄ first made by M. Gregory (S₂Cl₂ + NH₃); X-ray structure by M. J. Bueger, 1936.
 1839 Vulcanization of natural rubber latex by heating it with S discovered by Charles Goodyear (USA).
 1865 Prospectors boring for petroleum in Louisiana discovered a great S deposit beneath a 150-m thick layer of quicksand.
 1891-4 H. Frasch developed commercial recovery of S by superheated water process.
 1912 E. Beckmann showed that rhombohedral sulfur was S₈ by cryoscopy in molten iodine.
 1923 V. B. Goldschmid's geochemical classification includes "chalcophiles" (p. 648).
 1926 Isotopes ³³S and ³⁴S discovered by F. W. Aston who previously (1920) had only detected ³²S in his mass spectrometer.
 1935 Molecular structure of *cyclo*-S₈ established by X-ray methods (B. E. Warren and J. T. Burwell).
 1944 Sulfur first produced from sour natural gas; by 1971 this source, together with crude oil, accounted for nearly one-third of world production.
 1950 SF₄ first isolated by G. A. Silvery and G. H. Cady.
 1951 Sulfur nmr signals (from ³³S) first detected by S. S. Dharmatti and H. E. Weaver.
 1972 Sulfur and H₂SO₄ detected in the atmosphere of the planet Venus by USSR Venera 8 (subsequently confirmed in 1978 by US Venus Pioneer 2).
 1973 S₁₈ and S₂₀ synthesized and characterized by M. Schmidt, A. Kutoglu, and their coworkers.
 1975 The metallic and superconducting properties of polymeric (SN)_x discovered independently by two groups in the USA (p. 727).

in a major campaign in the West was at the Battle of Crécy (26 August 1346), but the guns lacked all power of manoeuvre and the devastating victory of Edward III was due chiefly to the long-bow men whom the French were also encountering for the first time. By 1415, however, gunpowder was decisive in Henry V's siege of Harfleur, and its increasing use in mobile field guns, naval artillery, and hand-held firearms was a dominant feature of world history for the next 500 y. Parallel with these activities, but largely independent of them, was the European development of the alchemy and chemistry of sulfur, and the growth of the emerging chemical

industry based on sulfuric acid (p. 708). Some of the key points in this story are summarized in the Panel and a fuller treatment can be found in standard references.⁽⁵⁻⁸⁾

⁵ J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 10, Chap. 57, pp. 1-692, Longmans, Green, London, 1930.

⁶ *Gmelins Handbuch der Anorganischen Chemie*, System Number 9A *Schwefel*, pp. 1-60, Verlag Chemie, Weinheim/Bergstrasse, 1953.

⁷ M. E. WEEKS, *Discovery of the Elements*, Sulfur, pp. 52-73, Journal of Chemical Education, Easton, 1956.

⁸ T. K. DERRY and T. I. WILLIAMS, *A Short History of Technology*, Oxford University Press, Oxford, 1960 (consult index).

15.1.2 Abundance and distribution

Sulfur occurs, mainly in combined form, to the extent of about 340 ppm in the crustal rocks of the earth. It is the sixteenth element in order of abundance, closely following barium (390 ppm) and strontium (384 ppm), and being about twice as abundant as the next element carbon (180 ppm). Earlier estimates placed its global abundance in the range 300–1000 ppm. Sulfur is widely distributed in nature but only rarely is it sufficiently concentrated to justify economic mining. Its ubiquity is probably related to its occurrence in nature in both inorganic and organic compounds, and to the fact that it can occur in at least five oxidation states: -2 (sulfides, H_2S and organosulfur compounds), -1 (disulfides, S_2^{2-}), 0 (elemental S), $+4$ (SO_2) and $+6$ (sulfates). The three most important commercial sources are:

- (1) elemental sulfur in the caprock salt domes in the USA and Mexico, and the sedimentary evaporite deposits in south-eastern Poland;
- (2) H_2S in natural gas and crude oil, and organosulfur compounds in tar sands, oil shales and coal (the latter two also contain pyrites inclusions);
- (3) pyrites (FeS_2) and other metal-sulfide minerals.

Volcanic sources of the free element are also widespread; they have been of great economic importance until this century but are now little used. They occur throughout the mountain ranges bordering the Pacific Ocean, and also in Iceland and the Mediterranean region, notably in Turkey, Italy and formerly also in Sicily and Spain.

Elemental sulfur in the caprock of salt domes was almost certainly produced by the anaerobic bacterial reduction of sedimentary sulfate deposits (mainly anhydrite or gypsum, p. 648). The strata are also associated with hydrocarbons; these are consumed as a source of energy by the anaerobic bacteria, which use sulfur instead of O_2 as a hydrogen acceptor to produce CaCO_3 , H_2O and H_2S . The H_2S

may then be oxidized to colloidal sulfur, or may form calcium hydrosulfide and polysulfide, which reacts with CO_2 generated by the bacteria to precipitate crystalline sulfur and secondary calcite. Alternatively, H_2S may escape from the system and the limestone caprock will then be free of sulfur. Indeed, of over 400 salt-dome structures known to exist in the coastal and offshore area of the Gulf of Mexico, only about 12 contain commercial deposits of sulfur (5 in Louisiana, 5 in Texas and 2 in Mexico). The mining operations are described in the Section 15.1.3.

The great evaporite basin deposits of elemental sulfur in Poland were discovered only in 1953 but have since had a dramatic impact on the economy of that country which, by 1985, was one of the world's leading producers (p. 649). The sulfur occurs in association with secondary limestone, gypsum and anhydrite, and is believed to be derived from hydrocarbon reduction of sulfates assisted by bacterial action. The H_2S so formed is consumed by other bacteria to produce sulfur as waste — this accumulates in the bodies of the bacteria until death, when the sulfur remains.

The next great natural occurrence of sulfur is as H_2S in sour natural gas and as organosulfur compounds in crude oil. Again, distribution is widespread. Although commercial production of elemental sulfur from such sources was first effected only in 1944 (in the USA) it now represents a major source of the element in the USA, Canada and France, and this growth has been one of the most significant trends in world sulfur production during the past few decades. Sulfur, of course, also occurs in many plant and animal proteins, and three of the principal amino-acid residues contain sulfur: cysteine, $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$; cystine $\{-\text{SCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}\}_2$; and methionine, $\text{MeSCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$.

Oil shales represent a further source of sulfur though here (unlike the tar sands which yield crude oil and H_2S) the sulfur is predominantly in the form of pyrites. US oil shales contain about 0.7% S of which about 80% is pyritic; other

major reserves are in Brazil, the former USSR, China and Africa, though these do not at present seem to be used as an industrial source of sulfur. Coal also contains about 1–2% S and is thus as huge a potential source of the element as it is an actual present source of air pollution (p. 698). From over 3×10^9 tonnes of coal mined annually, only some 500 000 tonnes of sulfur are recovered (as H_2SO_4) from a potential 50 million tonnes.

The third great source of sulfur and its compounds is from the mineral sulfides. V. M. Goldschmid's geochemical classification of the elements (1923), which has formed the basis of all subsequent developments in the field, proposed four main groups of elements: chalcophile, siderophile, lithophile and atmophile.⁽⁹⁾ Of these the chalcophiles (Greek *χαλκος*, *chalcos*, copper; *φιλος*, *philos*, loving) are associated with copper, specifically as sulfides. Elements which occur mainly as sulfide minerals are predominantly from Groups 11–16 of the periodic table (together with iron, molybdenum and, to a lesser extent, some of the platinum metals as shown in Fig. 15.1. Some

examples of the more important sulfide minerals are listed in Table 15.1, and a further discussion of the structural chemistry and reactivity of metal sulfides is on p. 676. Pyrites (fool's gold, FeS_2) is one of the most abundant of all sulfur minerals and is a major source of the element (see above). It often occurs in massive lenses but may also appear in veins or in disseminated zones. The largest commercial deposits extend from Seville (Spain) westward into Portugal and, at the Rio Tinto mines in Huelva Province, one of the lenses is 1.5 km long and 240 m wide with a sulfur content of 48% (pure FeS_2 has 53.4% S). Other major deposits are in the former USSR, Japan, Italy, Cyprus and Scandinavia. The most important non-ferrous metal sulfides are those of Cu, Ni, Zn, Pb and As.

Finally, sulfur occurs in many localities as the sulfates of electropositive elements (see Chapters 4 and 5) and to a lesser extent as sulfates of Al, Fe, Cu and Pb, etc. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) are particularly notable but are little used as a source of sulfur because of high capital and operating costs. Similarly, by far the largest untapped source of sulfur is in the oceans as the dissolved sulfates of Mg, Ca and K. It has been estimated that there are some 1.5×10^9 cubic km of water in the oceans of the world and that 1 cubic km of sea-water contains approximately 1 million tonnes of sulfur combined as sulfate.

⁹ R. W. FAIRBRIDGE, *Encyclopedia of Geochemistry and Environmental Sciences*, Van Nostrand, New York, 1972. See sections on Geochemical Classification of the Elements; Sulfates; Sulfate Reduction—Microbial; Sulfides; Sulfosalts; Sulfur; Sulfur Cycle; Sulfur Isotope Fractionation in Biological Processes, etc., pp. 1123–58.

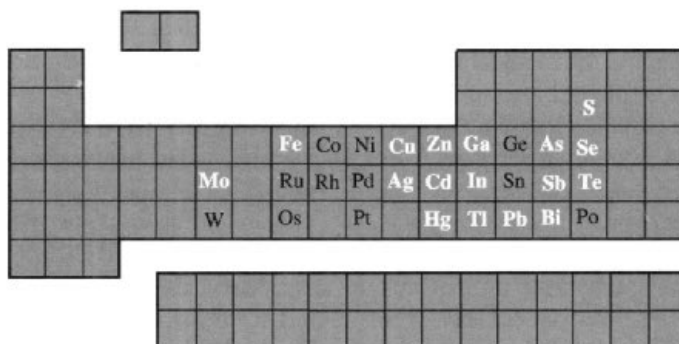


Figure 15.1 Position of the chalcophilic elements in the periodic table: these elements (particularly those in white) tend to occur in nature as sulfide minerals; the tendency is much less pronounced for the elements in normal black type.

Table 15.1 Some sulfide minerals (those in bold are the more prevalent or important)

Name	Idealized formula	Name	Idealized formula
Molybdenite	MoS₂	Galena (Pb glance)	PbS
Tungstenite	WS ₂	Realgar	As₄S₄
Alabandite	MnS	Orpiment	As₂S₃
Pyrite (fool's gold)	FeS₂	Dimorphite	As ₄ S ₃
Marcasite	FeS₂	Stibnite	Sb₂S₃
Pyrrhotite	Fe_{1-x}S	Bismuthinite	Bi ₂ S ₃
Laurite	RuS ₂	Pentlandite	(Fe,Ni) ₉ S ₈
Linnaeite	Co ₃ S ₄	Chalcopyrite	CuFeS₂
Millerite	NiS	Bornite	Cu₃FeS₄
Cooperite	PtS	Arsenopyrite	FeAsS
Chalcocite (Cu glance)	Cu₂S	Cobaltite	CoAsS
Argentite (Ag glance)	Ag ₂ S	Enargite	Cu ₃ AsS ₄
Sphalerite (Zn blende)	ZnS	Bournoite	CuPbSbS ₃
Wurtzite	ZnS	Proustite	Ag ₃ AsS ₃
Greenockite	CdS	Pyrrargyrite	Ag ₃ SbS ₃
Cinnabar (vermillion)	HgS	Tetrahedrite^(a)	Cu₁₂As₄S₁₃^(a)

^(a)There is a second series in which As is replaced by Sb; in both series Cu is often substituted in part by Fe, Ag, Zn, Hg or Pb.

The global geochemical sulfur cycle has been extensively studied in recent years for both commercial and environmental reasons.^(10–17)

15.1.3 Production and uses of elemental sulfur

Sulfur is produced commercially from one or more sources in over seventy countries of

¹⁰ M. V. IVANOV and J. R. FRENET (eds.), *The Global Biogeochemical Sulfur Cycle*, SCOPE Report 19, Wiley, Chichester, 1983, 495 pp.

¹¹ A. MÜLLER and B. KREBS (eds.), *Sulfur: Its Significance for Chemistry, for the Geo-, Bio-, and Cosmo-sphere and Technology*, Elsevier, Amsterdam, 1984, 512 pp.

¹² P. BRIMBLECOMBE and A. Y. LEIN (eds.), *Evolution of the Global Biogeochemical Sulfur Cycle*, SCOPE Report 39, Wiley, Chichester, 1989, 276 pp.

¹³ E. S. SALZMAN and W. J. COOPER (eds.), *Biogenic Sulfur in the Environment*, ACS Symposium Series No. 393, Amer. Chem. Soc., Washington, DC, 1989, 584 pp.

¹⁴ W. L. ORR and C. M. WHITE (eds.), *Geochemistry of Sulfur in Fossil Fuels*, ACS Symposium Series, No. 429, Amer. Chem. Soc., Washington, DC, 1990, 720 pp.

¹⁵ H. R. KROUSE and V. A. GRINENKO (eds.), *Stable Isotopes; Natural and Anthropogenic Sulfur in the Environment*, SCOPE Report 43, Wiley, Chichester, 1991, 466 pp.

¹⁶ R. W. HOWARTH, J. W. B. STEWART and M. V. IVANOV (eds.), *Sulfur Cycling on the Continents*, SCOPE Report 48, Wiley, Chichester, 1992, 372 pp.

Table 15.2 Main producers of sulfur in 1985 (in megatonnes)⁽¹⁸⁾

World	USA	USSR	Canada	Poland	China	Japan	Others
54.0	11.4	9.7	6.7	5.1	2.9	2.5	15.7

the world, and production of all forms in 1985 amounted to 54.0 million tonnes. The main producers are shown in Table 15.2. Until the beginning of this century, sulfur was obtained mainly by mining volcanic deposits of the element, but this now accounts for less than 5% of the total. During the first half of this century the prime method of production was the process developed by H. Frasch in 1891–4. This involves forcing superheated water into submerged sulfur-bearing strata and then forcing the molten element to the surface by compressed air (see Panel). This is the method used to obtain sulfur from the caprock of salt domes in the

¹⁷ D. A. DUNNETTE and R. J. O'BRIEN (eds.), *The Science of Global Change: The Impact of Human Activities on the Environment*, ACS Symposium Series No. 483, Amer. Chem. Soc., Washington, DC, 1992, 498 pp.

¹⁸ W. BÜCHNER, R. SCHLIEBS, G. WINTER and K. H. BÜCHEL, (transl. by D. R. TERRELL), *Industrial Inorganic Chemistry*, VCH, Weinheim, 1989, pp. 105–8.

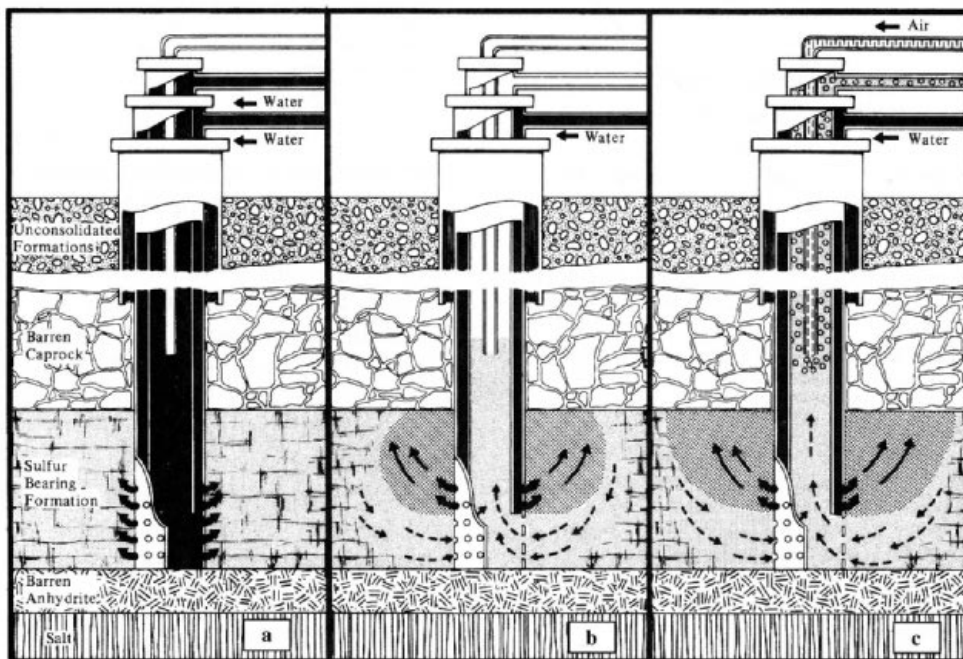
The Frasch Process for Mining Elemental Sulfur¹⁹

The ingenious process of melting subterranean sulfur with superheated water and forcing it to the surface with compressed air was devised and perfected by Herman Frasch in the period 1891–4. Originally designed to overcome the problems of recovering sulfur from the caprock of salt domes far below the swamps and quicksands of Louisiana, the method is now also extensively used elsewhere to extract native sulfur.

The caprock typically occurs some 150–750 m beneath the surface and the sulfur-bearing zone is typically about 30 m thick and contains 20–40% S. Using oil-well drilling techniques a cased 200 mm (8-inch) pipe is sunk through the caprock to the bottom of the S-bearing layer. Its lower end is perforated with small holes. Inside this pipe a 100 mm (4-inch) pipe is lowered to within a short distance of the bottom and, finally, a concentric 25-mm (1-inch) compressed-air pipe is lowered to a point rather more than half-way down to the bottom of the well as shown in Fig. a. Superheated water at 165°C is forced down the two outer pipes and melts the surrounding sulfur (mp 119°C). As liquid sulfur is about twice as dense as water under these conditions, it flows to the bottom of the well; the pumping of water down the 100-mm pipe is discontinued, but the static pressure of the hot water being pumped down the outer 200-mm pipe forces the liquid sulfur some 100 m up the 100-mm pipe as shown in Fig. b. Compressed air is then forced down the central 25-mm pipe to aerate the molten sulfur and carry it to the surface where it emerges from the 100-mm annulus Fig. (c). One well can extract sulfur (~35 000 tonnes) from an area of about 2000 m² (0.5 acre) and new wells must continually be sunk. Bleed-water wells must also be sunk to remove the excess of water pumped into the strata.

A Frasch mine can produce as much as 2.5 million tonnes of sulfur per annum. Such massive operations clearly require huge quantities of mining water (up to 5 million gallons daily) and abundant power supplies for the drilling, pumping and superheating operations.

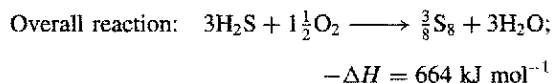
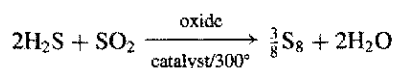
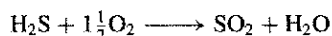
The sulfur can be piped long distances in liquid form or transported molten in ships, barges or rail cars. Alternatively it can be prilled or handled as nuggets or chunks. Despite the vast bulk of liquid sulfur mined by the Frasch process it is obtained in very pure form. There is virtually no selenium, tellurium or arsenic impurity, and the product is usually 99.5–99.9% pure.



¹⁹W. HAYNES, *Brimstone: The Stone that Burns*, Van Nostrand, Princeton, 1959, 308 pp. (The story of the Frasch sulfur industry.)

Gulf Coast region of the USA and Mexico, and from the evaporite basin deposits in west Texas, Poland, the former USSR and Iran.

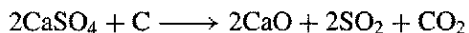
Recovery from sour natural gas and from crude oil was first developed in the USA in 1944, and by 1970 these sources exceeded the total volume of Frasch-mined sulfur for the first time. Canada (Alberta) and France are the principal producers from sour natural gas, which contains 15–20% H₂S. The USA and Japan are the largest producers from petroleum refineries. The phenomenal growth of these sources is clear from the following figures (in 10⁶ tonnes): <0.5 (1950); 2.5 (1960); 15 (1972); >25 (1985). Recovery from sour natural gas involves first separating out the H₂S by absorption in mono-ethanolamine and then converting it to sulfur by a process first developed by C. F. Claus in Germany about 1880. In this process one-third of the H₂S is burned to produce SO₂, water vapour, and sulfur vapour; the SO₂ then reacts with the remaining H₂S in the presence of oxide catalysts such as Fe₂O₃ or Al₂O₃ to produce more H₂O and S vapour:



Multiple reactors achieve 95–96% conversion and recovery, and stringent air pollution legislation has now pushed this to 99%. A similar sequence of reactions is used for sulfur production from crude oil except that the organosulfur compounds must first be removed from the refinery feed and converted to H₂S by a hydrogenation process before the sulfur can be recovered.

The third major source of sulfur is pyrite and related sulfide minerals. The ore is roasted to secure SO₂ gas which is then usually used directly for the manufacture of H₂SO₄ (p. 708). Again air pollution by SO₂ gas emissions has been the subject of increasing legislation and control during the past three decades (p. 698).

The proportion of sulfur and S-containing compounds recovered by these various methods has been changing rapidly and frequently depends on the nature of local sources available. The comparative figures for 1985 are: sour natural gas 38%, Frasch S 28%, pyrites 18%, miscellaneous 16% (includes metallurgy, crude oil, coal, gypsum, tar sands and flue gases). Estimated reserves on the basis of present technology and prices are summarized in Table 15.3; these can increase more than tenfold if coal, gypsum, anhydrite and sea-water are included. At present these latter sources are economic only under special conditions though, as we have already seen (p. 648), vast quantities of SO₂ are lost from industrial coal each year. Recovery of useful sulfur compounds from anhydrite (and gypsum) can be achieved by two main routes. The Müller–Kühne process used in the UK and Austria involves the roasting of anhydrite with clay, sand and coke in a rotary kiln at 1200–1400°:



The emergent SO₂ is then fed into a contact process for H₂SO₄ (p. 708). Alternatively, ammonia and CO₂ can be passed into a gypsum slurry to give ammonium sulfate for use in fertilizers:



This double decomposition route was developed in Germany and has been used in the UK since 1971.

The pattern of uses of sulfur and its compounds in the chemical industry is illustrated in the

Table 15.3 Estimated world reserves of sulfur

Source	Natural gas	Petroleum	Native ore	Pyrite	Sulfide ore	Dome	Total
S/10 ⁶ tonne	690	450	560	380	270	150	2500

flow chart below. Most sulfur is converted via SO_2/SO_3 into sulfuric acid which accounts, for example, for some 88% of the contained sulfur used in the USA. The proportion of sulfur used in making the extensive number of end products is shown in Fig. 15.2. Indeed, the uses of sulfur and its principal compounds are so widely spread throughout industry that a nation's consumption of sulfur is often used as a reliable measure of its economic development. Thus, the USA, the former USSR, Japan and Germany lead the world in industrial production and rank similarly in the consumption of sulfur. Further details of industrial uses will be found in subsequent sections dealing with specific compounds of sulfur, and various review books are available.⁽²⁰⁻²²⁾

²⁰ J. R. WEST (ed.), *New Uses of Sulfur*, Advances in Chemistry Series No. 140, Am. Chem. Soc., Washington, DC, 1975, 230 pp.

²¹ D. J. BOURNE (ed.), *New Uses of Sulfur — II*, Advances in Chemistry Series No. 165, Am. Chem. Soc., Washington, DC 1978, 282 pp.

²² U. H. F. SANDER, H. FISCHER, U. ROTHE and R. KOLA, (Engl. edn. prepared by A. I. MORE), *Sulfur, Sulfur Dioxide, Sulfuric Acid: Industrial Chemistry and Technology*, British Sulfur Corporation, London, 1984, 428 pp.

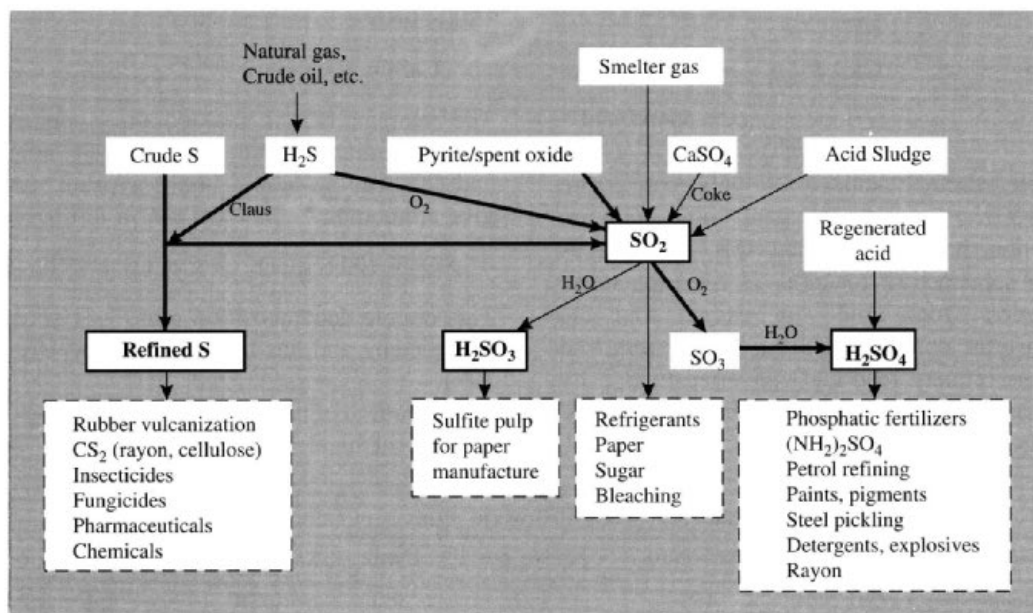
15.1.4 Allotropes of sulfur⁽²³⁻²⁵⁾

The allotropy of sulfur is far more extensive and complex than for any other element (except perhaps carbon, after the synthesis of the innumerable fullerene clusters, p. 279). This arises partly because of the great variety of molecular forms that can be achieved by —S—S— catenation and partly because of the numerous ways in which the molecules so formed can be arranged within the crystal. In fact, S—S bonds are very variable and flexible: interatomic distances cover an enormous range, 180–260 pm (depending to some extent on the amount of multiple bonding), whilst bond angles S—S—S vary from 90° to 180° and dihedral angles S—S—S—S from 0° to 180° (Fig. 15.3). Estimated S—S bond energies may be as high as 430 kJ mol^{-1} and the unrestrained —S—S— single-bond energy of 265 kJ mol^{-1} is exceeded amongst homonuclear single bonds only by those of H_2 (435 kJ mol^{-1}) and C—C

²³ J. DONOHUE, *The Structures of the Elements*, Sulfur, pp. 324–69, Wiley, New York, 1974.

²⁴ B. MEYER, *Chem. Revs.* **76**, 367–88, (1976).

²⁵ M. SCHMIDT, Chap. 1, pp. 1–12, in ref. 21.



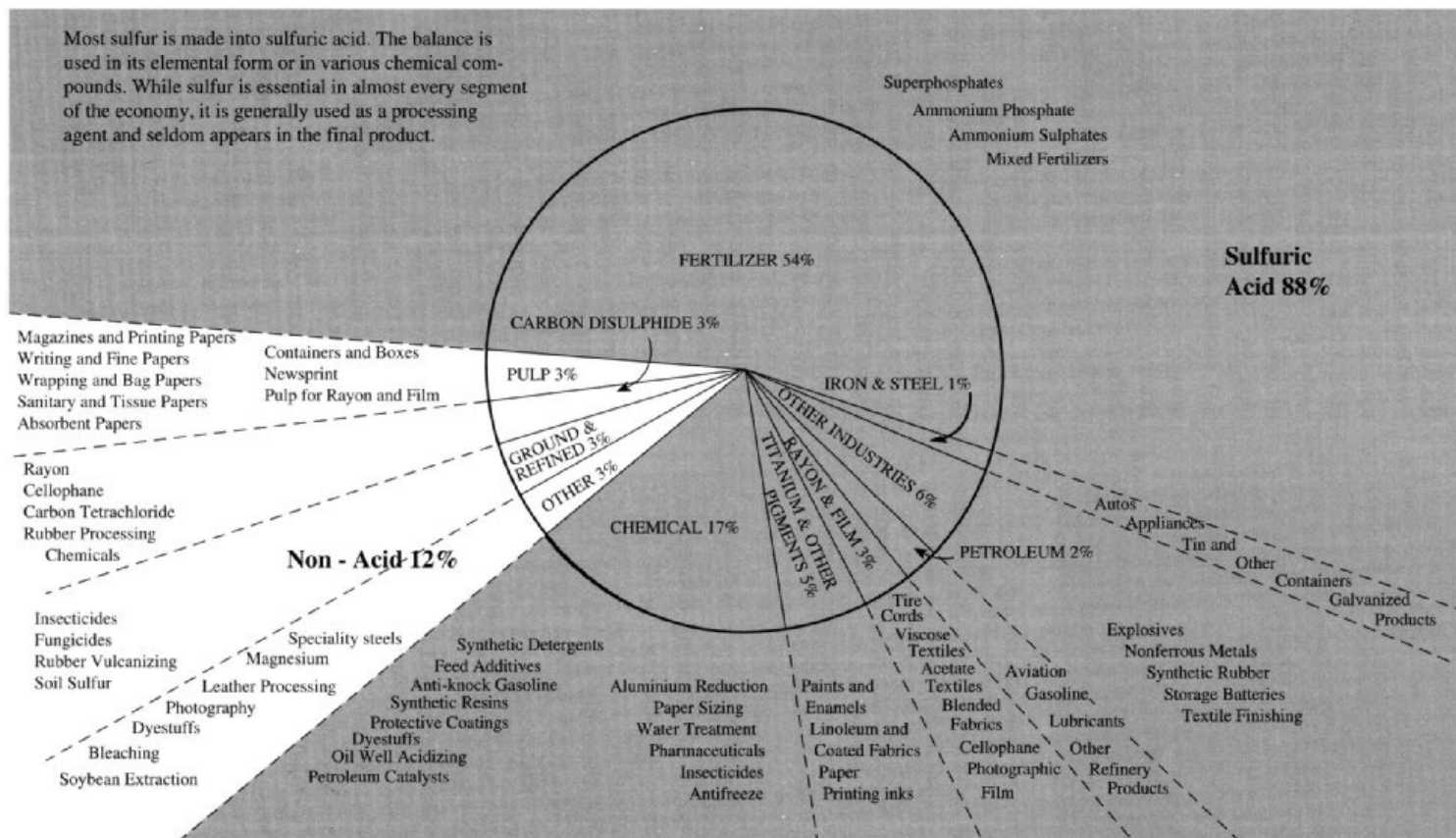


Figure 15.2 Sulfur's uses as acid and as non-acid.

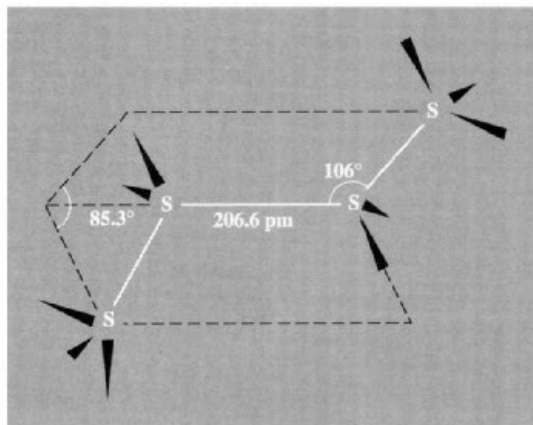


Figure 15.3 Portion of an unrestrained- S_n -chain showing typical values for the S-S-S bond angle (106°) and S-S-S-S dihedral angle (85.3°). Possible alternative orientations of the bonds from the 2 inner S atoms, and possible directions for extensions of the chain from the 2 outer S atoms are indicated by the black lines. (See also p. 656.)

(330 kJ mol^{-1}). Again, the amazing temperature dependence of the properties of liquid sulfur have attracted attention for over a century since the rapid and reversible gelation of liquid sulfur was first observed in the temperature range $160\text{--}195^\circ\text{C}$. Major advances have been achieved during the past 25 y in our knowledge of the molecular structure of many of the crystalline allotropes of sulfur and of the complex molecular equilibria occurring in the liquid and gaseous states. Sulfur is also unique in the extent to which new allotropes can now be purposefully synthesized using kinetically controlled reactions that rely on the great strength of the S-S bond once it is formed, and over

a dozen new elemental sulfur rings, *cyclo-S_n*, have been synthesized. Fortunately, several excellent reviews are available,^(23–25) and these can be consulted for fuller details and further references. It will be convenient to start with some of the classic allotropes (now known to contain *cyclo-S₈* molecules), and then to consider in turn other cyclic oligomers (*cyclo-S_n*) various chain polymers (*catena-S_n*), certain unstable small molecules S_n ($n = 2\text{--}5$) and, finally, the properties of liquid and gaseous sulfur.

The commonest (and most stable) allotrope of sulfur is the yellow, orthorhombic α -form to which all other modifications eventually revert at room temperature. Commercial roll sulfur, flowers of sulfur (sublimed) and milk of sulfur (precipitated) are all of this form. It was shown to contain S_8 molecules by cryoscopy in iodine (E. Beckmann, 1912) and was amongst the first substances to be examined by X-ray crystallography (W. H. Bragg, 1914), but the now familiar crown structure of *cyclo-S₈* was not finally established until 1935.⁽²³⁾ Various representations of the idealized D_{4d} molecular structure are given in Fig. 15.4. The packing of the molecules within the crystal has been likened to a crankshaft arrangement extending in two different directions and leads to a structure which is very complex.⁽²³⁾ Orthorhombic α - S_8 has a density of 2.069 g cm^{-3} , is a good electrical insulator when pure, and is an excellent thermal insulator, the extremely low thermal conductivity being similar to those of the very best insulators such as mica (p. 356) and wood. Some solubilities in common solvents are in Table 15.4.

At about 95.3° α - S_8 becomes unstable with respect to β -monoclinic sulfur in which the packing of the S_8 molecules is altered and their

Table 15.4 Solubilities of α -orthorhombic sulfur (at 25°C unless otherwise stated)

Solvent	CS_2	S_2Cl_2	Me_2CO	C_6H_6	CCl_4	Et_2O	C_6H_{14}	EtOH
g S per 100 g solvent ($T^\circ\text{C}$)	35.5 ^(a)	17 ^(b) (21°)	2.5	2.1	0.86 ^(c)	0.283 (23°)	0.25 (20°)	0.065

^(a)55.6 at 60° . ^(b)97 at 110° . ^(c)1.94 at 60° .

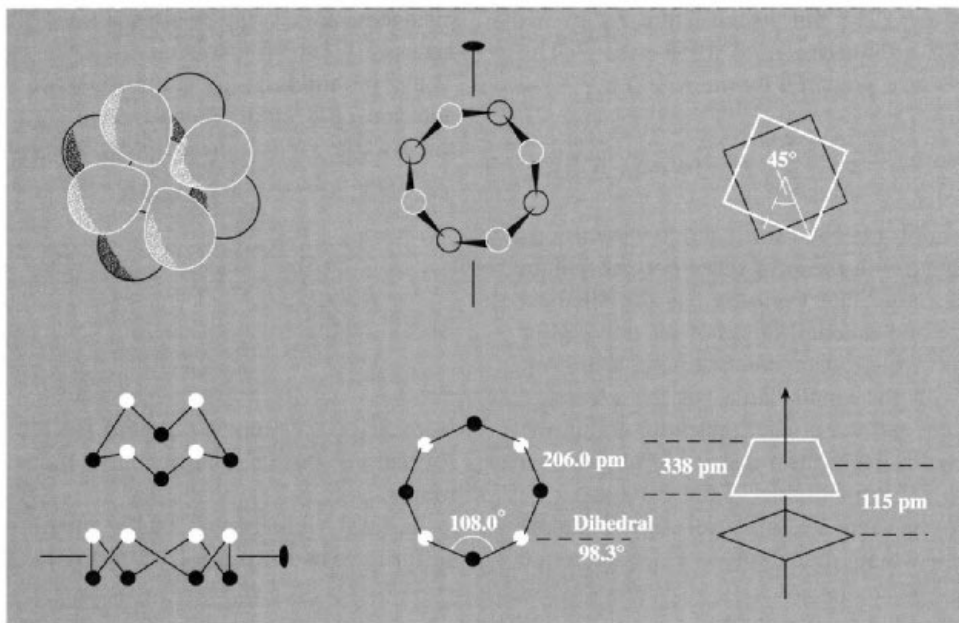


Figure 15.4 Various representations of the molecule cyclo-S_8 found in α -orthorhombic, β -monoclinic, and γ -monoclinic sulfur.

orientation becomes partly disordered.⁽²⁶⁾ This results in a lower density ($1.94\text{--}2.01\text{ g cm}^{-3}$), but the dimensions of the S_8 rings in the two allotropes are very similar. The transition is somewhat sluggish even above 100° , and this enables a mp of metastable single crystals of $\alpha\text{-S}_8$ to be obtained: a value of 112.8° is often quoted but microcrystals may melt as high as 115.1° . Monoclinic $\beta\text{-S}_8$ has a “mp” which is usually quoted as 119.6° but this can rise to 120.4° in microcrystals or may be as low as 114.6° . The uncertainty arises because the S_8 ring is unstable above $\sim 119^\circ$ and begins to form other species which progressively depress the mp. The situation is reminiscent of the equilibria accompanying the melting of anhydrous phosphoric acid (p. 518). Monoclinic $\beta\text{-S}_8$ is best prepared by crystallizing liquid sulfur at about 100° and then cooling it rapidly to room temperature to retard the formation of orthorhombic $\alpha\text{-S}_8$; under these conditions

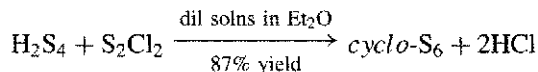
$\beta\text{-S}_8$ can be kept for several weeks at room temperature before reverting to the more stable α -form.

A third crystalline modification, γ -monoclinic sulfur, was first obtained by W. Muthmann in 1890. It is also called nacreous or mother-of-pearl sulfur and can be made by slowly cooling a sulfur melt that has been heated above 150° , or by chilling hot concentrated solutions of sulfur in EtOH, CS_2 or hydrocarbons. However, it is best prepared as pale-yellow needles by the mechanistically obscure reaction of pyridine with copper(I) ethyl xanthate, CuSSCOEt . Like α - and β -sulfur, γ -monoclinic sulfur comprises cyclo-S_8 molecules but the packing is more efficient and leads to a higher density (2.19 g cm^{-3}). It reverts slowly to $\alpha\text{-S}_8$ at room temperature but rapid heating leads to a mp of 106.8° .

We now consider other homocyclic polymorphs of sulfur containing 6–20 S atoms per ring. A rhombohedral form, ϵ -sulfur, was first prepared by M. R. Engel in 1891 by the reaction of concentrated HCl on a saturated solution of thiosulfate HS_2O_3^- at 0° . It was shown to be

²⁶ L. K. TEMPLETON, D. H. TEMPLETON and A. ZALKIN, *Inorg. Chem.* **15**, 1999–2001 (1976).

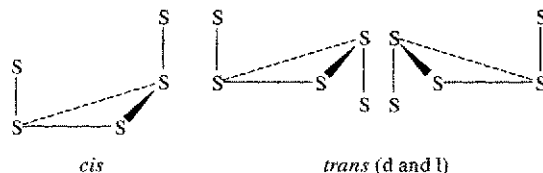
hexameric in 1914 but its structure as *cyclo-S*₆ was not established until 1958–61.⁽²³⁾ The allotrope is best prepared by the reaction



The ring adopts the chair form and its dimensions are compared with those of other polymorphs in Table 15.5. Note that *cyclo-S*₆ has the smallest bond angle and dihedral angle of all poly-sulfur species for which data are available and this, together with the small "hole" at the centre of the molecule and the efficient packing within the crystal, lead to the highest density of any known polymorph of sulfur (Table 15.6).

In *cyclo-S*₆ and *cyclo-S*₈ all the S atoms are equivalent with essentially equal interatomic

distances, angles and conformations. This is not necessarily so for all homocyclic molecules. Thus, in building up cumulated $-\text{S}_n-$ bonds, addition of S atoms to an *S*₃ unit can occur in three ways: *cis* (c), *d-trans* (dt), and *l-trans* (lt):



Both *S*₆ (chair) and *S*₈ (crown) are all *-cis* conformations, but larger rings have more complex motifs.

At least eight further cyclic modifications of sulfur have been synthesized during the past 25 y

Table 15.5 Dimensions of some sulfur molecules. Average values are given except for *S*₇ where deviations from the mean are more substantial (see text)

Molecule	Interatomic distance/pm	Bond angle	Dihedral angle
<i>S</i> ₂ (matrix at 20 K)	188.9	—	—
<i>cyclo-S</i> ₆	205.7	102.2°	74.5°
<i>cyclo-S</i> ₇	199.3–218.1	101.5°–107.5°	0.3°–107.6°
<i>cyclo-S</i> ₈ (α)	203.7	107.8°	98.3°
<i>cyclo-S</i> ₈ (β)	204.5	107.9°	—
<i>cyclo-S</i> ₁₀	205.6	106.2°	–77° and +123°
<i>cyclo-S</i> ₁₂	205.3	106.5°	86.1°
<i>cyclo-S</i> ₁₈	205.9	106.3°	84.4°
<i>cyclo-S</i> ₂₀	204.7	106.5°	83.0°
<i>catena-S</i> _x	206.6	106.0°	85.3°

Table 15.6 Some properties of sulfur allotropes

Allotrope	Colour	Density/g cm ⁻³	Mp or decomp. point/°C
<i>S</i> ₂ (g) or matrix at 20 K	Blue-violet	—	Very stable at high temp
<i>S</i> ₃ (g)	Cherry red	—	Stable at high temp
<i>S</i> ₆	Orange red	2.209	<i>d</i> > 50°
<i>S</i> ₇	Yellow	2.182 (–110°)	<i>d</i> 39°
α- <i>S</i> ₈	Yellow	2.069	112.8° (see text)
β- <i>S</i> ₈	Yellow	1.94–2.01	119.6° (see text)
γ- <i>S</i> ₈	Light yellow	2.19	106.8° (see text)
<i>S</i> ₉	Intense yellow	—	Stable below rt
<i>S</i> ₁₀	Pale yellow green	2.103 (–110°C)	<i>d</i> > 0°
<i>S</i> ₁₁	—	—	—
<i>S</i> ₁₂	Pale yellow	2.036	148°
<i>S</i> ₁₈	Lemon yellow	2.090	m 128°(d)
<i>S</i> ₂₀	Pale yellow	2.016	m 124°(d)
<i>S</i> _∞	Yellow	2.01	104°(d)

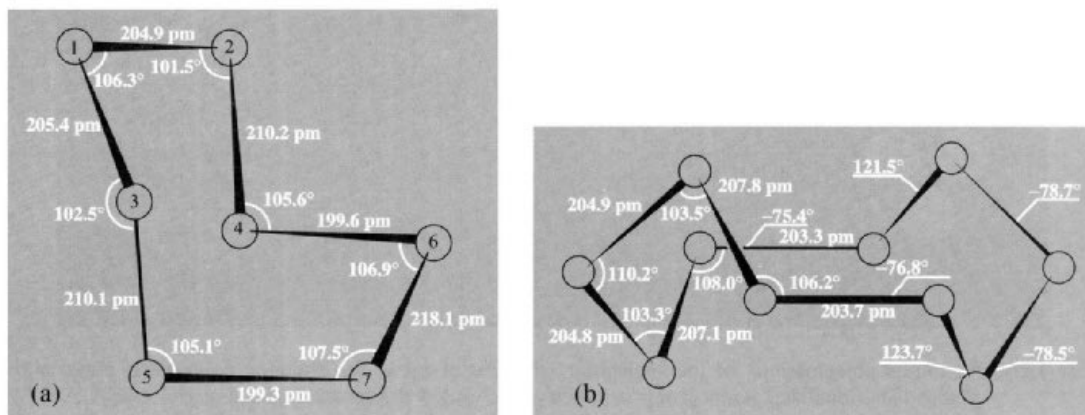
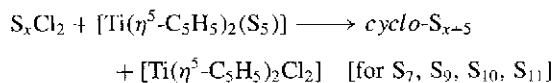
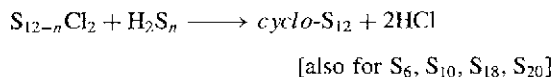
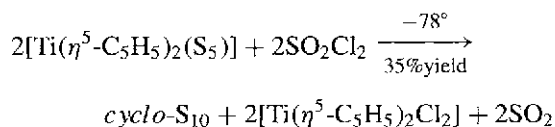


Figure 15.5 (a) Molecular structure of *cyclo-S*₇ showing the large distance S(6)–(7) and alternating interatomic distances away from this bond; the point group symmetry is approximately *C*_s. (b) Molecular structure of *cyclo-S*₁₀ showing interatomic distances, bond angles and dihedral angles; the distance between the 2 “horizontal” bonds is 541 pm.

by the elegant work of M. Schmidt and his group. The method is to couple two compounds which have the desired combined number of S atoms and appropriate terminal groups, e.g.:



A variant is the ligand displacement and coupling reaction:



The preparation and structures of the reactants are on p. 683 (*H*₂*S*_{*n*}), p. 689 (*S*_{*x*}*Cl*₂), and p. 670 $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{S}_5)]$.

*S*₇ is known in four crystalline modifications; one of these, obtained by crystallization from *CS*₂ at -78° , rapidly disintegrates to a powder at room temperature, but an X-ray study at -110° showed it to consist of *cyclo-S*₇ molecules with

the dimensions shown in Fig. 15.5(a).⁽²⁷⁾ Notable features are the very large interatomic distance S(6)–S(7) (218.1 pm) which probably arises from the almost zero dihedral angle between the virtually coplanar atoms S(4) S(6) S(7) S(5), thus leading to maximum repulsion between nonbonding lone-pairs of electrons on adjacent S atoms. As a result of this weakening of S(6)–S(7), the adjacent bonds are strengthened (199.5 pm) and there are further alternations of bond lengths (210.2 and 205.2 pm) throughout the molecule.

The structure of *cyclo-S*₁₀ is shown in Fig. 15.5(b).⁽²⁸⁾ The molecule belongs to the very rare point group symmetry *D*₂ (three orthogonal twofold axes of rotation as the only symmetry elements). The mean interatomic distance and bond angle are close to those in *cyclo-S*₁₂ (Table 15.5) and the molecule can be regarded as composed of two identical *S*₅ units obtained from the *S*₁₂ molecule (Fig. 15.6).

*Cyclo-S*₁₂ occupies an important place amongst the cyclic oligomers of sulfur. In a

²⁷ R. STEUDEL, R. REINHARDT and F. SCHUSTER, *Angew. Chem. Int. Edn. Engl.* **16**, 715 (1977).

²⁸ R. REINHARDT, R. STEUDEL and F. SCHUSTER, *Angew. Chem. Int. Edn. Engl.* **17**, 57–8 (1978).

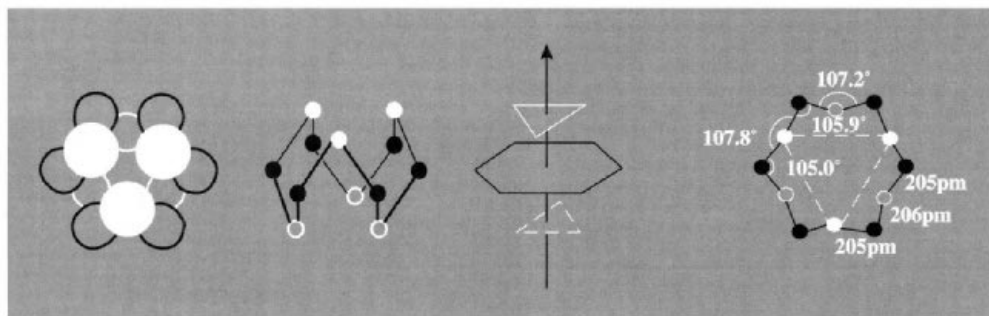
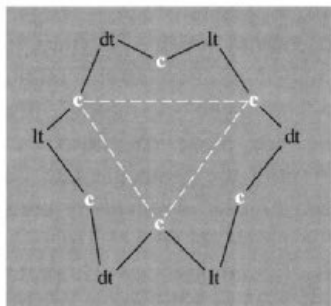


Figure 15.6 Various representations of the molecular structure of *cyclo-S*₁₂ showing S atoms in three parallel planes. The idealized point group symmetry is D_{3d} and the mean dihedral angle is $86.1 \pm 5.5^\circ$. In the crystal the symmetry is slightly distorted to C_{2h} and the central group of 6 S atoms deviate from coplanarity by ± 14 pm.

classic paper by L. Pauling⁽²⁹⁾ the molecule had been predicted to be unstable, though subsequent synthesis showed it to be second only to *cyclo-S*₈ in stability. In fact, the basic principles underlying Pauling's prediction remain valid but he erroneously applied them to two sets of S atoms in two parallel planes whereas the configuration adopted has S atoms in three parallel planes. Several representations of the structure are in Fig. 15.6. Using the nomenclature of p. 656 it can be seen that, unlike *S*₆ and *S*₈, the conformation of all S atoms is not *cis*: the S atoms in upper and lower planes do indeed have this conformation but the 6 atoms in the central plane are alternately *d-trans* and *l-trans* leading to the sequence:



*Cyclo-S*₁₂ was first prepared in 1966 in 3% yield by reacting *H*₂*S*₄ with *S*₂*Cl*₂ but a better

route is the reaction between dilute solutions of *H*₂*S*₈ and *S*₄*Cl*₂ in *Et*₂*O* (18% yield). It can also be extracted from liquid sulfur. The stability of the allotrope can be gauged from its mp (148°), which is higher than that of any other allotrope and nearly 30° above the temperature at which the *S*₈ ring begins to decompose.

Two allotropes of *cyclo-S*₁₈ are known. The structure of the first is shown in Fig. 15.7(a): if we take 3 successive atoms out of the *S*₁₂ ring then the 9-atom fragment combines with a second one to generate the structure. Alternatively, the structure can be viewed as two parallel 9-atom helices (see below), one right-handed and one left-handed, mutually joined at each end by the *cis* atoms *S*(5) and *S*(14). Interatomic distances vary between 204–211 pm (mean 206 pm), bond angles between 103.7–108.3° (mean 106.3°), and dihedral angles between 79.1–90.0° (mean 84.5°). This form of *cyclo-S*₁₈ is formed by the reaction between *H*₂*S*₈ and *S*₁₀*Cl*₂ and forms lemon-coloured crystals, mp 128°, which can be stored in the dark for several days without apparent change. The second form of *cyclo-S*₁₈ has the molecular structure shown in Fig. 15.7(b): this has twice the 8-atom repeat motif *cis-cis-trans-cis-trans-cis-trans-cis* (one with *d-trans* and the other with *l-trans*) joined at each end by further bridging single *trans*-sulfur atoms which constitute the 2 extreme atoms of the elongated ring.

²⁹ L. PAULING, *Proc. Natl. Acad. Sci. USA* **35**, 495–9 (1949).

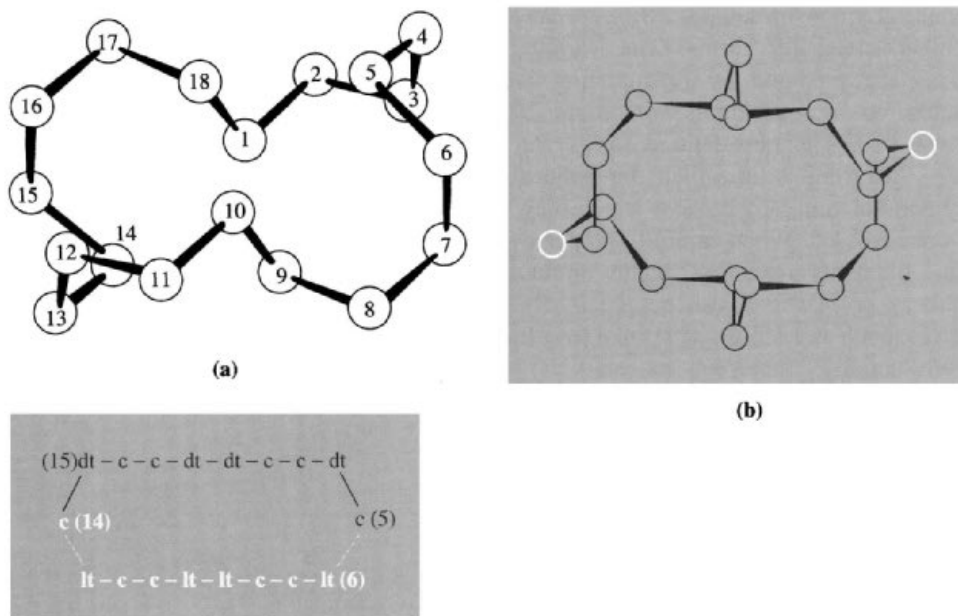


Figure 15.7 (a) The molecular structure of one form of *cyclo-S*₁₈, together with the conformational sequence of the two helical subunits.⁽³⁰⁾ (b) The molecular structure of the second form of *cyclo-S*₁₈ showing the *trans*-configuration of the S atoms at the extreme ends of the elongated rings.⁽²⁵⁾

Pale yellow crystals of *cyclo-S*₂₀, mp 124° (decomp), d 2.016 g cm⁻³, have been made by the reaction of H₂S₁₀ and S₁₀Cl₂. The molecular structure is shown in Fig. 15.8⁽³¹⁾ The interatomic S-S distances vary between 202.3–210.4 pm (mean 204.2 pm), the angles S-S-S between 104.6–107.7° (mean 106.4°), and the dihedral angles between 66.3–89.9° (mean 84.7°). In this case the conformation motif is -c-It-It-It-c- repeated 4 times and the abnormally long bond required to achieve ring closure is notable; it is also this section of the molecule which has the smallest dihedral angles thereby incurring increased repulsion between adjacent nonbonding lone-pairs of electrons. Consistent with this the adjacent bonds are the shortest in the molecule.

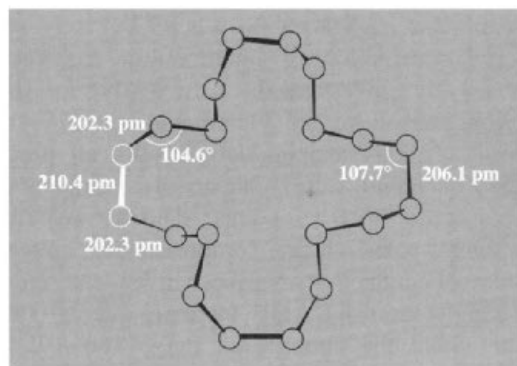


Figure 15.8 Molecular structure of *cyclo-S*₂₀ viewed along the [001] direction.⁽³¹⁾ The 2 adjacent S atoms with the longest interatomic distance are shown in white.

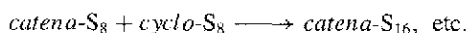
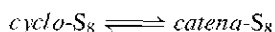
Solid polycatenasulfur comes in many forms: it is present in rubbery S, plastic (χ)S, lamina S, fibrous (ψ, ϕ), polymeric (μ) and insoluble (ω)S, supersublimation S, white S and the commercial product Crystex. All these are metastable mixtures of allotropes containing more or less

³⁰ T. DEBAERDEMAEKER and A. KUTOGLU, *Naturwissenschaften* **60**, 49 (1973).

³¹ T. DEBAERDEMAEKER, E. HELLNER, A. KUTOGLU, M. SCHMIDT and E. WILHELM, *Naturwissenschaften* **60**, 300 (1973).

defined concentrations of helices (S_{∞}), *cyclo*- S_8 , and other molecular forms. The various modifications are prepared by precipitating S from solution or by quenching *hot* liquid S (say from 400°C). The best-defined forms are fibrous ($d \sim 2.01 \text{ g cm}^{-3}$) in which the helices are mainly parallel, and lamella S in which they are partly criss-crossed. When carefully prepared by drawing filaments from hot liquid sulfur, fibrous rubbery or plastic S can be repeatedly stretched to as much as 15 times its normal length without substantially impairing its elasticity. All these forms revert to *cyclo*- $S_8(\alpha)$ at room temperature and this has caused considerable difficulty in obtaining their X-ray structures.⁽²³⁾ However, it is now established that fibrous S consists of infinite chains of S atoms arranged in parallel helices whose axes are arranged on a close-packed (hexagonal) net 463 pm apart. The structure contains both left-handed and right-handed helices of radius 95 pm and features a repeat distance of 1380 pm comprising 10 S atoms in three turns as shown in Fig. 15.9. Within each helix the interatomic distance S–S is 206.6 pm, the bond angle S–S–S is 106.0°, and the dihedral angle S–S–S–S is 85.3°.

The constitution of liquid sulfur has been extensively investigated, particularly in the region just above the remarkable transition at 159.4°. At this temperature virtually all properties of liquid sulfur change discontinuously, e.g. specific heat (λ point), density, velocity of sound, polarizability, compressibility, colour, electrical conductivity, surface tension and, most strikingly, viscosity, which increases over 10 000-fold within the temperature range 160–195°C before gradually decreasing again. The phenomena can now be interpreted at least semi-quantitatively by a 2-step polymerization theory involving initiation and propagation:



The polymerization is photosensitive, involves diradicals and leads to chain lengths that exceed 200 000 S atoms at $\sim 180^\circ\text{C}$ before dropping slowly to ~ 1000 S at 400° and ~ 100 S at 600° .

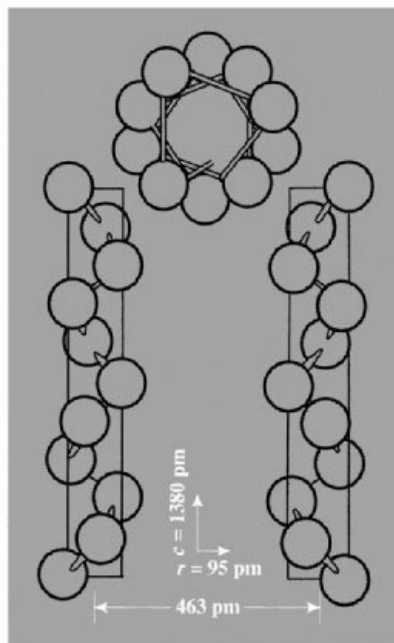


Figure 15.9 The structure of right-handed and left-handed S_{∞} helices in fibrous sulfur (see text).

Polymeric S_{∞} is dark yellow with an absorption edge at 350 nm (cf. H_2S_n , p. 683) but the colour is often obscured either by the presence of trace organic impurities or, in pure S, by the presence of other highly coloured species such as the dark cherry-red trimer S_3 or the deeper-coloured diradicals S_4 and S_5 .

The saturated vapour pressure above solid and liquid sulfur is given in Table 15.7. The molecular composition of the vapour has long been in contention but, mainly as a result of the work of J. Birkowitz and others⁽²⁴⁾ is now known to contain all molecules S_n with $2 \leq n \leq 10$ including odd-numbered species. The actual concentration

Table 15.7 Vapour pressure of crystalline *cyclo*- $S_8(\alpha)$ and liquid sulfur

$p/\text{mmHg}^{(a)}$	10^{-5}	10^{-3}	10^{-1}	1	10	100	760
$T/^\circ\text{C}$	39.0	81.1	141	186	244.9	328	444.61
$p/\text{atm}^{(a)}$	1	2	5	10	50	100	200
$T/^\circ\text{C}$	444.61	495	574	644	833	936	1035

^(a) 1 mmHg \approx 133.322 Pa; 1 atm = 101 325 Pa

of each species depends on both temperature and pressure. In the saturated vapour up to 600°C S_8 is the most common species followed by S_6 and S_7 , and the vapour is green. Between 620–720°C S_7 and S_6 are slightly more prevalent than S_8 but the concentration of all three species falls rapidly with respect to those of S_2 , S_3 and S_4 , and above 720°C S_2 is the predominant species. At lower pressures S_2 is even more prominent, accounting for more than 80% of all vapour species at 530°C and 100 mmHg, and 99% at 730°C and 1 mmHg. This vapour is violet. The vapour above FeS_2 at 850°C is also S_2 .

The best conditions for observing S_3 are 440°C and 10 mmHg when 10–20% of vapour species comprise this deep cherry-red bent triatomic species; like ozone, p. 607, it has a singlet ground state. The best conditions for S_4 are 450°C and 20 mmHg (concentration $\sim 20\%$) but the structure is still not definitely established and may, in fact be a strained ring, an unbranched diradical chain, or a branched-chain isostructural with $SO_3(g)$ (p. 703).

The great stability of S_2 in the gas phase at high temperature is presumably due to the essentially double-bond character of the molecule and to the increase in entropy ($T\Delta S$) consequent on the breaking up of the single-bonded S_n oligomers. As with O_2 (p. 606) the ground state is a triplet level $^3\Sigma_g^-$ but the splitting within the triplet state is far larger than with O_2 and the violet colour is due to the transition $B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ at $31\,689\text{ cm}^{-1}$. The corresponding $B \rightarrow X$ emission is observed whenever S compounds are burned in a reducing flame and the transition can be used for the quantitative analytical determination of the concentration of S compounds. There is also a singlet $^1\Delta$ excited state as for O_2 . The dissociation energy $D_0^0(S_2)$ is 421.3 kJ mol^{-1} , and the interatomic distance in the gas phase 188.7 pm (cf. Table 15.5).

15.1.5 Atomic and physical properties

Several physical properties of sulfur have been mentioned in the preceding section; they vary

markedly with the particular allotrope and its physical state.

Sulfur ($Z = 16$) has 4 stable isotopes of which ^{32}S is by far the most abundant in nature (95.02%). The others are ^{33}S (0.75%), ^{34}S (4.21%), and ^{36}S (0.02%). These abundances vary somewhat depending on the source of the sulfur, and this prevents the atomic weight of sulfur being quoted for general use more precisely than 32.066(6) (p. 17). The variability is a valuable geochemical indication of the source of the sulfur and the isotope ratios of sulfur-containing impurities can even be used to identify the probable source of petroleum samples.^(15,32) In such work it is convenient to define the abundance ratio of the 2 most abundant isotopes ($R = ^{32}S/^{34}S$) and to take as standard the value of 22.22 for meteoritic troilite (FeS). Deviations from this standard ratio are then expressed in parts per thousand (sometimes confusingly called "per mil" or ‰):

$$\delta^{34}S = 1000(R_{\text{sample}} - R_{\text{std}})/R_{\text{std}}$$

On this definition, $\delta^{34}S$ is zero for meteoritic troilite; dissolved sulfate in ocean water is enriched +20‰ in ^{34}S , as are contemporary evaporite sulfates, whereas sedimentary sulfides are depleted in ^{34}S by as much as -50‰ due to fractionation during bacterial reduction to H_2S .

In addition to the 4 stable isotopes sulfur has at least 9 radioactive isotopes, the one with the longest half-life being ^{35}S which decays by β^- activity ($E_{\text{max}} 0.167\text{ MeV}$, $t_{1/2} 87.5\text{ d}$). ^{35}S can be prepared by $^{35}Cl(n,p)$, $^{34}S(n,\gamma)$ or $^{34}S(d,p)$ and is commercially available as S_{element} , H_2S , $SOCl_2$ and $KSCN$. The β^- radiation has a similar energy to that of ^{14}C ($E_{\text{max}} 0.155\text{ MeV}$) and similar counting techniques can be used (p. 276). The maximum range is 300 mm in air and 0.28 mm in water, and effective shielding is provided by a perspex screen 3–10 mm thick. The preparation of many ^{35}S -containing compounds has been

³² H. NIELSEN, Sulfur isotopes, in E. JÄGER and J. C. HUNZIKER (eds.), *Lectures in Isotope Geology*, pp. 283–312, Springer-Verlag, Berlin, 1979.

reviewed⁽³³⁾ and many of these have been used for mechanistic studies, e.g. the reactions of the specifically labelled thiosulfate ions $^{35}\text{SSO}_3^{2-}$ and $\text{S}^{35}\text{SO}_3^{2-}$. Another ingenious application, which won Barbara B. Askins the US Inventor of the Year award for 1978, is the use of ^{35}S for intensifying under-exposed photographic images: prints or films are immersed in dilute aqueous alkaline solutions of ^{35}S -thiourea, which complexes all the silver in the image (including invisibly small amounts), and the alkaline medium converts this to immobile, insoluble Ag^{35}S ; the film so treated is then overlaid with unexposed film which reproduces the image with heightened intensity as a result of exposure to the β^- activity.

The isotope ^{33}S has a nuclear spin quantum number $I = \frac{3}{2}$ and so is potentially useful in nmr experiments (receptivity to nmr detection 17×10^{-6} that of the proton). The resonance was first observed in 1951 but the low natural abundance of ^{33}S (0.75%) and the quadrupolar broadening of many of the signals has so far restricted the amount of chemically significant work appearing on this resonance.⁽³⁴⁾ However, more results are expected now that pulsed fourier-transform techniques have become generally available.

The S atom in the ground state has the electronic configuration $[\text{Ne}]3s^23p^4$ with 2 unpaired p electrons (3P_1). Other atomic properties are: ionization energy $999.30 \text{ kJ mol}^{-1}$, electron affinities $+200$ and -414 kJ mol^{-1} for the addition of the first and second electrons respectively, electronegativity (Pauling) 2.5, covalent radius 103 pm and ionic radius of S^{2-} 184 pm. These properties can be compared with those of the other elements in Group 16 on p. 754.

³³ R. H. HERBER, Sulfur-35, in R. H. HERBER (ed.), *Inorganic Isotopic Syntheses*, pp. 193–214, Benjamin, New York, 1962.

³⁴ C. RODGER, N. SHEPPARD, C. MCFARLANE and W. MCFARLANE, in R. H. HARRIS and B. E. MANN (eds.), *NMR and the Periodic Table*, pp. 401–2, Academic Press, London, 1978. H. C. E. MCFARLANE and W. MCFARLANE, in J. MASON (ed.) *Multinuclear NMR*, Plenum Press, New York, 1987, pp. 417–35.

15.1.6 Chemical reactivity

Sulfur is a very reactive element especially at slightly elevated temperatures (which presumably facilitates cleavage of S–S bonds). It unites directly with all elements except the noble gases, nitrogen, tellurium, iodine, iridium, platinum and gold, though even here compounds containing S bonded directly to N, Te, I, Ir, Pt and Au are known. Sulfur reacts slowly with H_2 at 120° , more rapidly above 200° , and is in reversible thermodynamic equilibrium with H_2 and H_2S at higher temperatures. It ignites in F_2 and burns with a livid flame to give SF_6 ; reaction with chlorine is more sedate at room temperature but rapidly accelerates above this to give (initially) S_2Cl_2 (p. 689). Sulfur dissolves in liquid Br_2 to form S_2Br_2 , which readily dissociates into its elements; iodine has been used as a cryoscopic solvent for sulfur (p. 654) and no binary compound is formed (directly) even at elevated temperature (see, however, p. 691). Oxidation of sulfur by (moist?) air is very slow at room temperature though traces of SO_2 are formed; the ignition temperature of S in air is $250\text{--}260^\circ$. Pure dry O_2 does not react at room temperature though O_3 does. Likewise direct reaction with N_2 has not been observed but, in a discharge tube, activated N reacts. All other non-metals (B, C, Si, Ge; P, As, Sb; Se) react at elevated temperatures. Of the metals, sulfur reacts in the cold with all the main group representatives of Groups 1, 2, 13, Sn, Pb and Bi, and also Cu, Ag and Hg (which even tarnishes at liquid-air temperatures). The transition metals (except Ir, Pt and Au) and the lanthanides and actinides react more or less vigorously on being heated with sulfur to form binary metal sulfides (p. 676).

The reactivity of sulfur clearly depends sensitively on the molecular complexity of the reacting species. Little systematic work has been done. *Cyclo-S*₈ is obviously less reactive than the diradical *catena-S*₈, and smaller oligomers in the liquid or vapour phase also complicate the picture. In the limit atomic sulfur, which can readily be generated photolytically, is an extremely reactive species. As with atomic oxygen and the various