ERRATUM TO

Part II
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In the original publication Part II opener, (page 159), Illustrations and text were mistakenly left out of the print and online versions of this book. Please see the next page for the missing content.

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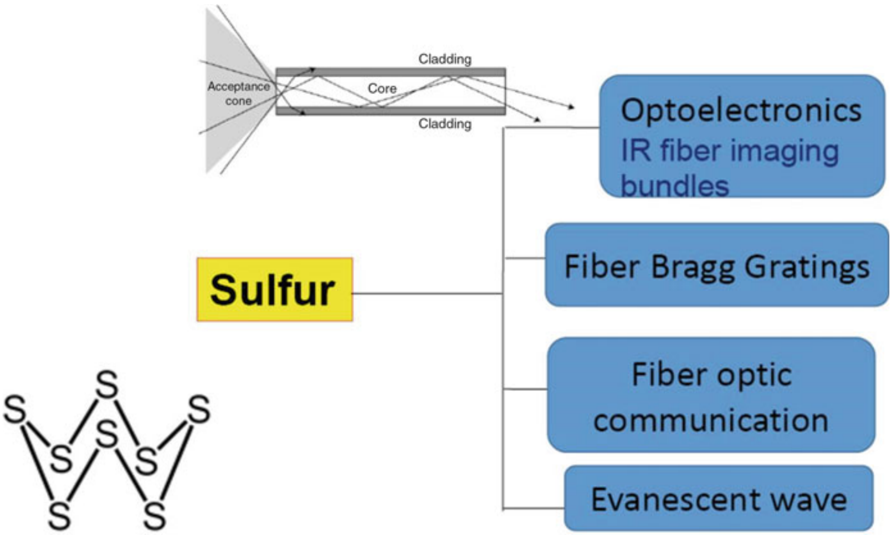
Part II
Sulfur



Sulfur- The Element

S - 16 - Ne $3s^2$ $3p^4$

Introduction

Sulfur is a polyatomic non-metallic chemical element with symbol S and atomic number 16. The term sulfur/sulphur originates from Sanskrit sulvere and Latin sulphurium. It has an atomic weight 32.059; 32.076, melts at. 115.21°C; and has a boiling point at 444.61°C. Specific gravity (rhombic) 2.07, (monoclinic) 1.957 (20°C). Sulfur is referred to in bible as brimstone (burn stone) in English. It is widely distributed in nature as pyrites (iron sulfide; FeS), galena (lead sulfide; PbS), spharelite (zinc sulfide; (Zn, Fe)S), cinnabar (mercury sulfide; HgS)), stibnite (antimony sulfide, Sb_2S_3), gypsum (calcium sulphate dihydrate; $CaSO_4{\cdot}2H_2O$), epsom salts (heptahydrate magnesium sulphate; $MgSO_4{\cdot}7H_2O$), celestite (strontium sulphate; ($SrSO_4$), barite (barium sulphate; $BaSO_4$), alunite (potassium aluminium sulfate; $KAl_3(SO_4)_2(OH)_6$) etc.

Sulfur is a pale yellow, odorless, brittle solid, which is insoluble in water but soluble in carbon disulfide. In every state, whether gas, liquid or solid, elemental sulfur occurs in more than one allotropic form or modification. Amorphous or "plastic" sulfur is obtained by fast cooling of the crystalline form. X-ray studies indicate that amorphous sulfur may have a helical structure with eight sulfur atoms per spiral. Crystalline sulfur seems to be made of rings, each containing eight sulfur atoms, amorphous sulfur may have a helical which fit together to give a normal X-ray pattern. Twenty-one isotopes of sulfur are now recognized. Four occur in natural sulfur, none of which is radioactive. Sulfur is essential to life. It is a minor component of fats, body fluids, and skeletal minerals. Sulfur is essential to all living things. It is taken up as sulfate from the soil (or seawater) by plants and algae. It is used to make two of the essential amino acids needed to make proteins. It is also needed in some co-enzymes. The average human contains 140 grams and takes in about 1 gram a day, mainly in proteins.

- Elemental sulfur is produced as a byproduct of removing sulfur-containing contaminants from natural gas and petroleum fertilizers, and in the manufacture of sulfuric acid.

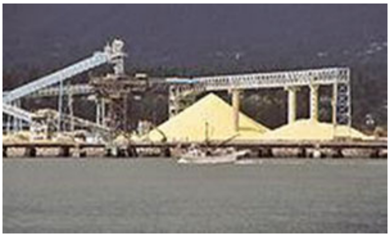
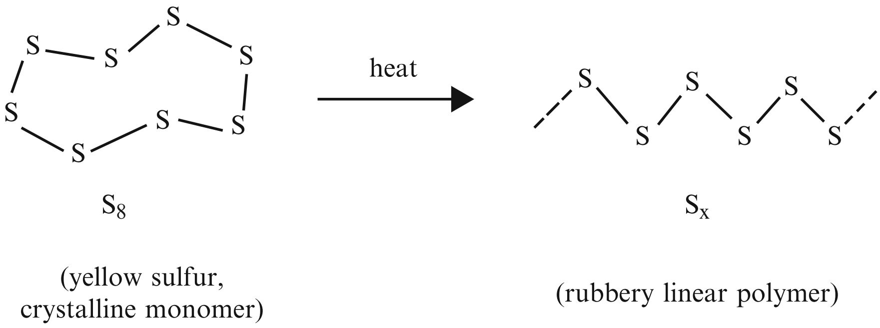
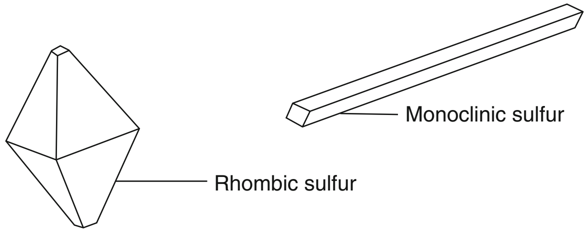


Fig. 1 Sulfur recovered from hydrocarbons in Alberta, stockpiled for shipment in North Vancouver, B.C., Canada. [1]





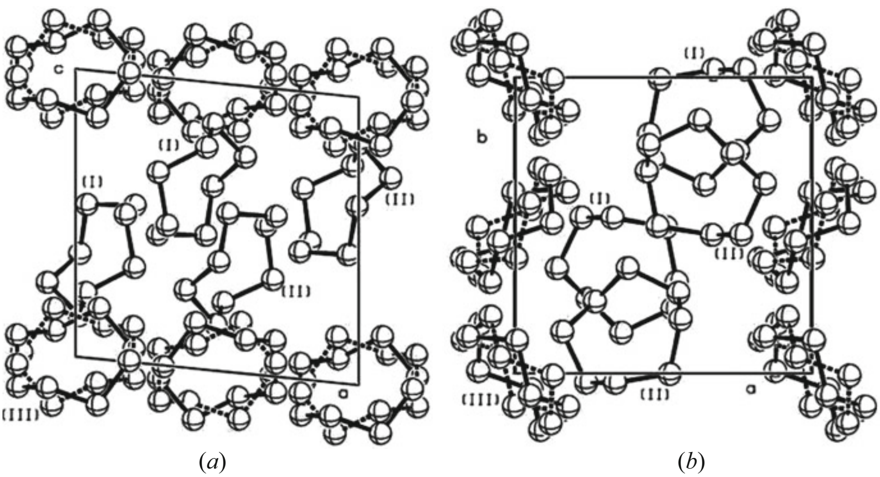
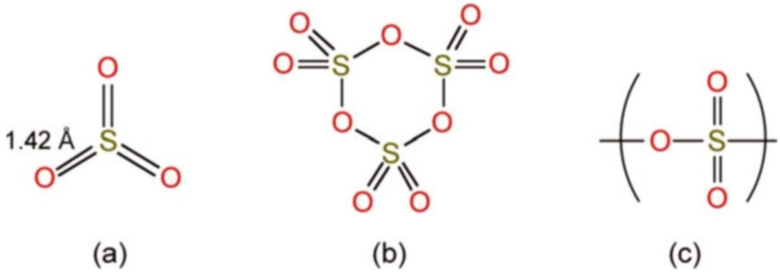


Fig. 2 Illustration of the crystal structure of monoclinic sulfur, viewed (a) along the b axis and (b) along the c axis. The three S8 molecules in the asymmetric unit are denoted as (I) (atoms S1-S8), (II) (atoms S9-S16) and the disordered molecule (III) (atoms S17-S24, S17' – S24') Copyright permission obtained [2].



S_2, disulfur

S_2 is the predominant species in sulfur vapour above 720°C. at low pressure (1mm Hg) at 530°C it comprises 99% of vapour species. It is a singlet diradical like dioxygen with an S-S bond length of 188.7 pm. The blue colour of burning sulfur is due to emission of light by the S_2 molecule produced in the flame.

S_3, trisulfur

S_3 is found in sulfur vapour, comprising 10% of vapour species at 440°C and 10mm Hg. It is cherry red in colour. Its structure is bent, similar to ozone, O_3.

S_4, tetrasulfur

This has been detected in the vapour phase but has not been fully characterised. Various forms, (e.g chains, branched chains and rings) have been proposed. The latest view, based on theoretical calculationsis that it has a ring structure.

Solid cyclo-sulfur allotropes

i) cyclo-S_5, pentasulfur - This has not been isolated, but has been detected in molten sulfur.
ii) S_6, cyclo- hexasulfur - This was first prepared by M.R. Engel in 1891 by reacting concentrated HCl with thiosulfate, $HS_2O_3^-$. Cyclo-S_6 is orange-red and forms a rhombohedral crystal. It is called ρ-sulfur, ε-sulfur, Engel's sulfur and Aten's sulfur.
iii) cyclo-S_6.cyclo-S_{10} adduct - This is produced from a solution of cyclo-S_6 and cyclo-S_{10} in CS_2. It has a density midway between cyclo-S_6 and cyclo-S_{10}. The crystal consists of alternate layers of cyclo-S_6 and cyclo-S_{10}. For all the elements this may be the only allotrope which contains molecules of different sizes.
iv) S_7, cyclo- heptasulfur - It is a bright yellow solid. Four (α-, β-, γ-, δ-) forms of cyclo-heptasulfur are known. Two forms (γ-, δ-) have been characterised. The cyclo-S_7 ring has an unusual range of bond lengths of 199.3pm - 218.1pm.
v) **Cyclo-S_8**

α- Sulfur - α-sulfur is the form most commonly found in nature. When pure it has a greenish-yellow colour (traces of cyclo-S_7 in commercially available samples make it appear yellower). It is practically insoluble in water and is a good electrical insulator with poor thermal conductivity. It is quite soluble in carbon disulfide 35.5g/100g solvent at 25°C. It has a rhombohedral crystal structure. This is the predominant form found in “flowers of sulfur”, “roll sulfur” and “milk of sulfur”. It contains S_8 puckered rings, alternatively called a crown shape. The S-S bond lengths are all 206pm and the S-S-S angles are 108° with a dihedral angle of 98°. At 95.3°C α-sulfur converts to β-sulfur.

β- Sulfur - This is a yellow solid with a monoclinic crystal form. Like the α- form it contains puckered S_8 rings and only differs from it in the way the rings are packed in the crystal. It is less dense than the α-form. It is unusual because it is only stable above 95.3°C, below this it converts to α-sulfur. It can be prepared by crystallising at 100°C and cooling rapidly to slow down formation of α-sulfur. It has a melting point variously quoted as 119.6°C and 119.8°C but as it decomposes to other forms at around this temperature the observed melting point can vary from this. The ca. 119°C melting point has been termed the “ideal melting point” and the typical lower value (114.5°) when decomposition occurs, the “natural melting point”.

γ- Sulfur - This form was first prepared by F.W Muthmann in 1890, sometimes called “nacreous sulfur” or “mother of pearl sulfur” because of its appearance, it crystallises in pale yellow monoclinic needles. It contains puckered S_8 rings like α-sulfur and β-sulfur and only differs from them in the way that these rings are packed. It is the densest form of the three. It can be prepared by slowly cooling molten sulfur that has been heated above 150°C or by chilling solutions of sulfur in carbon disulfide, ethyl alcohol or hydrocarbons. It is found in nature as the mineral rosickyite.

cyclo- S_n, (n=9-15, 18, 20) - These allotropes have been synthesised by various methods for example, reacting titanocene pentasulfide and a dichlorosulfane of suitable sulfur chain length, $S_{n-5}Cl_2$. S_{12}, S_{18} and S_{20} can be prepared from S_8.

Unlike α-sulfur and cyclo-S_6 the rings contain S-S bond lengths and S-S-S bond angle that differ one from another.

Cyclo-S_{12} is the second most stable cyclo- allotrope after cyclo-S_8. Its structure can be visualised as having sulfur atoms in three parallel planes, 3 in the top, 6 in the middle and three in the bottom.

Two forms (α-, β-) of cyclo-S_9 are known one of which has been characterised. Two forms of cyclo-S_{18} are known where the conformation of the ring is different. To differentiate these structures rather than use the normal crystallographic convention of α-, β- etc. which in other cyclo-S_n compounds refer to different packings of essentially the same conformer, these two conformers have been termed endo- and exo-.

Solid catena sulfur allotropes - The production of pure forms of catena-sulfur has proved to be extremely difficult. Purity of the starting material and the thermal history of the sample posing major constraints.

(i) **ψ- Sulfur** - This form, also called (confusingly) fibrous sulfur or ω1-sulfur, has been well characterised. It has a density of 2.01g cm^{-3} (α-sulfur 2.069g cm^{-3}) and decomposes around its melting point of 104°C. It consists of parallel helical sulfur chains. These chains have both left and right handed "twists" and a 95pm. The S-S bond length is 206.6pm, the S-S-S bond angle is 106° and the dihedral angle is 85.3°. (Comparable figures for α-sulfur are 203.7pm, 107.8° and 98.3°).

(ii) **Lamina sulfur** - This has not been well characterised but is believed to consist of criss-crossed helices. It is also called χ-sulfur or ω2-sulfur.

Catena sulfur forms - The naming of the different forms is very confusing and care has to be taken to determine what is being described as the same names are used interchangeably.

Amorphous sulfur - This is the quenched product of molten sulfur (>160°C). Its form changes from an initial plastic form gradually to a glassy form, hence its other names of plastic, glassy or vitreous sulfur. It is also called χ-sulfur. It contains a complex mixture of catena-sulfur forms mixed with cyclo-forms.

Insoluble sulfur - This is obtained by washing quenched liquid sulfur with CS_2. It is sometimes called polymeric sulfur, μ-S or ω-S.

φ- Sulfur, fibrous sulfur - This is a mixture of the allotropic ψ- form and γ-cycloS_8.

ω- Sulfur - This is a commercially available product prepared from amorphous sulfur that has NOT been stretched prior to extraction of soluble forms with CS_2. It sometimes called "white sulfur of Das" or super sublimated sulfur.. It is a mixture of ψ-sulfur and lamina sulfur. The composition depends on the exact method of production and the samples history. One well known commercial form is "Crystex". ω- Sulfur is used in the vulcanization of rubber.

λ- Sulfur - This name is given to the molten sulfur immediately after melting. Cooling this gives predominantly β-sulfur.

μ- Sulfur - This name is applied to solid insoluble sulfur and the melt prior to quenching.

π- Sulfur - Dark coloured liquid formed when λ-sulfur is left to stay molten. Contains mixture of S_n rings.

S_∞ - This term is applied to biradical catena- chains in sulfur melts or the chains in the solid.

Applications of elemental Sulfur:
Sulfur is a component of black gun powder, and is used in the vulcanisation of natural rubber and a fungicide. It is also used extensively in making phosphatic fertilizers. A tremendous tonnage is used to produce sulfuric acid. It is used in making sulfite paper and other papers as a fumigant, and in the bleaching of dried fruits. The element is a good electrical insulator. Some important compounds of

sulfur include calcium sulfate, ammonium sulfate, carbon disulfide, sulfur dioxide and hydrogen sulfide. Of these carbon disulfide, hydrogen sulfide and sulfur dioxide particularly should be handled carefully.

References

1. https://en.wikipedia.org/wiki/Sulfur
2. David, Ibberson, Cox & Wood (2006). Acta Crystallographica B62, pp. 953–959.