

Sulfur

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Sulfur or **sulphur** (see spelling differences) is a chemical element with symbol **S** and atomic number 16. It is an abundant, multivalent nonmetal. Under normal conditions, sulfur atoms form cyclic octatomic molecules with chemical formula S₈. Elemental sulfur is a bright yellow crystalline solid at room temperature. Chemically, sulfur reacts with all elements except for gold, platinum, iridium, tellurium and the noble gases.

Elemental sulfur occurs naturally as the element (native sulfur), but most commonly occurs in combined forms as sulfide and sulfate minerals. Being abundant in native form, sulfur was known in ancient times, being mentioned for its uses in ancient India, ancient Greece, China, and Egypt. In the Bible, sulfur is called *brimstone*.^[5] Today, almost all elemental sulfur is produced as a byproduct of removing sulfur-containing contaminants from natural gas and petroleum. The greatest commercial use of the element is the production of sulfuric acid for sulfate and phosphate fertilizers, and other chemical processes. The element sulfur is used in matches, insecticides, and fungicides. Many sulfur compounds are odoriferous, and the smells of odorized natural gas, skunk scent, grapefruit, and garlic are due to organosulfur compounds. Hydrogen sulfide gives the characteristic odor to rotting eggs and other biological processes.

Sulfur is an essential element for all life, but almost always in the form of organosulfur compounds or metal sulfides. Three amino acids (cysteine, cystine, and methionine) and two vitamins (biotin and thiamine) are organosulfur compounds. Many cofactors also contain sulfur including glutathione and thioredoxin and iron–sulfur proteins. Disulfides, S–S bonds, confer mechanical strength and insolubility of the protein keratin, found in outer skin, hair, and feathers. Sulfur is one of the core chemical elements needed for biochemical functioning and is an elemental macronutrient for all organisms.

Characteristics

Physical properties

Sulfur, ¹⁶S



Spectral lines of sulfur

General properties

Name, symbol	sulfur, S
Alternative name	sulphur
Appearance	lemon yellow sintered microcrystals

Sulfur in the periodic table

Atomic number (<i>Z</i>)	16
Group, block	group 16 (chalcogens), p-block
Period	period 3
Element category	□ polyatomic nonmetal
Standard atomic weight (<i>A</i> _r)	32.06 ^[1] (32.059– 32.076) ^[2]
Electron configuration	[Ne] 3s ² 3p ⁴
per shell	2, 8, 6



When burned, sulfur melts to a blood-red liquid and emits a blue flame that is best observed in the dark.

Sulfur forms polyatomic molecules with different chemical formulas, the best-known allotrope being octasulfur, cyclo-S₈. The point group of cyclo-S₈ is D_{4d} and its dipole moment is 0 D.^[9] Octasulfur is a soft, bright-yellow solid that is odorless, but impure samples have an odor similar to that of matches.^[10] It melts at 115.21 °C (239.38 °F), boils at 444.6 °C (832.3 °F) and sublimates easily.^[5] At 95.2 °C (203.4 °F), below its melting temperature, cyclo-octasulfur changes from α-octasulfur to the β-polymorph.^[11] The structure of the S₈ ring is virtually unchanged by this phase change, which affects the intermolecular interactions. Between its melting and boiling temperatures, octasulfur changes its allotrope again, turning from β-octasulfur to γ-sulfur, again accompanied by a lower density but increased viscosity due to the formation of polymers.^[11] At higher temperatures, the viscosity decreases as

depolymerization occurs. Molten sulfur assumes a dark red color above 200 °C (392 °F). The density of sulfur is about 2 g·cm⁻³, depending on the allotrope; all of the stable allotropes are excellent electrical insulators.

Chemical properties

Sulfur burns with a blue flame with formation of sulfur dioxide, which has a suffocating and irritating odor. Sulfur is insoluble in water but soluble in carbon disulfide and, to a lesser extent, in other nonpolar organic solvents, such as benzene and toluene. The first and second ionization energies of sulfur are 999.6 and 2252 kJ·mol⁻¹, respectively. Despite such figures, the +2 oxidation state is rare, with +4 and +6 being more common. The fourth and sixth ionization energies are 4556 and 8495.8 kJ·mol⁻¹, the magnitude of the figures caused by electron transfer between orbitals; these states are only stable with strong oxidants such as fluorine, oxygen,

Physical properties

Phase	solid
Melting point	388.36 K (115.21 °C, 239.38 °F)
Boiling point	717.8 K (444.6 °C, 832.3 °F)
Density near r.t.	alpha: 2.07 g/cm ³ beta: 1.96 g/cm ³ gamma: 1.92 g/cm ³
when liquid, at m.p.	1.819 g/cm ³
Critical point	1314 K, 20.7 MPa
Heat of fusion	mono: 1.727 kJ/mol
Heat of vaporization	mono: 45 kJ/mol
Molar heat capacity	22.75 J/(mol·K)

Vapor pressure

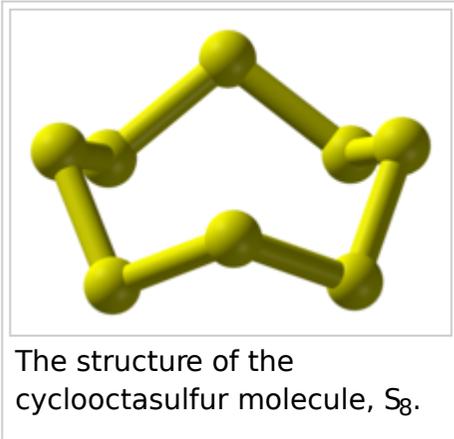
P (Pa)	1	10	100	1 k	10 k	100 k
at T (K)	375	408	449	508	591	717

Atomic properties

Oxidation states	6, 5, 4, 3, 2, 1, -1, -2 (a strongly acidic oxide)
Electronegativity	Pauling scale: 2.58
Ionization energies	1st: 999.6 kJ/mol 2nd: 2252 kJ/mol 3rd: 3357 kJ/mol (more)
Covalent radius	105±3 pm
Van der Waals radius	180 pm

and chlorine. Sulfur reacts with nearly all other elements with the exception of gold, platinum, iridium, nitrogen, tellurium, iodine and the noble gases. Some of those reactions need elevated temperatures.^[12]

Allotropes



Sulfur forms over 30 solid allotropes, more than any other element.^[13] Besides S₈, several other rings are known.^[14] Removing one atom from the crown gives S₇, which is more deeply yellow than S₈. HPLC analysis of "elemental sulfur" reveals an equilibrium mixture of mainly S₈, but with S₇ and small amounts of S₆.^[15] Larger rings have been prepared, including S₁₂ and S₁₈.^{[16][17]}

Amorphous or "plastic" sulfur is produced by rapid cooling of molten sulfur—for example, by pouring it

into cold water. X-ray crystallography studies show that the amorphous form may have a helical structure with eight atoms per turn. The long coiled polymeric molecules make the brownish substance elastic, and in bulk this form has the feel of crude rubber. This form is metastable at room temperature and gradually reverts to crystalline molecular allotrope, which is no longer elastic. This process happens within a matter of hours to days, but can be rapidly catalyzed.

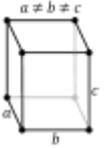
Isotopes

Sulfur has 25 known isotopes, four of which are stable: ³²S (94.99 ± 0.26%), ³³S (0.75 ± 0.02%), ³⁴S (4.25 ± 0.24%), and ³⁶S (0.01 ± 0.01%).^{[18][19]} Other than ³⁵S, with a half-life of 87 days and formed in cosmic ray spallation of ⁴⁰Ar, the radioactive isotopes of sulfur have half-lives less than 3 hours.

When sulfide minerals are precipitated, isotopic equilibration among solids and liquid may cause small differences in the δS-34 values of co-genetic minerals. The differences between minerals can be used to estimate the temperature of equilibration. The δC-13 and δS-34 of coexisting carbonate minerals and sulfides can be used to determine the pH and oxygen fugacity of the ore-

Miscellanea

Crystal structure orthorhombic



Thermal conductivity 0.205 W/(m·K)
(amorphous)

Electrical resistivity 2 × 10¹⁵ Ω·m
(at 20 °C)
(amorphous)

Magnetic ordering diamagnetic^[3]

Bulk modulus 7.7 GPa

Mohs hardness 2.0

CAS Number 7704-34-9

History

Discovery Chinese^[4]
(before 2000 BCE)

Recognized as an element by Antoine Lavoisier
(1777)

Most stable isotopes of sulfur

iso	NA	half-life	DM	DE (MeV)	DP
32S	94.99%	is stable with 16 neutrons			
33S	0.75%	is stable with 17 neutrons			
34S	4.25%	is stable with 18 neutrons			
35S	trace	87.32 d	β ⁻	0.167	³⁵ Cl
36S	0.01%	is stable with 20 neutrons			

bearing fluid during ore formation.

In most forest ecosystems, sulfate is derived mostly from the atmosphere; weathering of ore minerals and evaporites contribute some sulfur. Sulfur with a distinctive isotopic composition has been used to identify pollution sources, and enriched sulfur has been added as a tracer in hydrologic studies. Differences in the natural abundances can be used in systems where there is sufficient variation in the ^{34}S of ecosystem components. Rocky Mountain lakes thought to be dominated by atmospheric sources of sulfate have been found to have different $\delta^{34}\text{S}$ values from lakes believed to be dominated by watershed sources of sulfate.

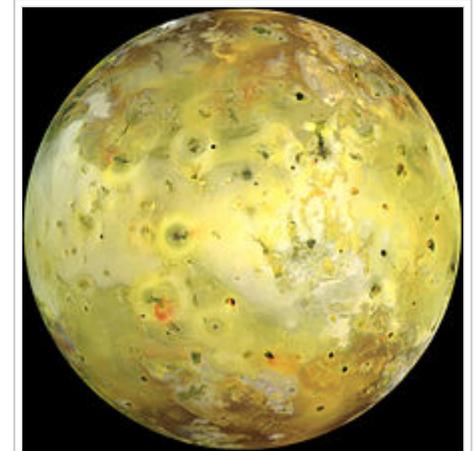
Natural occurrence

^{32}S is created inside massive stars, at a depth where the temperature exceeds 2.5×10^9 K, by the fusion of one nucleus of silicon plus one nucleus of helium.^[20] As this is part of the alpha process that produces elements in abundance, sulfur is the 10th most common element in the universe.

Sulfur, usually as sulfide, is present in many types of meteorites. Ordinary chondrites contain on average 2.1% sulfur, and carbonaceous chondrites may contain as much as 6.6%. It is normally present as troilite (FeS), but there are exceptions, with carbonaceous chondrites containing free sulfur, sulfates and other sulfur compounds.^[21] The distinctive colors of Jupiter's volcanic moon Io are attributed to various forms of molten, solid and gaseous sulfur.^[22]

On Earth, elemental sulfur can be found near hot springs and volcanic regions in many parts of the world, especially along the Pacific Ring of Fire; such volcanic deposits are currently mined in Indonesia, Chile, and Japan. Such deposits are polycrystalline, with the largest documented single crystal measuring $22 \times 16 \times 11$ cm.^[23] Historically, Sicily was a major source of sulfur in the Industrial Revolution.^[24]

Native sulfur is synthesised by anaerobic bacteria acting on sulfate minerals such as gypsum in salt domes.^{[25][26]} Significant deposits in salt domes occur along the coast of the Gulf of Mexico, and in evaporites in eastern Europe and western Asia. Native sulfur may be produced by geological processes alone. Fossil-based sulfur deposits from salt domes were until recently the basis for commercial production in the United States, Russia, Turkmenistan, and Ukraine.^[27] Currently, commercial production is still carried out in the Osiek mine in Poland. Such sources are now of secondary commercial importance, and most are no longer worked.



Most of the yellow and orange hues of Io are due to elemental sulfur and sulfur compounds deposited by active volcanoes.

Common naturally occurring sulfur compounds include the sulfide minerals, such as pyrite (iron sulfide), cinnabar (mercury sulfide), galena (lead sulfide), sphalerite (zinc sulfide) and stibnite (antimony sulfide); and the sulfates, such as gypsum (calcium sulfate), alunite (potassium aluminium sulfate), and barite (barium sulfate). On Earth, just as upon Jupiter's moon Io, elemental sulfur occurs naturally in volcanic emissions, including emissions from hydrothermal vents.

Source

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