

# Sulfur

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## 1 . Introduction :

**Sulfur** or **sulphur** is the chemical element that has the atomic number 16 . It is denoted with the symbol **S**. It is an abundant, multivalent non - metal. Sulfur in its native form is a yellow crystalline solid. In nature, it can be found as the pure element and as sulfide and sulfate minerals. It is an essential element for life and is found in two amino acids, cysteine and methionine. Its commercial uses are primarily in fertilizers, but it is also widely used in black gunpowder, matches, insecticides and fungicides. Elemental sulfur

crystals are commonly sought after by mineral collectors for their brightly colored polyhedron shapes. In nonscientific context it can also be referred to as *brimstone*.

Appearance	Lemon yellow crystals.
Name, Symbol, Number	Sulfur , S , 16
Element Category	Non metal
Group , Period , Block	16 , 3 , p
Standard atomic weight	32 g · mol <sup>-1</sup>
Electron configuration	[Ne] 3s <sup>2</sup> 3p <sup>4</sup>
Electrons per shell	2, 8, 6
Phase	Solid
Density	( alpha ) 2.07 g · cm <sup>-3</sup>
Density	( beta ) 1.96 g · cm <sup>-3</sup>
Density	( gamma ) 1.92 g · cm <sup>-3</sup>
Liquid density at m.p.	1.819 g · cm <sup>-3</sup>
Melting point	115.21 °C
Boiling point	444.6 ° C
Critical point	1314 K , 20.7 MPa
Heat of fusion	( mono ) 1.727 kJ · mol <sup>-1</sup>
Heat of vaporization	( mono ) 45 kJ · mol <sup>-1</sup>
Specific heat capacity	( 25 °C ) 22.75 J · mol <sup>-1</sup> · K <sup>-1</sup>
Oxidation states	6 , 5 , 4 , 3 , 2 , 1 , -1 , -2 ( strongly acidic oxide )
Ionization energies	1 <sup>st</sup> : 999.6 kJ · mol <sup>-1</sup>
	2 <sup>nd</sup> : 2252 kJ · mol <sup>-1</sup>
	3 <sup>rd</sup> : 3357 kJ · mol <sup>-1</sup>
Covalent radius	105 ± 3 pm
Van der Waals radius	180 pm
Crystal structure	Ortho rhombic
Magnetic ordering	diamagnetic
Electrical resistivity	( 20 °C ) ( amor phous ) 2 × 10 <sup>15</sup> Ω · m

Thermal conductivity	( 300 K ) ( amorphous ) 0.205 W · m <sup>-1</sup> · K <sup>-1</sup>
Bulk modulus	7.7 GPa
Mohs hardness	2.0

### Main article : Isotopes of sulfur

<sup>32</sup> S	95.02 %	<sup>32</sup> S is stable with 16 neutrons			
<sup>33</sup> S	0.75 %	<sup>33</sup> S is stable with 17 neutrons			
<sup>34</sup> S	4.21 %	<sup>34</sup> S is stable with 18 neutrons			
<sup>35</sup> S	syn	87.32 d	β <sup>-</sup>	0.167	<sup>35</sup> Cl
<sup>36</sup> S	0.02 %	<sup>36</sup> S is stable with 20 neutrons			

## 2 . History

Sulfur ( Sanskrit, *sulvari* ; Latin *sulfur* or *sulpur* ) was known in ancient times and is referred to in the Torah ( Genesis ) .

English translations of the Bible commonly referred to burning sulfur as " brim stone ", giving rise to the name of ' fire and brim stone ' sermons, in which listeners are reminded of the fate of eternal damnation that await the unbelieving and unrepentant. It is from this part of the Bible that Hell is implied to " smell of sulfur ", although sulfur, in itself, is in fact odorless. The " smell of sulfur " usually refers to either the odor of hydrogen sulfide, e.g. from rotten egg, or of burning sulfur, which produces sulfur dioxide, the smell associated with burnt matches. The smell emanating from raw sulfur originates from a slow oxidation in the presence of air. Hydrogen sulfide is the principal odor of untreated sewage and is one of several unpleasant smelling sulfur-containing components of flatulence ( along with sulfur-containing mercaptans ) .

A natural form of sulfur known as *shiliuhuang* was known in China since the 6th century BC and found in Hanzhong . By the 3rd century, the Chinese discovered that sulfur could be extracted from pyrite . Chinese Daoists were interested in sulfur's flammability and

its reactivity with certain metals, yet its earliest practical uses were found in traditional Chinese medicine . A Song Dynasty military treatise of 1044 AD described different formulas for Chinese black powder, which is a mixture of potassium nitrate (  $\text{KNO}_3$  ) , charcoal, and sulfur. Early alchemists gave sulfur its own alchemical symbol which was a triangle at the top of a cross.

In 1777 Antoine Lavoisier helped convince the scientific community that sulfur was an element and not a compound. In 1867, sulfur was discovered in underground deposits in Louisiana and Texas. The overlying layer of earth was quicksand, prohibiting ordinary mining operations, therefore the Frasch process was developed.

### **2 . 1 . Spelling and etymology**

The element has traditionally been spelled *sulphur* in the United Kingdom ( since the 14th Century ) , most of the Common wealth including India, Malaysia, South Africa, and Hong Kong, along with the rest of the Caribbean and Ireland, but *sulfur* in the United States, while both spellings are used in Australia, New Zealand, Canada, and the Philippines. IUPAC adopted the spelling “sulfur” in 1990 , as did the Royal Society of Chemistry Nomenclature Committee in 1992 and the Qualifications and Curriculum Authority for England and Wales recommended its use in 2000 .

In Latin, the word is variously written *sulpur*, *sulphur* , and *sulfur* ( the Oxford Latin Dictionary lists the spellings in this order ) . It is an original Latin name and not a Classical Greek loan, so the *ph* variant does not denote the Greek letter  $\phi$ . Sulfur in Greek is *thion* (  $\theta\epsilon\acute{\iota}\omicron\nu$  ) , whence comes the prefix thio - . The simplification of the Latin word's p or ph to an f appears to have taken place towards the end of the classical period, with the f spelling becoming dominant in the medieval period .

### **3 . Characteristics**

Sulfur melts to a blood - red liquid. When burned, it emits a blue flame.

At room temperature, sulfur is a soft, bright - yellow solid. Elemental sulfur has only a faint odor, similar to that of matches. The odor associated with rotten eggs is due to hydrogen sulfide (  $\text{H}_2\text{S}$  ) and organic sulfur compounds rather than elemental sulfur. Sulfur burns with a blue flame that emits sulfur dioxide, notable for its peculiar suffocating odor due to dissolving in the mucosa to form dilute sulfurous acid. Sulfur itself is insoluble in water, but soluble in carbon disulfide — and to a lesser extent in other non-polar organic solvents such as benzene and toluene. Common oxidation states of sulfur include  $-2$  ,  $+2$  ,  $+4$  and  $+6$  . Sulfur forms stable compounds with all elements except the noble gases. Sulfur in the solid state ordinarily exists as cyclic crown - shaped  $\text{S}_8$  molecules.

The crystallography of sulfur is complex . Depending on the specific conditions, the sulfur allotropes form several distinct crystal structures, with rhombic and monoclinic  $\text{S}_8$  best known.

A noteworthy property of sulfur is that its viscosity in its molten state, unlike most other liquids, increases above temperatures of  $200^\circ\text{C}$  due to the formation of polymers. The molten sulfur assumes a dark red color above this temperature. At higher temperatures, however, the viscosity is decreased as depolymerization occurs.

Amorphous or " plastic " sulfur can be produced through the rapid cooling of molten sulfur. X - ray crystallography studies show that the amorphous form may have a helical structure with eight atoms per turn . This form is metastable at room temperature and gradually reverts back to crystalline form. This process happens within a matter of hours to days but can be rapidly catalyzed.

### **3 . 1 . Allotropes of Sulfur**

Sulfur forms more than 30 solid allotropes, more than any other element . Besides  $\text{S}_8$  , several other rings are known . Removing one atom from the crown gives  $\text{S}_7$ , which is more deeply yellow than  $\text{S}_8$ . HPLC analysis of " elemental sulfur " reveals an equilibrium mixture of mainly  $\text{S}_8$ , but also  $\text{S}_7$  and small amounts of  $\text{S}_6$  . Larger rings have been prepared, including  $\text{S}_{12}$  and  $\text{S}_{18}$  . By contrast, sulfur's lighter neighbor oxygen only exists in two states of allotropic significance:

O<sub>2</sub> and O<sub>3</sub>. Selenium, the heavier analogue of sulfur, can form rings but is more often found as a polymer chain.

### 3.2. Isotopes of Sulfur

Sulfur has 25 known isotopes, four of which are stable: <sup>32</sup>S (95.02%), <sup>33</sup>S (0.75%), <sup>34</sup>S (4.21%), and <sup>36</sup>S (0.02%). Other than <sup>35</sup>S, the radioactive isotopes of sulfur are all short lived. <sup>35</sup>S is formed from cosmic ray spallation of <sup>40</sup> argon in the atmosphere. It has a half-life of 87 days.

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 carbonates and sulfides can be used to determine the pH and oxygen fugacity of the ore-bearing fluid during ore formation.

In most forest ecosystems, sulfate is derived mostly from the atmosphere; weathering of ore minerals and evaporites also 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 also be used in systems where there is sufficient variation in the <sup>34</sup>S of ecosystem components. Rocky Mountain lakes thought to be dominated by atmospheric sources of sulfate have been found to have different δS-34 values from lakes believed to be dominated by watershed sources of sulfate.

### 3.3. Occurrence

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. Sicily is also famous for its sulfur mines. Sulfur deposits are polycrystalline, and the largest documented single crystal measured 22 x 16 x 11 cm<sup>3</sup>.

Significant deposits of elemental sulfur also exist in salt domes along the coast of the Gulf of Mexico, and in evaporites in eastern Europe and western Asia. The sulfur in these deposits is believed to come from the action of anaerobic bacteria on sulfate minerals, especially gypsum, although apparently native sulfur may be produced by geological processes alone, without the aid of living organisms. However, fossil-based sulfur deposits from salt domes are the basis for commercial production in the United States, Poland, Russia, Turkmenistan, and Ukraine.

Sulfur recovered from hydrocarbons in Alberta, stockpiled for shipment at Vancouver, B.C.

Sulfur production through hydrodesulfurization of oil, gas, and the Athabasca Oil Sands has produced a surplus — huge stockpiles of sulfur now exist throughout Alberta, Canada.

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 ) . It occurs naturally in volcanic emissions , such as from hydrothermal vents, and from bacterial action on decaying sulfur - containing organic matter.

The distinctive colors of Jupiter's volcanic moon , Io , are from various forms of molten, solid and gaseous sulfur. There is also a dark area near the Lunar crater Aristarchus that may be a sulfur deposit.

Sulfur 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 % . Sulfur in meteorites is normally present entirely as troilite ( FeS ), but other sulfides are found in some meteorites, and carbonaceous chondrites contain free sulfur , sulfates , and possibly other sulfur compounds .

## **4 . Extraction and production**

### **4 . 1 . Extraction from natural resources**

Sulfur is extracted by mainly two processes: the Sicilian process and the Frasch process. The Sicilian process, which was first used in Sicily, was used in ancient times to get sulfur from rocks present in volcanic regions. In this process, the sulfur deposits are piled and stacked in brick kilns built on sloping hillsides, and with airspaces between them. Then powdered sulfur is put on top of the sulfur deposit and ignited. As the sulfur burns, the heat melts the sulfur deposits, causing the molten sulfur to flow down the sloping hillside. The molten sulfur can then be collected in wooden buckets .

The second process used to obtain sulfur is the Frasch process. In this method, three concentric pipes are used: the outermost pipe contains super heated water, which melts the sulfur, and the innermost pipe is filled with hot compressed air, which serves to create foam and pressure. The resulting sulfur foam is then expelled through the middle pipe .

The Frasch process produces sulfur with a 99.5 % purity content, and which needs no further purification. The sulfur produced by the Sicilian process must be purified by distillation.

### **4 . 2 . Production from hydrogen sulfide**

#### **4 . 2 . 1 . Chemically**

The Claus process is used to extract elemental sulfur from hydrogen sulfide produced in hydrodesulfurization of petroleum or from natural gas.

#### **4 . 2 . 2 . Biologically**

In the biological route, hydrogen sulfide (  $H_2S$  ) from natural gas or refinery gas is absorbed with a slight alkaline solution in a wet scrubber . Or the sulfide is produced by biological sulfate reduction. In the subsequent process step, the dissolved sulfide is biologically converted to elemental sulfur. This solid sulfur is removed from the



reactor. This process has been built on commercial scale. The main advantages of this process are:

1. No use of expensive chemicals,
2. The process is safe as the  $H_2S$  is directly absorbed in an alkaline solution,
3. No production of a polluted waste stream,
4. Re - usable sulfur is produced, and
5. The process occurs under ambient conditions.

The biosulfur product is different from other processes in which sulfur is produced because the sulfur is hydrophilic. Next to straightforward reuses as source for sulfuric acid production, it can also be applied as sulfur fertilizer .

## 5 . Chemistry

### 5 . 1 . Inorganic compounds

When dissolved in water, hydrogen sulfide is acidic and will react with metals to form a series of metal sulfides. Natural metal sulfides are common, especially those of iron. Iron sulfide is called pyrite, the so - called *fool's gold* . Pyrite can show semiconductor properties.<sup>[18]</sup> Galena, a naturally occurring lead sulfide, was the first semiconductor discovered, and found a use as a signal rectifier in the "cat's whiskers" of early crystal radios.

Polymeric sulfur nitride has metallic properties even though it does not contain any metal atoms. This compound also has unusual electrical and optical properties. This polymer can be made from tetra sulfur tetra nitride  $S_4 N_4$ .

Phosphorus sulfides are useful in synthesis . For example,  $P_4S_{10}$  and its derivatives Lawesson's reagent and naphthalen-1,8- diyl 1,3,2,4 - dithiadiphosphetane 2 , 4 - disulfide are used to replace oxygen from some organic molecules with sulfur .

- Sulfides (  $S^{2-}$  ) , a complex family of compounds usually derived from  $S^{2-}$  . Cadmium sulfide (  $Cd S$  ) is an example.

- Sulfites (  $\text{SO}_3^{2-}$  ), the salts of sulfurous acid (  $\text{H}_2\text{SO}_3$  ) which is generated by dissolving  $\text{SO}_2$  in water. Sulfurous acid and the corresponding sulfites are fairly strong reducing agents. Other compounds derived from  $\text{SO}_2$  include the pyrosulfite or metabisulfite ion ( $\text{S}_2\text{O}_5^{2-}$ ).
- Sulfates (  $\text{SO}_4^{2-}$  ), the salts of sulfuric acid. Sulfuric acid also reacts with  $\text{SO}_3$  in equimolar ratios to form pyro sulfuric acid (  $\text{H}_2\text{S}_2\text{O}_7$  ).
- Thiosulfates (  $\text{S}_2\text{O}_3^{2-}$  ). Sometimes referred as thiosulfites or " hypo sulfites ", Thio sulfates are used in photographic fixing (HYPO) as reducing agents. Ammonium thiosulfate is being investigated as a cyanide replacement in leaching gold .
- Sodium dithionite,  $\text{Na}_2\text{S}_2\text{O}_4$  , is the highly reducing dianion derived from hyposulfurous/dithionous acid.
- Sodium dithionate (  $\text{Na}_2\text{S}_2\text{O}_6$  ) .
- Poly thionic acids (  $\text{H}_2\text{S}_n\text{O}_6$  ) , where  $n$  can range from 3 to 80.
- Peroxy mono sulfuric acid (  $\text{H}_2\text{SO}_5$  ) and peroxy disulfuric acids (  $\text{H}_2\text{S}_2\text{O}_8$  ) , made from the action of  $\text{SO}_3$  on concentrated  $\text{H}_2\text{O}_2$  , and  $\text{H}_2\text{SO}_4$  on concentrated  $\text{H}_2\text{O}_2$  respectively.
- Sodium poly sulfides (  $\text{Na}_2\text{S}_x$  )
- Sulfur hexa fluoride,  $\text{S F}_6$  , a dense gas at ambient conditions, is used as nonreactive and nontoxic propellant
- Sulfur nitrides are chain and cyclic compounds containing only S and N. Tetra sulfur tetra nitride  $\text{S}_4\text{N}_4$  is an example.
- Thio cyanates contain the  $\text{S CN}^-$  group . Oxidation of thio cyanoate gives thio cyanogen, (  $\text{S CN}$  )<sub>2</sub> with the connectivity NCS - SCN.

## 5 . 2 . Organic compounds

Many of the unpleasant odors of organic matter are based on sulfur-containing compounds such as methyl mercaptan and dimethyl sulfide. Thiols and sulfides are used in the odoriation of natural gas, notably, 2- methyl - 2 - propanethiol ( t - butyl mercaptan ) . The odor of garlic and " skunk stink " are also caused by sulfur - containing organic compounds. Not all organic sulfur compounds smell unpleasant; for example, grapefruit mercaptan, a sulfur - containing

mono terpenoid is responsible for the characteristic scent of grapefruit . It should be noted that this thiol is present in very low concentrations. In larger concentrations, the odor of this compound is that typical of all thiols, unpleasant.

Sulfur - containing organic compounds include the following :  
(  $R$  ,  $R'$  , and  $R$  are organic groups such as  $CH_3$  ):

- Thio ethers have the form  $R - S - R'$  . These compounds are the sulfur equivalents of ethers.
- Sulfonium ions have the formula  $RR'S - 'R''$  , i.e. where three groups are attached to the cationic sulfur center. Di methyl sulfonio propionate ( DMSP ;  $(CH_3)_2 S^+ CH_2 CH_2 COO^-$  ) is a sulfonium ion , which is important in the marine organic sulfur cycle.
- Thiols ( also known as mercaptans ) have the form  $R - SH$ . These are the sulfur equivalents of alcohols.
- Thiolates ions have the form  $R - S^-$  . Such anions arise upon treatment of thiols with base.
- Sulfoxides have the form  $R - S(=O) - R'$  . The simplest sulfoxide, DMSO , is a common solvent.
- Sulfones have the form  $R - S(=O)_2 - R'$  . A common sulfone is sulfolane  $C_4H_8 SO_2$  .

## 6 . Applications

One of the direct uses of sulfur is in vulcanization of rubber, where poly sulfides crosslink organic polymers. Sulfur is a component of gunpowder. It reacts directly with methane to give carbon disulfide, which is used to manufacture cellophane and rayon .

Elemental sulfur is mainly used as a precursor to other chemicals. Approximately 85 % ( 1989 ) is converted to sulfuric acid (  $H_2SO_4$  ) , which is of such prime importance to the world's economies that the production and consumption of sulfuric acid is an indicator of a nation's industrial development. For example, more sulfuric acid is produced in the United States every year than any other industrial chemical . The principal use for the acid is the extraction of phosphate ores for the production of fertilizer

manufacturing. Other applications of sulfuric acid include oil refining, wastewater processing, and mineral extraction .

Sulfur compounds are also used in detergents, fungicides, dyestuffs, and agrichemicals. In silver - based photography sodium and ammonium thiosulfate are used as " fixing agents" .

Sulfur is an ingredient in some acne treatments.

An increasing application is as fertilizer. Standard sulfur is hydrophobic and therefore has to be covered with a surfactant by bacteria in the ground before it can be oxidized to sulfate. This makes it a slow release fertilizer, which cannot be taken up by the plants instantly, but has to be oxidized to sulfate over the growth season. Sulfur also improves the use efficiency of other essential plant nutrients, particularly nitrogen and phosphorus . Biologically produced sulfur particles are naturally hydrophilic due to a biopolymer coating. This sulfur is therefore easier to disperse over the land ( via spraying as a diluted slurry ) , and results in a faster release

Sulfites, derived from burning sulfur, are heavily used to bleach paper. They are also used as preservatives in dried fruit.

Magnesium sulfate, better known as Epsom salts , can be used as a laxative, a bath additive, an exfoliant, a magnesium supplement for plants, or a desiccant.

### **6 . 1 . Specialized applications**

Sulfur is used as a light - generating medium in the rare lighting fixtures known as sulfur lamps.

### **6 . 2 . Historical applications**

In the late 18th century , furniture makers used molten sulfur to produce decorative inlays in their craft. Because of the sulfur dioxide produced during the process of melting sulfur, the craft of sulfur inlays was soon abandoned. Molten sulfur is some times still used for setting steel bolts into drilled concrete holes where high shock resistance is desired for floor-mounted equipment attachment points.

Pure powdered sulfur was also used as a medicinal tonic and laxative. Sulfur was also used in baths for people who had fits .

### **6 . 3 . Fungicide and pesticide**

Sulfur is one of the oldest fungicides and pesticides. Dusting sulfur, elemental sulfur in powdered form, is a common fungicide for grapes, strawberry, many vegetables and several other crops. It has a good efficacy against a wide range of powdery mildew diseases as well as black spot. In organic production, sulfur is the most important fungicide. It is the only fungicide used in organically farmed apple production against the main disease apple scab under colder conditions. Biosulfur ( biologically produced elemental sulfur with hydrophillic characteristics ) can be used well for these applications.

Standard - formulation dusting sulfur is applied to crops with a sulfur duster or from a dusting plane. Wettable sulfur is the commercial name for dusting sulfur formulated with additional ingredients to make it water soluble. It has similar applications, and is used as a fungicide against mildew and other mold-related problems with plants and soil.

Sulfur is also used as an " organic " ( i.e. " green " ) insecticide ( actually an acaricide ) against ticks and mites. A common method of use is to dust clothing or limbs with sulfur powder. Some livestock owners set out a sulfur salt block as a salt lick.

### **7 . Biological role ( Sulfur assimilation )**

Sulfur is an essential component of all living cells.

Inorganic sulfur forms a part of iron - sulfur clusters, and sulfur is the bridging ligand in the  $Cu_A$  site of cytochrome c oxidase, a basic substance involved in utilization of oxygen by all aerobic life .

Sulfur may also serve as chemical food source for some primitive organisms : some forms of bacteria use hydrogen sulfide (  $H_2S$  ) in the place of water as the electron donor in a primitive photosynthesis-like process in which oxygen is the electron receptor.

The photosynthetic green and purple sulfur bacteria and some chemolithotrophs use elemental oxygen to carry out such oxidization of hydrogen sulfide to produce elemental sulfur ( $S^0$ ), oxidation state = 0. Primitive bacteria which live around deep ocean volcanic vents oxidize hydrogen sulfide in this way with oxygen.

The so - called sulfur bacteria, by contrast, " breathe sulfate " instead of oxygen. They use sulfur as the electron acceptor, and reduce various oxidized sulfur compounds back into sulfide, often into hydrogen sulfide. They also can grow on a number of other partially oxidized sulfur compounds ( e. g. thiosulfates, thionates, polysulfides, sulfites ). The hydrogen sulfide produced by these bacteria is responsible for the smell of some intestinal gases and decomposition products.

Sulfur is a part of many bacterial defense molecules. For example, though sulfur is not a part of the lactam ring, it is a part of most beta lactam antibiotics, including the penicillins, cephalosporins, and monobactams.

Sulfur is absorbed by plants via the roots from soil as the sulfate ion and reduced to sulfide before it is incorporated into cysteine and other organic sulfur compounds.

Sulfur is regarded as secondary nutrient although plant requirements for sulfur are equal to and sometimes exceed those for phosphorus. However sulfur is recognized as one of the major nutrients essential for plant growth, root nodule formation of legumes and plants protection mechanisms. Sulfur deficiency has become widespread in many countries in Europe. Because atmospheric inputs of sulfur will continue to decrease, the deficit in the sulfur input/output is likely to increase, unless sulfur fertilizers are used.

In plants and animals the amino acids cysteine and methionine contain sulfur, as do all polypeptides, proteins, and enzymes which contain these amino acids. Homocysteine and taurine are other sulfur-containing acids which are similar in structure, but which are not coded for by DNA, and are not part of the primary structure of proteins. Glutathione is an important sulfur -containing tripeptide

which plays a role in cells as a source of chemical reduction potential in the cell, through its sulfhydryl ( - SH ) moiety. Many important cellular enzymes use prosthetic groups ending with - SH moieties to handle reactions involving acyl-containing biochemicals: two common examples from basic metabolism are coenzyme A and alpha - lipoic acid.

Disulfide bonds ( S - S bonds ) formed between cysteine residues in peptide chains are very important in protein assembly and structure. These strong covalent bonds between peptide chains give proteins a great deal of extra toughness and resiliency. For example, the high strength of feathers and hair is in part due to their high content of S - S bonds and their high content of cysteine and sulfur ( eggs are high in sulfur because are necessary for feather formation ) The high disulfide content of hair and feathers contributes to their indige stibility , and also their odor when burned .

### **7 . 1 . Traditional medical role for elemental sulfur**

In traditional medical skin treatment which predates modern era of scientific medicine, elemental sulfur has been used mainly as part of creams to alleviate various conditions such as psoriasis, eczema and acne. The mechanism of action is not known, although elemental sulfur does oxidize slowly to sulfurous acid, which in turn ( though the action of sulfite ) acts as a mild reducing and antibacterial agent.

### **8 . Precautions**

Carbon disulfide , carbon oxysulfide , hydrogen sulfide , and sulfur dioxide should all be handled with care .

Although sulfur dioxide is sufficiently safe to be used as a food additive in small amounts, at high concentrations it reacts with moisture to form sulfurous acid which in sufficient quantities may harm the lungs, eyes or other tissues. In organisms without lungs such as insects or plants, it otherwise prevents respiration.

Hydrogen sulfide is toxic. Although very pungent at first, it quickly deadens the sense of smell , so potential victims may be unaware of its presence until death or other symptoms occur .

### **8 . 1 . Environmental impact**

The burning of coal and / or petroleum by industry and power plants generates sulfur dioxide (  $\text{SO}_2$  ) , which reacts with atmospheric water and oxygen to produce sulfuric acid ( $\text{H}_2\text{SO}_4$ ). This sulfuric acid is a component of acid rain, which lowers the pH of soil and freshwater bodies, sometimes resulting in substantial damage to the environment and chemical weathering of statues and structures. Fuel standards increasingly require sulfur to be extracted from fossil fuels to prevent the formation of acid rain. This extracted sulfur is then refined and represents a large portion of sulfur production. In coal fired power plants, the flue gases are sometimes purified. In more modern power plants that use syngas the sulfur is extracted before the gas is burned .



# Hydrogen sulfide

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## 1 . Introduction ;

**Hydrogen sulfide** ( or **hydrogen sulphide** ) is the chemical compound with the formula H<sub>2</sub>S . This colorless, toxic and flammable gas is partially responsible for the foul odor of rotten eggs and flatulence.

It often results from the bacterial break down of sulfites in nonorganic matter in the absence of oxygen, such as in swamps and sewers ( anaerobic digestion ). It also occurs in volcanic gases , natural gas and some well waters . The odor of H<sub>2</sub>S is commonly misattributed to elemental sulfur , which is in fact odorless . Hydrogen sulfide has numerous names .

Other Names	Sulfuretted hydrogen ; sulfane ; Hydrogen Sulfide ; sulfur hydride ; sulfurated hydrogen ; hydro sulfuric acid ; sewer gas ; stink damp ; rotten egg gas ; brimstone
Molecular Formula	H <sub>2</sub> S
Molar Mass	34 g / mol
Appearance	Colorless gas.
Density	1.363 g / L , gas .
Melting Point	- 82.30 °C
Boiling Point	- 60.28 °C
Solubility in Water	0.4 g / 100 mL ( 20 °C ) 0.25 g / 100 mL ( 40 °C )
Solubility	Soluble in CS <sub>2</sub> , methanol, acetone ; Very soluble in alkanol amine
Acidity ( pK <sub>a</sub> )	6.89 19 ± 2
Refractive index ( n <sub>D</sub> )	1.000644 ( 0 °C )
Specific heat capacity , C	1.003 J / g K
EU classification	Highly Flammable ( F+ ) Very Toxic ( T+ ) Dangerous for the environment ( N )
Flash Point	Flammable gas
Auto ignition Temperature	260 °C
Explosive limits	4.3 – 46 %

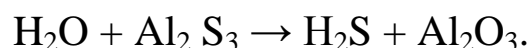
## 2 . Production

Hydrogen sulfide is obtained by its separation from sour gas, which is natural gas with high content of H<sub>2</sub>S. It can be produced by reacting hydrogen gas with molten elemental sulfur at about 450 °C. Hydrocarbons can replace hydrogen in this process .

Sulfate - reducing bacteria produce hydrogen sulfide under ambient conditions by the reduction of sulfate from elemental sulfur .

The standard lab preparation is to gently heat iron sulfide ( FeS ) with a strong acid in a Kipp generator.

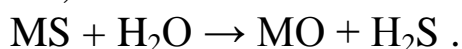
A less well known and more convenient alternative is to react aluminum sulfide with water :



Hydrogen Sulfide is also a by product of some reactions and caution should be used when production is likely as exposure can be fatal.

## 3 . Occurrence

Small amounts of hydrogen sulfide occur in crude petroleum but natural gas can contain up to 90 % . Volcanoes and hot springs emit some H<sub>2</sub>S , where it probably arises via the hydrolysis of sulfide minerals, i.e .



Normal concentration in clean air is about 0.0001- 0.0002 ppm .

About 10 % of total global emissions of H<sub>2</sub>S is due to human activity . By far the largest industrial route to H<sub>2</sub>S occurs in petroleum refineries: the hydro desulfurization process liberates sulfur from petroleum by the action of hydrogen. The resulting H<sub>2</sub>S is converted to elemental sulfur by partial combustion via the Claus process, which is a major source of elemental sulfur. Other anthropogenic sources of hydrogen sulfide include coke ovens , paper mills ( using the sulfate method ) , and tanneries. H<sub>2</sub>S arises from virtually anywhere where

elemental sulfur comes into contact with organic material, especially at high temperatures .

Hydrogen sulfide can be present naturally in well water. In such cases, ozone is often used for its removal. An alternative method uses a filter with manganese dioxide . Both methods oxidize sulfides to less toxic sulfates.

## **4 . Uses**

### **4 . 1 . Production of thio organic compounds**

Several organo sulfur compounds are produced using hydrogen sulfide . These include methane thiol , ethane thiol, and thio glycolic acid .

### **4 . 2 . Alkali metal sulfides**

Upon combining with alkali metal bases, hydrogen sulfide converts to alkali hydro sulfides such as sodium hydro sulfide and sodium sulfide, which are used in the degradation of biopolymers. The depilation of hides and the delignification of pulp by the Kraft process both are effected by alkali sulfides.

### **4 . 3 . In analytical chemistry**

Hydrogen sulfide used to have importance in analytical chemistry for well over a century, in the qualitative inorganic analysis of metal ions. For such small - scale laboratory use,  $H_2S$  was made as needed in a Kipp generator by reaction of sulfuric acid (  $H_2SO_4$  ) with ferrous sulfide  $Fe S$  . Kipp generators were superseded by the use of thioacetamide, an organic solid that converts in water to  $H_2S$ . In these analyses, heavy metal (and nonmetal) ions (e.g.  $Pb (II)$ ,  $Cu (II)$ ,  $Hg (II)$ ,  $As (III)$ ) are precipitated from solution upon exposure to  $H_2S$ . The components of the resulting precipitate redissolve with some selectivity.

#### **4 . 4 . A precursor to metal sulfides**

As indicated above, many metal ions react with hydrogen sulfide to give the corresponding metal sulfides. This conversion is widely exploited. In the purification of metal ores by flotation, mineral powders are often treated with hydrogen sulfide to enhance the separation. Metal parts are some times passivated with hydrogen sulfide. Catalysts used in hydro desulfurization are routinely activated with hydrogen sulfide, and the behavior of metallic catalysts used in other parts of a refinery is also modified using hydrogen sulfide .

#### **4 . 5 . Miscellaneous applications**

Hydrogen sulfide is also used in the separation of deuterium oxide, i.e. heavy water, from normal water via the Girdler Sulfide process.

#### **4 . 6 . Hibernation**

Scientists have discovered that hydrogen sulfide can induce hibernation in mice<sup>[4]</sup>, but not pigs , casting doubt on the effectiveness of the process in larger mammals.

### **5 . Safety**

Hydrogen sulfide is a highly toxic and flammable gas. Being heavier than air, it tends to accumulate at the bottom of poorly ventilated spaces. Although very pungent at first, it quickly deadens the sense of smell, so potential victims may be unaware of its presence until it is too late. For safe handling procedures, a hydrogen sulfide material safety data sheet ( MSDS ) should be consulted .

### **6 . Toxicity**

Hydrogen sulfide is considered a broad - spectrum poison, meaning that it can poison several different systems in the body, although the nervous system is most affected. The toxicity of H<sub>2</sub>S is comparable with that of hydrogen cyanide. It forms a complex bond with iron in the mitochondrial cyto chrome enzymes, thereby blocking oxygen from binding and stopping cellular respiration. Since

hydrogen sulfide occurs naturally in the environment and the gut, enzymes exist in the body capable of detoxifying it by oxidation to ( harmless ) sulfate. Hence, low levels of sulfide may be tolerated indefinitely .

At some threshold level, the oxidative enzymes will be overwhelmed. This threshold level is believed to average around 300 - 350 ppm. Many personal safety gas detectors, such as those used by utility, sewage and petrochemical workers, are set to alarm at as low as 5 to 10 ppm and to go into high alarm at 15 ppm .

An interesting diagnostic clue of extreme poisoning by H<sub>2</sub>S is the discoloration of copper coins in the pockets of the victim. Treatment involves immediate inhalation of amyl nitrite, injections of sodium nitrite, inhalation of pure oxygen, administration of bronchodilators to overcome eventual bronchospasm , and in some cases hyperbaric oxygen therapy ( HBO ) . HBO therapy has anecdotal support and remains controversial .

Exposure to lower concentrations can result in eye irritation, a sore throat and cough, nausea, shortness of breath, and fluid in the lungs. These symptoms usually go away in a few weeks. Long – term , low - level exposure may result in fatigue, loss of appetite, headaches, irritability, poor memory, and dizziness. Chronic exposures to low level H<sub>2</sub>S ( around 2 ppm ) has been implicated in increased miscarriage and reproductive health issues amongst Russian and Finnish wood pulp workers, but the reports hadn't ( as of circa 1995 ) been replicated. Higher concentrations of 700 - 800 ppm tend to be fatal.

- 0.0047 ppm is the recognition threshold, the concentration at which 50 % of humans can detect the characteristic odor of hydrogen sulfide , normally described as resembling " a rotten egg " .
- Less than 10 ppm has an exposure limit of 8 hours per day.
- 10 - 20 ppm is the borderline concentration for eye irritation.
- 50 - 100 ppm leads to eye damage.

- At 150 - 250 ppm the olfactory nerve is paralyzed after a few inhalations, and the sense of smell disappears, often together with awareness of danger,
- 320 - 530 ppm leads to pulmonary edema with the possibility of death.
- 530 - 1000 ppm causes strong stimulation of the central nervous system and rapid breathing, leading to loss of breathing ;
  - 800 ppm is the lethal concentration for 50% of humans for 5 minutes exposure ( LC50 ) .
- Concentrations over 1000 ppm cause immediate collapse with loss of breathing, even after inhalation of a single breath.

Hydrogen sulfide was used by the British as a chemical agent during World War One . It was not considered to be an ideal war gas, but while other gasses were in short supply it was used on two occasions in 1916 .

A series of suicide cases in Japan in which the victims killed themselves by producing toxic hydrogen sulfide fumes by mixing common household cleaning products have highlighted the danger posed by commonly used substances and prompted censorship of internet sites who posted advice for aspiring suicides .

## **7 . Function in the body**

Hydrogen sulfide is produced in small amounts by some cells of the mammalian body and has a number of biological functions. It is produced from cysteine by various enzymes. It acts as a vasodilator and is also active in the brain, where it increases the response of the NMDA receptor and facilitates long term potentiation , which is involved in the formation of memory. Eventually the gas is converted to sulfites and further oxidized to thiosulfate and sulfate. Due to its effects similar to NO (without its potential to form peroxides by interacting with superoxide), hydrogen sulfide is now recognized as a potential cardio protective agent . Vaso activity of garlic is caused by catabolism of the poly sulfide group in allicin to H<sub>2</sub>S , a reaction which could depend on reduction mediated by glutathione . In trisomy

21 ( the most common form of Down syndrome ) the body produces an excess of hydrogen sulfide .

## **8 . Induced hibernation**

In 2005 it was shown that mice can be put into a state of suspended animation-like hypothermia by applying a low dosage of hydrogen sulfide ( 81 ppm  $H_2S$  ) in the air. The breathing rate of the animals sank from 120 to 10 breaths per minute and their temperature fell from 37 ° C to just 2 ° C above ambient temperature (in effect, they had become cold- blooded). The mice survived this procedure for 6 hours and afterwards showed no negative health consequences . In 2006 it was shown that the blood pressure of mice treated in this fashion with hydrogen sulfide did not significantly decrease .

Such hibernation occurs naturally in many mammals and also in toads, but not in mice. ( Mice can fall into a state called clinical torpor when food shortage occurs ) . If the  $H_2S$  - induced hibernation can be made to work in humans, it could be useful in the emergency management of severely injured patients, and in the conservation of donated organs. In 2008, hypothermia induced by hydrogen sulfide for 48 hours was shown to reduce the extent of brain damage caused by experimental stroke in rats .

As mentioned above, hydrogen sulfide binds to cyto chrome oxidase and thereby prevents oxygen from binding, which leads to the dramatic slowdown of metabolism. Animals and humans naturally produce some hydrogen sulfide in their body ; researchers have proposed that the gas is used to regulate metabolic activity and body temperature, which would explain the above findings .

However, a 2008 study failed to reproduce the effect in pigs, concluding that the effects seen in mice were not present in larger mammals .

## **9 . Participant in the sulfur cycle**

Hydrogen sulfide is a central participant in the sulfur cycle, the biogeochemical cycle of sulfur on Earth. As mentioned above, sulfur -



reducing and sulfate - reducing bacteria derive energy from oxidizing hydrogen or organic molecules in the absence of oxygen by reducing sulfur or sulfate to hydrogen sulfide. Other bacteria liberate hydrogen sulfide from sulfur - containing amino acids .

Several groups of bacteria can use hydrogen sulfide as fuel, oxidizing it to elemental sulfur or to sulfate by using dissolved oxygen, metal oxides ( e.g. Fe oxyhydroxides and Mn oxides ) or nitrate as oxidant . The purple sulfur bacteria and the green sulfur bacteria use hydrogen sulfide as electron donor in photosynthesis, thereby producing elemental sulfur. ( In fact , this mode of photosynthesis is older than the mode of cyano bacteria, algae and plants which uses water as electron donor and liberates oxygen ) .

### **10 . H<sub>2</sub>S implicated in mass extinctions**

Hydrogen sulfide has been implicated in some of the several mass extinctions that have occurred in the Earth's past. The Permian mass extinction ( some times known as the " Great Dying " ) may have been caused by hydrogen sulfide. Organic residues from these extinction boundaries indicate that the oceans were anoxic ( oxygen depleted ) and had species of shallow plankton that metabolized H<sub>2</sub>S. The formation of H<sub>2</sub>S may have been initiated by massive volcanic eruptions, which emitted CO<sub>2</sub> and methane into the atmosphere which warmed the oceans, lowering their capacity to absorb oxygen which would otherwise oxidize H<sub>2</sub>S. The increased levels of hydrogen sulfide could have killed oxygen-generating plants as well as depleted the ozone layer causing further stress. Small H<sub>2</sub>S blooms have been detected in modern times in the Dead Sea and in the Atlantic ocean off the coast of Namibia .

## Sulfur Oxides

**Sulfur oxide (SO<sub>x</sub>)** refers to one or more of the following :

- 1 Lower sulfur oxides ( S<sub>n</sub>O , S<sub>7</sub>O<sub>2</sub> and S<sub>6</sub>O<sub>2</sub> )
- 2 Sulfur monoxide ( SO )
- 3 Sulfur dioxide ( SO<sub>2</sub> )
- 4 Sulfur trioxide ( SO<sub>3</sub> )
- 5 Higher sulfur oxides ( SO<sub>3+x</sub> where 0 < x ≤ 1)

# 1 . Lower sulfur oxides

## Structure of S<sub>2</sub>O

The **lower sulfur oxides** are a group of chemical compounds consisting of :

- SO , sulfur monoxide and its dimer S<sub>2</sub>O<sub>2</sub>
- Di sulfur monoxide, S<sub>2</sub>O
  - n sulfur monoxides , S<sub>n</sub>O , based on cyclic S<sub>n</sub> rings where n is 5 - 10
  - S<sub>7</sub> O<sub>2</sub>
  - polymeric oxides, poly sulfur oxides some times termed PSO ' s

Interest in the lower sulfur oxides has increased because of the need to under stand terrestrial atmospheric sulfur pollution and the finding that the extraterrestrial atmospheres of Io, one of Jupiters moons, and Venus contain significant amounts of sulfur oxides. Some compounds reported by early workers such as the blue " sesquioxide" , S<sub>2</sub> O<sub>3</sub>, formed by dissolving sulfur in liquid SO<sub>3</sub> appears to be a mixture of poly sulfate salts of the S<sub>4</sub><sup>2+</sup> and S<sub>8</sub><sup>2+</sup> ions .

## Sulfur monoxide , monomer ( SO ) and dimer ( S<sub>2</sub>O<sub>2</sub> )

These are stable molecules that have been trapped at low temperature .

## Di sulfur monoxide , S<sub>2</sub>O

S<sub>2</sub> O has a non linear structure , like sulfur dioxide, SO<sub>2</sub>, ozone, O<sub>3</sub> and S<sub>3</sub>. The S - S bond is 188.4pm, the S - O bond is 146.5 pm and the S S O angle is 117.88. The two dipole moment components are  $\mu_a = 0.875$  D and  $\mu_b = 1.18$  D

## Tri sulfur monoxide, S<sub>3</sub>O

This unstable neutral molecule has been found in the gas phase using neutralization - reionization mass spectrometry. Both ring and chain structures were found .

### **S<sub>n</sub> O :**

A number of monoxides S<sub>n</sub> O are known where n = 5 - 10 , where the oxygen is bonded to one member of the S<sub>n</sub> sulfur ring . They can be prepared by oxidizing the related cyclo - S<sub>n</sub> elemental sulfur rings ( these are allotropes of sulfur ) with tri fluoro per oxo acetic acid , C F<sub>3</sub> C (O) OOH . The compounds are all dark coloured and decompose to give sulfur and sulfur dioxide .

### **S<sub>6</sub> O<sub>2</sub> , S<sub>7</sub> O<sub>2</sub> :**

S<sub>6</sub> O<sub>2</sub> and S<sub>7</sub> O<sub>2</sub> can be prepared by oxidizing cyclo - S<sub>6</sub> and cyclo - S<sub>7</sub> respectively, with tri fluoro per oxo acetic acid, although crystalline S<sub>6</sub> O<sub>2</sub> has not been isolated .

### **Polymeric sulfur oxides**

These have been studied to determine whether they are a factor in the observed colour of Io .

## 2 . Sulfur monoxide ( S O , S<sub>2</sub>O<sub>2</sub> )

### 1 . Introduction :

**Sulfur monoxide** is a chemical compound with formula SO . It is an unstable species only found in the gas phase where it is in equilibrium with a dimeric form, S<sub>2</sub>O<sub>2</sub> ( some times called di sulfur di oxide ) which can be represented as O S S O. Sulfur monoxide has been detected around Io , one of Jupiter's moons , both in the atmosphere ' and in the plasma torus . It has also been found in the atmosphere of Venus , in the Hale - Bopp comet and in interstellar space .

### 2 . Structure and bonding :

The SO molecule has a triplet ground state similar to dioxygen, O<sub>2</sub> , with two unpaired electrons . The S – O bond length of 148.1 pm is similar to that found in lower sulfur oxides ( e.g. S<sub>8</sub>O, S – O = 148 pm ) but is longer than the S – O bond in gaseous S<sub>2</sub>O ( 146 pm ) , SO<sub>2</sub> ( 143.1 pm ) and SO<sub>3</sub> ( 142 pm ) .

Disulfur dioxide , S<sub>2</sub>O<sub>2</sub>, is a dimer, that is, a molecule consisting of two identical simpler molecules. It is a planar molecule (a molecule that has two dimensional characteristics) with C<sub>2v</sub> symmetry. Two SO units are joined via the sulfur atoms and the oxygen atoms in a *cis* configuration. The S - O bond length is 145.8 pm, shorter than in the monomer, and the S - S bond length is 202.45 pm. The OSS angle is 112.7°. It has a dipole moment,  $\mu = 3.17$  D .

### 3 . Production and reactions :

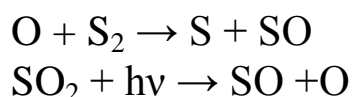
In the laboratory sulfur monoxide be made reacting sulfur dioxide with sulfur vapour in a glow discharge and in single bubble sono luminescence of concentrated sulfuric acid containing some dissolved noble gas

Production of the transient SO molecule as a reagent in organic syntheses has been investigated. Research has centered on using compounds that decompose under reaction conditions to "

extrude " SO . Examples include the decomposition of the relatively simple molecule thiirane 1- oxide :



as well as more complex examples e.g. a tri sulfide oxide ,  $\text{C}_{10}\text{H}_6\text{S}_3\text{O}$  . On Io the production of SO is believed to be both volcanic and also photochemical. The principal photochemical reactions proposed are :



The SO molecule is thermodynamically unstable . The transient SO molecule can be trapped by the formation of transition metal complexes .As a ligand SO can bond in a number different ways:

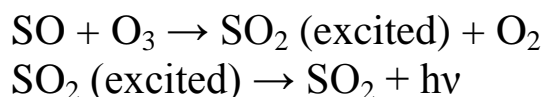
- $\sigma$  donation forming a bent bond with the metal
- bridging across 2 or 3 metal centres via sulfur
- edge on bridging

SO inserts into alkenes, alkynes and dienes producing molecules with three membered rings containing sulfur .

The triplet ground state molecule with two unpaired electrons can be excited by near infrared light to the singlet state with no unpaired electrons. The singlet state is believed be more reactive than the ground state triplet state, in the same way that singlet oxygen is more reactive than the triplet ground state . Sulfur monoxide may have some biological activity, the formation of transient SO in porcine coronary artery has been inferred from the reaction products .

#### 4 . Uses :

A chemilumines conce detector for sulfur has been reported that is based on the reactions :



### 3 . Sulfur dioxide ( SO<sub>2</sub> )

#### *Contents*

- 1 Introduction
- 2 Preparation
- 3 Structure and bonding
- 4 Reactions
- 5 Uses
  - 5.1 Precursor to sulfuric acid
  - 5.2 As a preservative
  - 5.3 In winemaking
  - 5.4 As a reducing agent
  - 5.5 Biochemical and biomedical roles
  - 5.6 As a refrigerant
  - 5.7 As a reagent and solvent in the laboratory
- 6 Emissions
- 7 Temperature dependence of aqueous solubility
- 8 Safety

#### **1 . Introduction :**

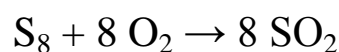
**Sulfur dioxide** ( also **sulphur dioxide** ) is the chemical compound with the formula SO<sub>2</sub> . It is produced by volcanoes and in various industrial processes. Since coal and petroleum often contain sulfur compounds, their combustion generates sulfur dioxide. Further oxidation of SO<sub>2</sub> , usually in the presence of a catalyst such as NO<sub>2</sub> , forms H<sub>2</sub>SO<sub>4</sub> , and thus acid rain . This is one of the causes for concern over the environmental impact of the use of these fuels as power sources .

Other Names	Sulfur ( IV ) oxide Sulfurous anhydride
Molecular Formula	SO <sub>2</sub>
Molar Mass	64 g / mol
Appearance	Colorless gas
Density	2.551 g / L ( gas )

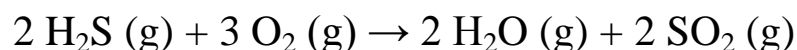
	1.46 g / cm <sup>3</sup> ( liquid , -10 ° C )
Melting Point	-75.5 °C
Boiling Point	-10.0 °C
Solubility in water	22.97 g / 100 mL ( 0 °C ) 11.58 g / 100 mL ( 20 °C ) 9.4 g / 100 mL ( 25 °C )
Solubility	Very soluble in acetone , methyl isobutyl ketone , acetic acid , alcohol soluble in sulfuric acid
Acidity ( pK <sub>a</sub> )	1.81
Viscosity	0.403 cP ( 0 ° C )
Molecular shape	Bent , C <sub>2v</sub> O – S – O = 119 °
Dipole Moment	1.62 D
EU classification	Toxic ( T ) Corrosive ( C )
Flash point	Non - flammable
LD <sub>50</sub>	3000 ppm ( 30 min inhaled, mouse)

## 2 . Preparation :

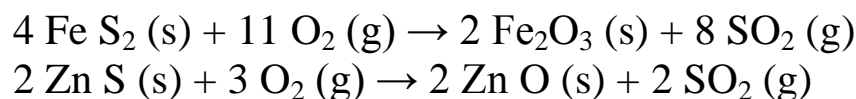
Sulfur dioxide can be prepared by burning sulfur:



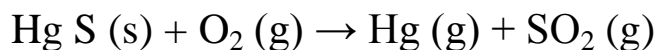
The combustion of hydrogen sulfide and organo sulfur compounds proceeds similarly.



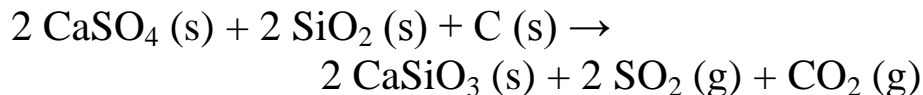
The roasting of sulfide ores such as pyrites, sphalerite ( zinc blende ) , and cinnabar ( mercury sulfide ) also releases SO<sub>2</sub> :







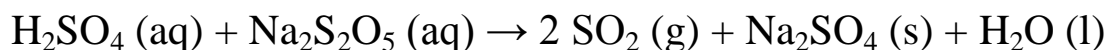
Sulfur dioxide is a by - product in the manufacture of calcium silicate cement :  $\text{Ca SO}_4$  is heated with coke and sand in this process :



Action of hot sulfuric acid on copper turnings produces sulfur dioxide .



It can also be prepared with sodium meta bisulfite :



This is an exothermic reaction.

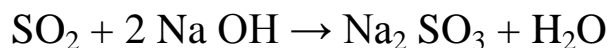
### 3 . Structure and bonding :

$\text{SO}_2$  is a bent molecule with  $C_{2v}$  symmetry point group. In terms of electron-counting formalisms, the sulfur atom has an oxidation state of +4, a formal charge of 0, and is surrounded by 5 electron pairs and can be described as a hypervalent molecule. From the perspective of molecular orbital theory, most of these valence electrons are engaged in S – O bonding.

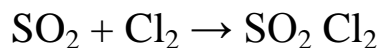
The S – O bonds are shorter in  $\text{SO}_2$  ( 143.1 pm ) than in sulfur monoxide, SO (148.1 pm), whereas the O – O bonds are longer in ozone ( 127.8 pm ) than in di oxygen ,  $\text{O}_2$  ( 120.7 pm ) . The mean bond energy is greater in  $\text{SO}_2$  ( 548 kJ / mol ) than in SO ( 524 kJ / mol ) , where as it is less in  $\text{O}_3$  ( 297 kJ / mol ) than in  $\text{O}_2$  ( 490 kJ / mol ) . These pieces of evidence lead chemists to conclude that the S–O bonds in sulfur dioxide have a bond order of at least 2, unlike the O – O bonds in ozone, which have a bond order of 1.5 .

### 4 . Reactions :

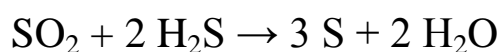
basic solutions with sulfur dioxide affords sulfite salts :



Featuring sulfur in the + 4 oxidation state, sulfur dioxide is a reducing agent. It is oxidized by halogens to give the sulfonyl halides, such as sulfonyl chloride :



How ever, on rare occasions, it can also act as an oxidizing agent: in the Claus process, sulfur dioxide is reduced by hydrogen sulfide to give elemental sulfur :



Sulfur dioxide can bind to metal ions as a ligand, typically where the transition metal is in oxidation state 0 or +1.<sup>[4]</sup> Many different bonding modes (geometries) are recognized, but in most cases the ligand is mono dentate, attached to the metal through sulfur, which can be either planar and pyramidal  $\eta^1$  .

## **5 . Uses :**

### **5 . 1 . Precursor to sulfuric acid**

Sulfur dioxide is an intermediate in the production of sulfuric acid, being converted to sulfur trioxide, and then to oleum, which is made into sulfuric acid. Sulfur dioxide for this purpose is made when sulfur combines with oxygen. The method of converting sulfur dioxide to sulfuric acid is called the contact process. Several billion kilograms are produced annually for this purpose.

### **5 . 2 . As a preservative**

Sulfur dioxide is sometimes used as a preservative for dried apricots and other dried fruits owing to its antimicrobial properties, and it is sometimes called E220 when used in this way. As a preservative, it maintains the appearance of the fruit and prevents rotting. Its presence gives the fruit a distinctive chemical taste .

### **5 . 3 . In Wine making**

Sulfur dioxide is an important compound in winemaking, and is designated as parts per million in wine, E number: E220 . It is present even in so - called unsulphurated wine at concentrations of up to 10 milligrams per liter . It serves as an antibiotic and antioxidant, protecting wine from spoilage by bacteria and oxidation. It also helps to keep volatile acidity at desirable levels. Sulfur dioxide is responsible for the words "contains sulfites" found on wine labels. Wines with SO<sub>2</sub> concentrations below 10 ppm do not require "contains sulfites" on the label by US and EU laws. The upper limit of SO<sub>2</sub> allowed in wine is 350 ppm in the US, in the EU is 160 ppm for red wines and 210 ppm for white and rosé wines. In low concentrations SO<sub>2</sub> is mostly undetectable in wine, but at over 50ppm, SO<sub>2</sub> becomes evident in the nose and taste of wine .

SO<sub>2</sub> is also a very important element in winery sanitation. Wineries and equipment must be kept clean, and because bleach cannot be used in a winery, a mixture of SO<sub>2</sub>, water, and citric acid is commonly used to clean and sanitize equipment. Compounds of ozone ( O<sub>3</sub> ) are now used extensively as cleaning products in wineries due to their efficiency, and because these compounds do not affect the wine or equipment .

### **5 . 4 . As a Reducing agent :**

Sulfur dioxide is also a good reductant . In the presence of water, sulfur dioxide is able to decolorize substances. Specifically it is a useful reducing bleach for papers and delicate materials such as clothes. This bleaching effect normally does not last very long. Oxygen in the atmosphere reoxidizes the reduced dyes, restoring the color. In municipal waste water treatment sulfur dioxide is used to treat chlorinated wastewater prior to release. Sulfur dioxide reduces free and combined chlorine to chloride.

### **5 . 5 . Biochemical and biomedical roles :**

Sulfur dioxide is toxic in large amounts. It or its conjugate base bisulfite is produced biologically as an intermediate in both sulfate-

reducing organisms and in sulfur oxidizing bacteria as well. Sulfur dioxide has no role in mammalian biology. Sulfur dioxide blocks nerve signals from the pulmonary stretch receptors ( PSR's ) and abolishes the Hering - Breuer inflation reflex .

### **5 . 6 . As a Refrigerant :**

Being easily condensed and possessing a high heat of evaporation, sulfur dioxide is a candidate material for refrigerants. Prior to the development of freons, sulfur dioxide was used as a refrigerant in home refrigerators.

### **5 . 7 . As a Reagent and solvent in the laboratory :**

Sulfur dioxide is a versatile inert solvent that has been widely used for dissolving highly oxidizing salts. It is also used occasionally as a source of the sulfonyl group in organic synthesis. Treatment of aryl diazonium salts with sulfur dioxide and cuprous chloride affords the corresponding aryl sulfonyl chloride .

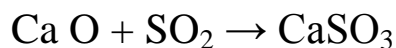
### **6 . Emissions :**

According to the United States Environmental Protection Agency ( EPA ) ( as presented by the *2002 World Almanac* or in chart form ) , the following amount of sulfur dioxide was released in the U.S. per year, measured in thousands of short tons :

<b>* 1999</b>	18 ,867
<b>* 1998</b>	19 ,491
<b>* 1997</b>	19 ,363
<b>* 1996</b>	18 ,859
<b>* 1990</b>	23 ,678
<b>* 1980</b>	25 ,905
<b>* 1970</b>	31 ,161

Due largely to the US EPA 's Acid Rain Program, the U.S. has witnessed a 33 percent decrease in emissions between 1983 and 2002.

This improvement resulted from flue gas desulfurization, a technology that enables SO<sub>2</sub> to be chemically bound in power plants burning sulfur - containing coal or oil. In particular, calcium oxide (lime) reacts with sulfur dioxide to form calcium sulfite :



Aerobic oxidation of the Ca SO<sub>3</sub> gives Ca SO<sub>4</sub>, gypsum. Most gypsum sold in Europe comes from flue gas desulfurization.

New fuel additive catalysts, such as ferox, are being used in gasoline and diesel engines in order to lower the emission of sulfur oxide gases into the atmosphere. This is also done by forcing the sulfur into stable mineral salts and mixed mineral sulfates as opposed to sulfuric acid and sulfur oxides.

As of 2006, China is the world's largest sulfur dioxide polluter, with 2005 emissions estimated to be 25.49 million tons. This amount represents a 27 % increase since 2000, and is roughly comparable with U.S. emissions in 1980.

### 7 . Temperature dependence of aqueous solubility :

22 g / 100 ml ( 0 ° C )	15 g / 100 ml ( 10 ° C )
11 g / 100 ml ( 20 ° C )	9.4 g / 100 ml ( 25 ° C )
8 g / 100 ml ( 30 ° C )	6.5 g / 100 ml ( 40 ° C )
5 g / 100 ml ( 50 ° C )	4 g / 100 ml ( 60 ° C )
3.5 g / 100 ml ( 70 ° C )	3.4 g / 100 ml ( 80 ° C )
3.5 g / 100 ml ( 90 ° C )	3.7 g / 100 ml ( 100 ° C )

The values are tabulated for 101.3 kPa partial pressure of SO<sub>2</sub>. Solubility of gas in a liquid depends on the gas partial pressure according to Henry's law. The solubility is given for "pure water", i.e., water that contains only SO<sub>2</sub> in the amount at equilibrium with the gas phase. This " pure water " is going to be acidic. The solubility of SO<sub>2</sub> in neutral (or alkaline) water is generally going to be higher because

of the pH - dependent speciation of  $\text{SO}_2$  in the solution with the production of bisulfite and some sulfite ions.

### **8 . Safety :**

Sulfur dioxide is an allergen to which some consumers are sensitive.  $\text{SO}_2$  is associated with increased respiratory symptoms and disease, difficulty in breathing, and premature death .

## 4 . Sulfur trioxide ( SO<sub>3</sub> )

### Contents :

- 1 Introduction
- 2 Structure and bonding
- 3 Chemical reactions
- 4 Preparation
- 5 Structure of solid SO<sub>3</sub>
- 6 Application
- 7 In popular culture

### 1 . Introduction :

**Sulfur trioxide** ( also spelled **sulphur trioxide** ) is the chemical compound with the formula SO<sub>3</sub> . In the gaseous form, this species is a significant pollutant, being the primary agent in acid rain. It is prepared on massive scales as a precursor to sulfuric acid .

Other Names	Sulfuric anhydride Sulfan
Molecular Formula	SO <sub>3</sub>
Molar mass	80. g / mol
Density	1.92 g / cm <sup>3</sup> , liquid
Melting Point	16.9 ° C
Boiling Point	45 ° C
Solubility in Water	Hydrolyses
Std enthalpy of formation $\Delta_f H^\ominus_{298}$	- 397.77 kJ / mol
Standard molar entropy $S^\ominus_{298}$	256.77 J K <sup>-1</sup> mol <sup>-1</sup>
EU classification	Corrosive ( C )
Flash point	Non - flammable

## 2 . Structure and bonding :

Gaseous SO<sub>3</sub> is a trigonal planar molecule of D<sub>3h</sub> symmetry, as predicted by VSEPR theory.

In terms of electron - counting formalisms , the sulfur atom has an oxidation state of + 6 , a formal charge of 0 , and is surrounded by 6 electron pairs. From the perspective of molecular orbital theory, most of these electron pairs are non-bonding in character, as is typical for hypervalent molecules.

Sulfur trioxide also exhibits hybridization.

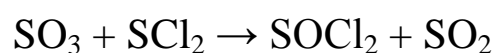
## 3 . Chemical reactions :

SO<sub>3</sub> is the anhydride of H<sub>2</sub>SO<sub>4</sub> . Thus , the following reaction occurs :



The reaction occurs both rapidly and exothermically, too violently to be used in large - scale manufacturing . At or above 340 °C , sulfuric acid, sulfur trioxide , and water coexist in significant equilibrium concentrations .

Sulfur trioxide also reacts with sulfur dichloride to yield the useful reagent, thionyl chloride .



SO<sub>3</sub> is a strong Lewis acid readily forming crystalline complexes with pyridine, dioxane and tri methyl amine which can be used as sulfonating agents .

## 4 . Preparation :

Sulfur trioxide can be prepared in the laboratory by the two - stage pyrolysis of sodium bisulfate . Sodium pyro sulfate is an intermediate product :



1. Dehydration at 315°C :



2. Cracking at 460°C :



This method will work for other metal bi sulfates , the controlling factor being the stability of the intermediate pyro sulfate salt.

Industrially  $\text{SO}_3$  is made by the contact process. Sulfur dioxide, generally made by the burning of sulfur or iron pyrite (a sulfide ore of iron), is first purified by electrostatic precipitation. The purified  $\text{SO}_2$  is then oxidized by atmospheric oxygen at between 400 and 600 °C over a catalyst consisting of vanadium pent oxide (  $\text{V}_2\text{O}_5$  ) activated with potassium oxide  $\text{K}_2\text{O}$  on kieselguhr or silica support. Platinum also works very well but is too expensive and is poisoned ( rendered ineffective ) much more easily by impurities.

The majority of sulphur trioxide made in this way is converted into sulfuric acid not by the direct addition of water, with which it forms a fine mist, but by absorption in concentrated sulfuric acid and dilution with water of the produced oleum.

## 5 . Structure of solid $\text{SO}_3$ :

The nature of solid  $\text{SO}_3$  is a surprisingly complex area because of structural changes caused by traces of water. Upon condensation of the gas, absolutely pure  $\text{SO}_3$  condenses into a trimer, which is often called  $\gamma - \text{SO}_3$ . This molecular form is a colorless solid with a melting point of 16.8 °C. It adopts a cyclic structure described as  $[\text{S} (= \text{O})_2 (\mu - \text{O})]_3$ .

If  $\text{SO}_3$  is condensed above 27 °C, then  $\alpha - \text{SO}_3$  forms, which has a melting point of 62.3°C.  $\alpha - \text{SO}_3$  is fibrous in appearance, like asbestos (with which it has no chemical relationship). Structurally, it is the polymer  $[\text{S} (= \text{O})_2 (\mu - \text{O})]_n$ . Each end of the polymer is terminated with OH groups ( hence  $\alpha - \text{SO}_3$  is not really a form of

$\text{SO}_3$  ) .  $B - \text{SO}_3$  , like the alpha form, is fibrous but of different molecular weight, consisting of an hydroxyl - capped polymer, but melts at  $32.5^\circ\text{C}$ . Both the gamma and the beta forms are metastable, eventually converting to the stable alpha form if left standing for sufficient time. This conversion is caused by traces of water .

Relative vapor pressures of solid  $\text{SO}_3$  are  $\alpha < \beta < \gamma$  at identical temperatures, indicative of their relative molecular weights. Liquid sulfur trioxide has vapor pressure consistent with the gamma form. Thus heating a crystal of  $\alpha - \text{SO}_3$  to its melting point results in a sudden increase in vapor pressure, which can be forceful enough to shatter a glass vessel in which it is heated. This effect is known as the " alpha explosion " .

$\text{SO}_3$  is aggressively hygroscopic. In fact , the heat of hydration is sufficient that mixtures of  $\text{SO}_3$  and wood or cotton can ignite. In such cases ,  $\text{SO}_3$  dehydrates these carbohydrates .

## **6 . Application :**

In process plant environment,  $\text{SO}_3$  gas is mixed into flue gas from combustion to make the ashes charged up before flowing through electrostatic precipitators. The electrostatic precipitators will then trap the ashes, making cleaner process emission possible.

## **7 . In popular culture :**

Sulfur trioxide is mentioned in the *Emergency!* episode " The Old Engine Cram " which aired in the United States on 20 September 1975.

## 5 . Higher Sulfur Oxides

**Higher sulfur oxides** are a group of chemical compounds with the formula  $\text{SO}_{3+x}$  where x lies between 0 and 1. They contain peroxy ( O – O ) groups and the oxidation state of sulfur is + 6 as in  $\text{SO}_3$  . Mono meric  $\text{SO}_4$  can be isolated at low temperatures (below  $78^\circ\text{K}$ ) following the reaction of  $\text{SO}_3$  and atomic oxygen or photolysis of  $\text{SO}_3$  / ozone mixtures. The favoured structure is :

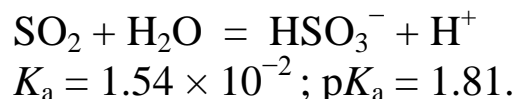
Colourless polymeric condensates are formed in the reaction of gaseous  $\text{SO}_3$  or  $\text{SO}_2$  with  $\text{O}_2$  in a silent electric discharge. The structure of the polymers is based on  $\beta$  -  $\text{SO}_3$  ( one of the three forms of solid  $\text{SO}_3$ ) with oxide bridges ( – O – ) replaced randomly by peroxide bridges ( – O – O – ). As such these compounds are non - stoichiometric.

# Sulfurous acid

## 1 . Introduction :

**Sulfurous acid** is the chemical compound with the formula  $\text{H}_2\text{SO}_3$  . There is no evidence that sulfurous acid exists in solution , but the molecule has been detected in the gas phase . The conjugate bases of this elusive acid are, however, common anions , bisulfite ( or hydrogen sulfite ) and sulfite.

Raman spectra of solutions of sulfur dioxide in water show only signals due to the  $\text{SO}_2$  molecule and the bisulfite ion,  $\text{HSO}_3^-$  . The intensities of the signals are consistent with the following equilibrium:



Aqueous solutions of sulfur dioxide, which sometimes are referred to as sulfurous acid are used as reducing agents and as disinfectants, as are solutions of bisulfite and sulfite salts. They are also mild bleaches , and are used for materials which may be damaged by chlorine - containing bleaches .

Molecular Formula	$\text{H}_2 \text{SO}_3$
Molar Mass	82 g / mol
EU Classification	Corrosive (C)
Flash Point	Non - flammable

# Sulfite

## Contents

- 1 Introduction
- 2 Structure
- 3 Commercial uses
  - 3.1 Wine
  - 3.2 Other food
- 4 Health risks

### 1 . Introduction ;

**Sulfites** ( also **sulphites** ) are compounds that contain the sulfite ion  $\text{SO}_2^{-3}$  ( additive IUPAC name : **tri oxido sulfate ( 2 - )** ) . The sulfite ion is the conjugate base of sulfurous acid. Although the acid itself is elusive, its salts are widely used .

### 2 . Structure

The structure of the sulfite anion can be described with three equivalent resonance structures. In each resonance structure, the sulfur atom is double-bonded to one oxygen atom with a formal charge of zero ( neutral ) , and sulfur is singly bonded to the other two oxygen atoms, which each carry a formal charge of  $-1$  , together accounting for the  $-2$  charge on the anion. There is also a non-bonded lone pair on the sulfur, so the structure predicted by VSEPR theory is trigonal pyramidal, as in ammonia (  $\text{NH}_3$  ) . In the hybrid resonance structure, the S - O bonds are equivalently of bond order one and one-third.

### 3 . Commercial uses

#### 3 . 1 . Wine

Sulfites occur naturally in all wines to some extent . Sulfites are commonly introduced to arrest fermentation at a desired time, and may also be added to wine as preservatives to prevent spoilage and oxidation at several stages of the wine making.

In the United States, wines bottled after mid - 1987 must have a label stating that they contain sulfites if they contain more than 10 parts per million .

In the European Union an equivalent regulation came into force in November 2005 . Organic wines are not necessarily sulfite –free .

### **3 . 2 . Other food**

Sulfites are often used as preservatives in dried fruits, and dried potato products.

Most beers no longer contain sulfites. Although shrimp is sometimes treated with sulfites on fishing vessels, the chemical may not appear on the label. In 1986, the Food and Drug Administration in the United States banned the addition of sulfites to all fresh fruit and vegetables that are eaten raw.

### **4 . Health risks**

Sulfites are used in increasing amounts as a food preservative or enhancer. They may come in various forms, such as :

- Sulfur dioxide
- Potassium bisulfite or potassium meta bisulfite
- Sodium bisulfite , sodium meta bisulfite or sodium sulfite

Sulfites are counted among the top nine food allergens, but a reaction to sulfite is not a true allergy . It may cause breathing difficulty within minutes after eating a food containing it,<sup>[6]</sup> but more commonly causes headaches and skin irritation within a few hours after consumption. Asthmatics and possibly people with salicylate sensitivity ( or aspirin sensitivity ) are at an elevated risk for reaction to sulfites. The reaction can, but not often , be fatal, and the individual must immediately go to the emergency room . Other symptoms include sneezing, swelling of the throat, and hives . In general, white and sweet ( dessert ) wines contain more sulfites than red wines.

Labeling regulations don't require that products indicate the presence of sulfites in foods other than wine ; however, many companies voluntarily label sulfite-containing foods. Regulations do exist that require that ingredients lists show sulfites if they were *added* to a product, but this requirement applies only if they were intentionally added in formulation and not if they are contained in an ingredient. If a product includes an ingredient that contains sulfites, such as dried fruit, then the ingredients label will list only " dried fruit " and is not required to indicate whether the dried fruit itself contains sulfites. Furthermore, the products most likely to contain sulfites ( fruits and alcoholic beverages ) do not require ingredients labels, so the presence of sulfites is usually undisclosed.

Sulfites are widely used to extend the shelf life of products. Because it is often difficult to know whether a food contains sulfites, many people do not realize that they may have a sensitivity to sulfite. Sulfites are also known to destroy vitamin B1 ( thiamin ) , a vitamin essential for metabolism of carbohydrates and alcohol .

# Bisulfite

## 1 . Introduction :

**Bisulfite** ion ( IUPAC- recommended nomenclature : **hydrogen sulfite** ) is the ion  $\text{HSO}_3^-$  . Salts containing the  $\text{HSO}_3^-$  ion are termed bi sulfites also known as sulfite lyes . For example, sodium bisulfite is  $\text{NaHSO}_3$ .

## 2 . Reactions

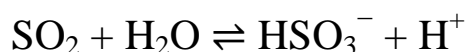
Bisulfite salts are typically prepared by treatment of alkaline solutions with excess sulfur dioxide :



$\text{HSO}_3^-$  is the conjugate base of sulfurous acid,  $\text{H}_2\text{SO}_3$  :



Sulfurous acid is not an isolable compound and does not appear to exist in solution either. An equilibrium that is much more consistent with spectroscopic evidence is given :



$\text{HSO}_3^-$  is a weakly acidic species with a  $\text{p}K_a$  of 6.97. Its conjugate base is the sulfite ion,  $\text{SO}_3^{2-}$  :



## 3 . Structure

Most evidence suggests that the proton in bisulfite ion is located on sulfur, giving rise to  $C_{3v}$  symmetry. There is, however, some evidence from  $^{17}\text{O}$  NMR spectroscopy to suggest that two tautomeric forms of  $\text{HSO}_3^-$  exist in dynamic equilibrium, one having  $C_{3v}$  symmetry ( protonated at sulfur ) and other  $C_s$  symmetry ( protonated at oxygen ). The  $C_{3v}$  structure is supported by X - ray crystallography



and, in aqueous solution, by Raman spectroscopy ( $\nu(\text{S} - \text{H}) = 2500 \text{ cm}^{-1}$ ).

#### **4 . Medicine**

Bisulfite salts are common additives to the drug epinephrine in order to prevent its oxidation to adrenochrome and resulting inactivation. Bisulfites can sometimes cause an allergic reaction. This is different from the common sulfa drugs allergy.

# Sulfuric acid

## Contents :

- 1 Introduction
- 2 Occurrence
  - 2.1 Extraterrestrial sulfuric acid
    - 2.1.1 Atmosphere of Venus
    - 2.1.2 On Europa's icy surface
- 3 Manufacture
- 4 Physical properties
  - 4.1 Forms of sulfuric acid
  - 4.2 Polarity and conductivity
- 5 Chemical properties
  - 5.1 Reaction with water
  - 5.2 Other reactions
- 6 Uses
  - 6.1 Sulfur - iodine cycle
- 7 History
- 8 Safety
  - 8.1 Laboratory hazards
  - 8.2 Industrial hazards
- 9 Legal restrictions
- 10 In fiction

## 1 . Introduction :

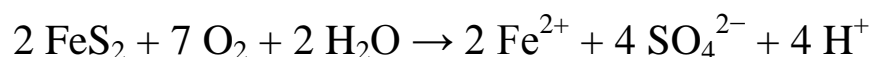
**Sulfuric ( or sulphuric ) acid** ,  $\text{H}_2\text{SO}_4$  , is a strong mineral acid. It is soluble in water at all concentrations. Sulfuric acid has many applications, and is one of the top products of the chemical industry. World production in 2001 was 165 million tonnes, with an approximate value of US\$8 billion. Principal uses include lead-acid batteries for cars and other vehicles, ore processing, fertilizer manufacturing, oil refining, wastewater processing, and chemical synthesis .

Other Names	Oil of vitriol
Molecular Formula	H <sub>2</sub> SO <sub>4</sub>
Molar Mass	98 g / mol
Appearance	Clear , Colorless , Odorless liquid
Density	1.84 g / cm <sup>3</sup> , liquid
Melting Point	10 °C
Boiling Point	337 °C
Solubility in Water	Miscible
Acidity ( pK <sub>a</sub> )	- 3
Viscosity	26.7 cP ( 20 ° C )
EU Classification	Corrosive ( C )
Flash Point	Non - flammable

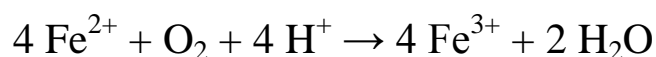
## 2 . Occurrence

Pure ( undiluted ) sulfuric acid is not encountered naturally on Earth, due to its great affinity for water. Apart from that, sulfuric acid is a constituent of acid rain, which is formed by atmospheric oxidation of sulfur dioxide in the presence of water - i.e., oxidation of sulfurous acid. Sulfur dioxide is the main byproduct produced when sulfur-containing fuels such as coal or oil are burned.

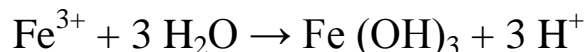
Sulfuric acid is formed naturally by the oxidation of sulfide minerals, such as iron sulfide. The resulting water can be highly acidic and is called acid mine drainage ( AMD ) or acid rock drainage ( ARD ) . This acidic water is capable of dissolving metals present in sulfide ores, which results in brightly - colored, toxic streams. The oxidation of iron sulfide pyrite by molecular oxygen produces iron ( II ) , or Fe<sup>2+</sup> :



The Fe<sup>2+</sup> can be further oxidized to Fe<sup>3+</sup> :



The  $\text{Fe}^{3+}$  produced can be precipitated as the hydroxide or hydrous oxide:



The iron (III) ion ( "ferric iron" ) can also oxidize pyrite. When iron (III) oxidation of pyrite occurs, the process can become rapid. pH values below zero have been measured in ARD produced by this process.

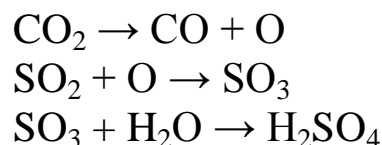
ARD can also produce sulfuric acid at a slower rate, so that the Acid Neutralization Capacity (ANC) of the aquifer can neutralize the produced acid. In such cases, the Total dissolved solids (TDS) concentration of the water can be increased from the dissolution of minerals from the acid-neutralization reaction with the minerals .

## **2 . 1 . Extra terrestrial sulfuric acid**

### **2 . 1 . 1 . Atmosphere of Venus**

Sulfuric acid is produced in the upper atmosphere of Venus by the Sun's photochemical action on carbon dioxide, sulfur dioxide, and water vapor. Ultraviolet photons of wavelengths less than 169 nm can photodissociate carbon dioxide into carbon monoxide and atomic oxygen.

Atomic oxygen is highly reactive. When it reacts with sulfur dioxide, a trace component of the Venusian atmosphere, the result is sulfur trioxide, which can combine with water vapor, another trace component of Venus's atmosphere, to yield sulfuric acid.



In the upper, cooler portions of Venus's atmosphere, sulfuric acid exists as a liquid, and thick sulfuric acid clouds completely obscure the planet's surface when viewed from above. The main cloud layer extends from 45 – 70 km above the planet's surface, with thinner hazes extending as low as 30 and as high as 90 km above the surface.

The permanent Venusian clouds produce a concentrated acid rain, as the clouds in the atmosphere of Earth produce water rain.

The atmosphere exhibits a sulfuric acid cycle. As sulfuric acid rain droplets fall down through the hotter layers of the atmosphere's temperature gradient, they are heated up and release water vapor, becoming more and more concentrated. When they reach temperatures above 300° C, sulfuric acid begins to decompose into sulfur trioxide and water, both in the gas phase. Sulfur trioxide is highly reactive and dissociates into sulfur dioxide and atomic oxygen, which oxidizes traces of carbon monoxide to form carbon dioxide.

Sulfur dioxide and water vapor rise on convection currents from the mid - level atmospheric layers to higher altitudes, where they will be transformed again into sulfuric acid, and the cycle repeats .

### **2 . 1 . 2 . On Europa 's icy surface**

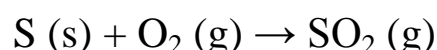
Infrared spectra from NASA's Galileo mission show distinct absorptions on Jupiter's moon Europa that have been attributed to one or more sulfuric acid hydrates. The interpretation of the spectra is somewhat controversial. Some planetary scientists prefer to assign the spectral features to the sulfate ion, perhaps as part of one or more minerals on Europa's surface .

### **3 . Manufacture :**

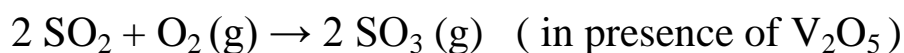
Sulfuric acid is produced from sulfur, oxygen and water via the conventional *contact process* ( DCDA ) or the *wet sulfuric acid process* ( WSA ) .

#### ***Description of the Contact process ( DCDA ) :***

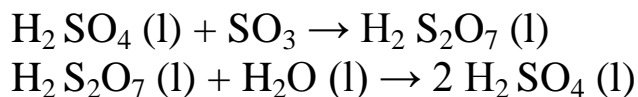
In the first step , sulfur is burned to produce sulfur dioxide .



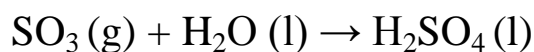
This is then oxidized to sulfur trioxide using oxygen in the presence of a vanadium ( V ) oxide catalyst .



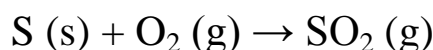
The sulfur trioxide is absorbed into 97 – 98 %  $\text{H}_2\text{SO}_4$  to form oleum (  $\text{H}_2\text{S}_2\text{O}_7$  ), also known as fuming sulfuric acid. The oleum is then diluted with water to form concentrated sulfuric acid.



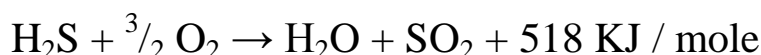
Note that directly dissolving  $\text{SO}_3$  in water is not practical due to the highly exothermic nature of the reaction between sulfur trioxide and water. The reaction forms a corrosive aerosol that is very difficult to separate, instead of a liquid.



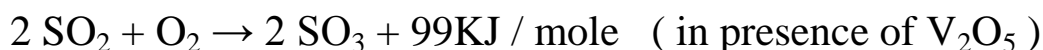
***Description of the Wet sulfuric acid process (WSA):***  
In the first step, sulfur is burned to produce sulfur dioxide.



or Hydrogen sulfide  $\text{H}_2\text{S}$  gas is incinerated to  $\text{SO}_2$  gas .



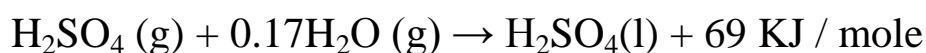
This is then oxidized to sulfur trioxide using oxygen in the presence of a vanadium ( V ) oxide catalyst .



The sulfur trioxide is hydrated into sulfuric acid  $\text{H}_2\text{SO}_4$  .



The last step is the condensation of the sulfuric acid to liquid 97 - 98 %  $\text{H}_2\text{SO}_4$



Another method is less known meta bisulfite method in which there is a meta bisulfite in the bottom of a beaker and pour in 12.6

molar concentration hydrochloric acid. Then said chemist would bubble the gas through nitric acid. The nitric acid will release brown/red vapors, and when the reaction is finished in converting the fumes will stop appearing indicating that there was a complete transfer. this method does not produce an inseparable mist which is quite convenient.

Prior to 1900, most sulfuric acid was manufactured by the chamber process .

## 4 . Physical properties

### 4 . 1 . Forms of sulfuric acid

Although nearly 100 % sulfuric acid can be made, this loses  $\text{SO}_3$  at the boiling point to produce 98.3 % acid. The 98 % grade is more stable in storage, and is the usual form of what is described as *concentrated sulfuric acid*. Other concentrations are used for different purposes . Some common concentrations are

- 10 % , *dilute sulfuric acid* for laboratory use,
- 34 % , *battery acid* ( used in lead - acid batteries ) ,
- 62 % , *chamber or fertilizer acid*,
- 74 % , *tower or Glover acid*,
- 97 % , *concentrated acid*.

Different purities are also available. Technical grade  $\text{H}_2\text{SO}_4$  is impure and often colored, but is suitable for making fertilizer. Pure grades such as United States Pharmacopoeia ( USP ) grade are used for making pharmaceuticals and dyestuffs.

When high concentrations of  $\text{SO}_3 (g)$  are added to sulfuric acid,  $\text{H}_2\text{S}_2\text{O}_7$  , called *pyro sulfuric acid* , *fuming sulfuric acid* or *oleum* or , less commonly, *Nordhausen acid* , is formed. Concentrations of oleum are either expressed in terms of %  $\text{SO}_3$  ( called % oleum ) or as %  $\text{H}_2\text{SO}_4$  ( the amount made if  $\text{H}_2\text{O}$  were added ) ; common concentrations are 40 % oleum ( 109 %  $\text{H}_2\text{SO}_4$  ) and 65 % oleum ( 114.6 %  $\text{H}_2\text{SO}_4$  ) . Pure  $\text{H}_2\text{S}_2\text{O}_7$  is a solid with melting point  $36^\circ\text{C}$ .

Pure sulphuric acid is an oily clear liquid and this explains the old name of the acid ( ' oil of vitriol ' ).

## 4.2. Polarity and conductivity

Anhydrous  $\text{H}_2\text{SO}_4$  is a very polar liquid, having a dielectric constant of around 100. It has a high electrical conductivity, caused by dissociation through protonating itself , a process known as auto protolysis .



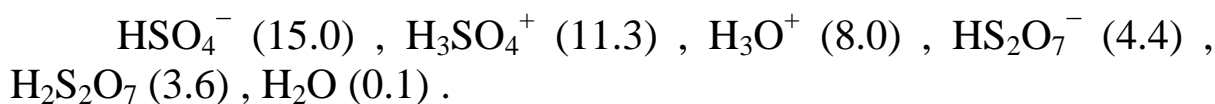
The equilibrium constant for the autoprotolysis is :

$$K_{\text{ap}} ( 25^\circ\text{C} ) = [ \text{H}_3\text{SO}_4^+ ] [ \text{HSO}_4^- ] = 2.7 \times 10^{-4} .$$

The comparable equilibrium constant for water ,  $K_{\text{w}}$  is  $10^{-14}$ , a factor of  $10^{10}$  ( 10 billion ) smaller.

In spite of the viscosity of the acid, the effective conductivities of the  $\text{H}_3\text{SO}_4^+$  and  $\text{HSO}_4^-$  ions are high due to an intra-molecular proton-switch mechanism (analogous to the Grotthuss mechanism in water), making sulfuric acid a good conductor. It is also an excellent solvent for many reactions .

The equilibrium is actually more complex than shown above; 100 %  $\text{H}_2\text{SO}_4$  contains the following species at equilibrium (figures shown as millimol per kg solvent) :



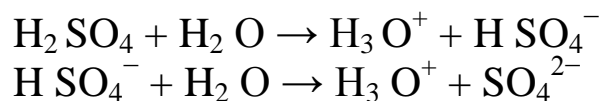
## 5. Chemical properties

### 5.1. Reaction with Water

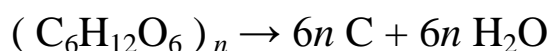
The hydration reaction of sulfuric acid is highly exothermic . One should always add the acid to the water rather than the water to the acid, because of the relative densities of these two liquids. Water is less dense than sulfuric acid, and will tend to float on top of it.



Thus, if water is added to the concentrated sulfuric acid, it can boil and splatter dangerously. This reaction is best thought of as the formation of hydronium ions:



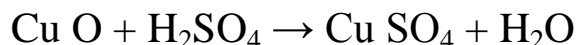
Because the hydration of sulfuric acid is thermodynamically favorable, sulfuric acid is an excellent dehydrating agent, and is used to prepare many dried fruits. The affinity of sulfuric acid for water is sufficiently strong that it will remove hydrogen and oxygen atoms from other compounds; for example, mixing starch (  $\text{C}_6\text{H}_{12}\text{O}_6$  )<sub>n</sub> and concentrated sulfuric acid will give elemental carbon and water which is absorbed by the sulfuric acid ( which becomes slightly diluted ) :



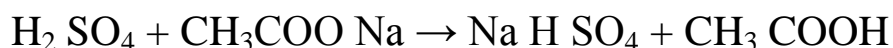
The effect of this can be seen when concentrated sulfuric acid is spilled on paper ; the cellulose reacts to give a burnt appearance, the carbon appears much as soot would in a fire. A more dramatic reaction occurs when sulfuric acid is added to a tablespoon of white sugar; a rigid column of black, porous carbon will quickly emerge. The carbon will smell strongly of caramel.

## 5 . 2 . Other Reactions

As an acid , sulfuric acid reacts with most bases to give the corresponding sulfate. For example, the blue copper salt copper (II) sulfate, commonly used for electroplating and as a fungicide, is prepared by the reaction of copper (II) oxide with sulfuric acid:

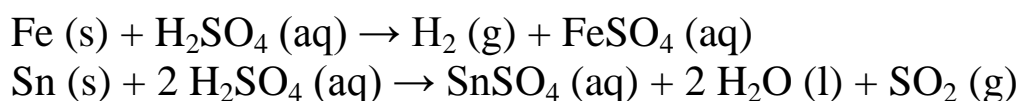


Sulfuric acid can also be used to displace weaker acids from their salts. Reaction with sodium acetate, for example, displaces acetic acid,  $\text{CH}_3\text{COOH}$ , and forms sodium bisulfate:



Similarly, reacting sulfuric acid with potassium nitrate can be used to produce nitric acid and a precipitate of potassium bisulfate. When combined with nitric acid, sulfuric acid acts both as an acid and a dehydrating agent, forming the nitronium ion  $\text{NO}_2^+$ , which is important in nitration reactions involving electrophilic aromatic substitution. This type of reaction, where protonation occurs on an oxygen atom, is important in many organic chemistry reactions, such as Fischer esterification and dehydration of alcohols.

Sulfuric acid reacts with most metals via a single displacement reaction to produce hydrogen gas and the metal sulfate. Dilute  $\text{H}_2\text{SO}_4$  attacks iron, aluminium, zinc, manganese, magnesium and nickel, but reactions with tin and copper require the acid to be hot and concentrated. Lead and tungsten, however, are resistant to sulfuric acid. The reaction with iron shown below is typical for most of these metals, but the reaction with tin produces sulfur dioxide rather than hydrogen.



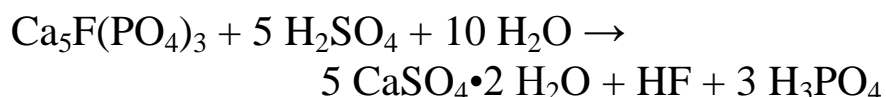
These reactions may be taken as typical: the hot concentrated acid generally acts as an oxidizing agent whereas the dilute acid acts as a typical acid. Hence hot concentrated acid reacts with tin, zinc and copper to produce the salt, water and sulphur dioxide, whereas the dilute acid reacts with metals high in the reactivity series (such as Zn) to produce a salt and hydrogen.

Sulfuric acid undergoes electrophilic aromatic substitution with aromatic compounds to give the corresponding sulfonic acids.

## 6 . Uses

Sulfuric acid is a very important commodity chemical, and indeed, a nation's sulfuric acid production is a good indicator of its industrial strength. The major use (60 % of total production worldwide) for sulfuric acid is in the "wet method" for the production of phosphoric acid, used for manufacture of phosphate fertilizers as well as tri sodium phosphate for detergents. In this

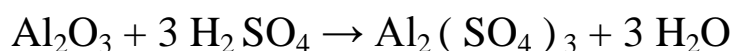
method, phosphate rock is used, and more than 100 million tonnes are processed annually. This raw material is shown below as fluorapatite, though the exact composition may vary. This is treated with 93% sulfuric acid to produce calcium sulfate, hydrogen fluoride ( HF ) and phosphoric acid. The HF is removed as hydrofluoric acid. The overall process can be represented as :



Sulfuric acid is used in large quantities by the iron and steelmaking industry to remove oxidation, rust and scale from rolled sheet and billets prior to sale to the automobile and white-goods industry. Used acid is often recycled using a Spent Acid Regeneration ( SAR ) plant. These plants combust spent acid with natural gas, refinery gas, fuel oil or other fuel sources. This combustion process produces gaseous sulfur dioxide (  $\text{SO}_2$  ) and sulfur trioxide (  $\text{SO}_3$  ) which are then used to manufacture "new" sulfuric acid. SAR plants are common additions to metal smelting plants, oil refineries, and other industries where sulfuric acid is consumed in bulk , as operating a SAR plant is much cheaper than the recurring costs of spent acid disposal and new acid purchases.

Ammonium sulfate, an important nitrogen fertilizer, is most commonly produced as a byproduct from coking plants supplying the iron and steel making plants. Reacting the ammonia produced in the thermal decomposition of coal with waste sulfuric acid allows the ammonia to be crystallized out as a salt ( often brown because of iron contamination ) and sold into the agro - chemicals industry.

Another important use for sulfuric acid is for the manufacture of aluminum sulfate, also known as paper maker's alum. This can react with small amounts of soap on paper pulp fibers to give gelatinous aluminum carboxylates, which help to coagulate the pulp fibers into a hard paper surface. It is also used for making aluminum hydroxide, which is used at water treatment plants to filter out impurities, as well as to improve the taste of the water. Aluminum sulfate is made by reacting bauxite with sulfuric acid :

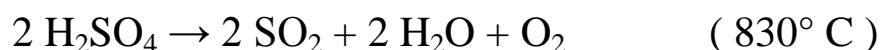


Sulfuric acid is used for a variety of other purposes in the chemical industry. For example, it is the usual acid catalyst for the conversion of cyclohexanone oxime to caprolactam, used for making nylon. It is used for making hydrochloric acid from salt via the Mannheim process. Much  $\text{H}_2\text{SO}_4$  is used in petroleum refining, for example as a catalyst for the reaction of iso-butane with isobutylene to give isooctane, a compound that raises the octane rating of gasoline (petrol). Sulfuric acid is also important in the manufacture of dyestuffs solutions and is the "acid" in lead-acid (car) batteries.

Sulfuric acid is also used as a general dehydrating agent in its concentrated form.

### 6.1. Sulfur - Iodine cycle

The sulfur - iodine cycle is a series of thermo-chemical processes used to obtain hydrogen. It consists of three chemical reactions whose net reactant is water and whose net products are hydrogen and oxygen.



The sulfur and iodine compounds are recovered and reused, hence the consideration of the process as a cycle. This process is endothermic and must occur at high temperatures, so energy in the form of heat has to be supplied.

The sulfur - iodine cycle has been proposed as a way to supply hydrogen for a hydrogen-based economy. It does not require hydrocarbons like current methods of steam reforming.

The sulfur - iodine cycle is currently being researched as a feasible method of obtaining hydrogen, but the concentrated, corrosive acid at high temperatures poses currently insurmountable safety hazards if the process were built on a large-scale.

## 7 . History

John Dalton's 1808 sulfuric acid molecule shows a central sulfur atom bonded to three oxygen atoms.

The discovery of sulfuric acid is credited to the 8th century Muslim chemist and alchemist, Jabir ibn Hayyan ( Geber ) . The acid was later studied by 9th century Persian physician and alchemist Ibn Zakariya al-Razi ( Rhazes ) , who obtained the substance by dry distillation of minerals including iron (II) sulfate hepta hydrate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and copper ( II ) sulfate penta hydrate ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . When heated, these compounds decompose to iron ( II ) oxide and copper ( II ) oxide, respectively, giving off water and sulfur trioxide, which combine to produce a dilute solution of sulfuric acid. This method was popularized in Europe through translations of Arabic and Persian treatises, as well as books by European alchemists, such as the 13th-century German Albertus Magnus.

Sulfuric acid was known to medieval European alchemists as *oil of vitriol*, *spirit of vitriol*, or simply *vitriol*, among other names. The word vitriol derives from the Latin vitreus, 'glass', referring to the glassy appearance of the sulfate salts, which also carried the name vitriol. Salts called by this name included copper(II) sulfate ( blue vitriol , or rarely Roman vitriol ) , zinc sulfate ( white vitriol ) , iron (II) sulfate ( green vitriol ) , iron ( III ) sulfate ( vitriol of Mars ) , and cobalt ( II ) sulfate ( red vitriol ) .

Vitriol was widely considered the most important alchemical substance, intended to be used as a philosopher's stone. Highly purified vitriol was used as a medium for reacting other substances. This was largely because the acid does not react with gold, production of which was often the final goal of alchemical processes. The importance of vitriol to alchemy is highlighted in the alchemical motto, *Visita Interiora Terrae Rectificando Invenies Occultum Lapidem* which is a backronym meaning ( ' Visit the interior of the earth and rectifying ( i.e. purifying ) you will find the hidden/secret stone ' ) , found in *L'Azoth des Philosophes* by the 15th Century alchemist Basilius Valentinus, .

In the 17<sup>th</sup> century, the German - Dutch chemist Johann Glauber prepared sulfuric acid by burning sulfur together with saltpeter ( potassium nitrate,  $\text{KNO}_3$  ), in the presence of steam. As saltpeter decomposes, it oxidizes the sulfur to  $\text{SO}_3$ , which combines with water to produce sulfuric acid. In 1736, Joshua Ward , a London pharmacist , used this method to begin the first large-scale production of sulfuric acid.

In 1746 in Birmingham, John Roebuck adapted this method to produce sulfuric acid in lead-lined chambers, which were stronger, less expensive, and could be made larger than the previously used glass containers. This *lead chamber process* allowed the effective industrialization of sulfuric acid production. After several refinements, this method remained the standard for sulfuric acid production for almost two centuries.

Sulfuric acid created by John Roebuck's process only approached a 35 – 40 % concentration . Later refinements to the lead-chamber process by French chemist Joseph - Louis Gay -Lussac and British chemist John Glover improved the yield to 78 % . However, the manufacture of some dyes and other chemical processes require a more concentrated product . Throughout the 18<sup>th</sup> century, this could only be made by dry distilling minerals in a technique similar to the original alchemical processes. Pyrite (iron disulfide,  $\text{FeS}_2$ ) was heated in air to yield iron (II) sulfate,  $\text{FeSO}_4$ , which was oxidized by further heating in air to form iron ( III ) sulfate,  $\text{Fe}_2 (\text{SO}_4)_3$  , which, when heated to 480 °C , decomposed to iron(III) oxide and sulfur trioxide, which could be passed through water to yield sulfuric acid in any concentration. However, the expense of this process prevented the large - scale use of concentrated sulfuric acid.

In 1831, British vinegar merchant Peregrine Phillips patented the contact process, which was a far more economical process for producing sulfur trioxide and concentrated sulfuric acid. Today, nearly all of the world's sulfuric acid is produced using this method.

## 8 . Safety

### 8 . 1 . Laboratory hazards

The corrosive properties of sulfuric acid are accentuated by its highly exothermic reaction with water. Burns from sulfuric acid are potentially more serious than those of comparable strong acids ( e.g. hydrochloric acid ) , as there is additional tissue damage due to dehydration and particularly secondary thermal damage due to the heat liberated by the reaction with water.

The danger is greater with more concentrated preparations of sulfuric acid, but even the normal laboratory " dilute " grade ( approximately 1 M , 10 % ) will char paper by dehydration if left in contact for a sufficient time. Therefore, solutions equal to or stronger than 1.5 M are labeled " CORROSIVE " , while solutions greater than 0.5 M but less than 1.5 M are labeled " IRRITANT ". Fuming sulfuric acid ( oleum ) is not recommended for use in schools due to it being quite hazardous.

The standard first aid treatment for acid spills on the skin is, as for other corrosive agents, irrigation with large quantities of water. Washing is continued for at least ten to fifteen minutes to cool the tissue surrounding the acid burn and to prevent secondary damage. Contaminated clothing is removed immediately and the underlying skin washed thoroughly .

Preparation of the diluted acid can also be dangerous due to the heat released in the dilution process. The concentrated acid is always added to water and not the other way round, to take advantage of the relatively high heat capacity of water. Addition of water to concentrated sulfuric acid leads to the dispersal of a sulfuric acid aerosol or worse, an explosion. Preparation of solutions greater than 6 M ( 35 % ) in concentration is most dangerous, as the heat produced may be sufficient to boil the diluted acid: efficient mechanical stirring and external cooling ( such as an ice bath ) are essential.

On a laboratory scale, sulfuric acid is advantageously diluted by pouring the concentrated version onto crushed ice . The ice used is

sufficiently chemically pure so as not to interfere with the intended use of the diluted acid .

## **8 . 2 . Industrial hazards**

Although sulfuric acid is non-flammable, contact with metals in the event of a spillage can lead to the liberation of hydrogen gas. The dispersal of acid aerosols and gaseous sulfur dioxide is an additional hazard of fires involving sulfuric acid.

Sulfuric acid is not considered toxic besides its obvious corrosive hazard, and the main occupational risks are skin contact leading to burns and the inhalation of aerosols. Exposure to aerosols at high concentrations leads to immediate and severe irritation of the eyes, respiratory tract and mucous membranes: this ceases rapidly after exposure, although there is a risk of subsequent pulmonary edema if tissue damage has been more severe. At lower concentrations, the most commonly reported symptom of chronic exposure to sulfuric acid aerosols is erosion of the teeth, found in virtually all studies: indications of possible chronic damage to the respiratory tract are inconclusive as of 1997. In the United States, the permissible exposure limit (PEL) for sulfuric acid is fixed at 1 mg / m<sup>3</sup>: limits in other countries are similar. Interestingly there have been reports of sulfuric acid ingestion leading to vitamin B12 deficiency with subacute combined degeneration. The spinal cord is most often affected in such cases, but the optic nerves may show demyelination, loss of axons and gliosis.

## **9 . Legal restrictions**

International commerce of sulfuric acid is controlled under the United Nations Convention Against Illicit Traffic in Narcotic Drugs and Psychotropic Substances, 1988, which lists sulfuric acid under Table II of the convention as a chemical frequently used in the illicit manufacture of narcotic drugs or psychotropic substances .

In the United States of America, sulfuric acid is included in List II of the list of essential or precursor chemicals established pursuant to the Chemical Diversion and Trafficking Act. Accordingly,



transactions of sulfuric acid — such as sales, transfers, exports from and imports to the United States — are subject to regulation and monitoring by the Drug Enforcement Administration .

## 10 . In Fiction

The use of sulfuric acid as a weapon in crimes of assault, known as " vitriol throwing " , has at times been sufficiently common ( if sensational ) to make its way into novels and short stories. Examples include the Sherlock Holmes short story *The Adventure of the Illustrious Client*, by Arthur Conan Doyle ; *The Love of Long Ago*, by Guy de Maupassant; and *Brighton Rock* by Graham Greene. A band, My Vitriol, take their name from its use as a weapon in *Brighton Rock*. An episode of *Saturday Night Live* hosted by Mel Gibson included a parody Western sketch about "Sheriff Josh Acid," who carries a flask of acid instead of a six shooter. The Batman villain Two-Face is said to have been disfigured as a result of a vitriol throw. In the George Orwell novel, *1984*, the protagonist swore his resistance to Big Brother and, among other things promises to resort to splashing a child with Sulfuric acid to avoid capture.

An interesting instance of sulfuric acid in fiction is shown in the pilot episode of the television show *MacGyver*, where the titular protagonist used a chocolate bar to stop a sulfuric acid leak. This concept was later confirmed to work by the television show *Mythbusters*.

# Oleum

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- 1 Introduction
- 2 Production
- 3 Applications
  - 3.1 Sulfuric acid production
  - 3.2 As an intermediate for transportation
  - 3.3 Organic chemistry
  - 3.4 Explosives Manufacture
- 4 Reactions

## 1 . Introduction :

**Oleum** ( Latin *oleum* = " oil " ) , or **fuming sulfuric acid** refers to a solution of various compositions of sulfur trioxide in sulfuric acid or sometimes more specifically to di sulfuric acid ( also known as pyro sulfuric acid ) .

Oleums can be described by the formula  $y \text{ SO}_3 \cdot \text{H}_2\text{O}$  where  $y$  is the total molar sulfur trioxide content. The value of  $y$  can be varied, to include different oleums . They can also be described by the formula  $\text{H}_2\text{SO}_4 \cdot x \text{ SO}_3$  where  $x$  is now defined as the molar free sulfur trioxide content. Oleum is generally assayed according to the free  $\text{SO}_3$  content by weight.

A value for  $x$  of 1 gives us the empirical formula  $\text{H}_2\text{S}_2\text{O}_7$  for disulfuric ( pyro sulfuric ) acid. Pure disulfuric acid itself is a solid at room temperature, melting at  $36^\circ\text{C}$  and rarely used either in the laboratory or industrial processes.

## 2 . Production

Oleum is produced in the contact process, where sulfur is oxidized to sulfur trioxide which is subsequently dissolved in concentrated sulfuric acid. Sulfuric acid itself is regenerated by dilution of part of the oleum.

The lead chamber process for sulfuric acid production was abandoned partly because it could not produce sulfur trioxide or concentrated sulfuric acid directly due to corrosion of the lead, and absorption of  $\text{NO}_2$  gas. Until this process was made obsolete by the contact process, oleum had to be obtained through indirect methods. Historically, the biggest production of oleum came from the distillation of iron sulfates at Nordhausen, from which the historical name Nordhausen sulfuric acid is derived.

### **3 . Applications**

#### **3 . 1 . Sulfuric acid production**

Oleum is an important intermediate in the manufacture of sulfuric acid due to its high enthalpy of hydration. When  $\text{SO}_3$  is added to water, rather than simply dissolving, it tends to form a fine mist of sulfuric acid, which is difficult to manage. However,  $\text{SO}_3$  added to concentrated sulfuric acid readily dissolves, forming oleum which can then be diluted with water to produce concentrated sulfuric acid .

#### **3 . 2 . As an intermediate for transportation**

Oleum is a useful form for transporting sulfuric acid compounds, typically in rail tank cars , between oil refineries ( which produce various sulfur compounds as a byproduct of refining ) and industrial consumers . Certain compositions of oleum are solid at room temperature, and thus is safer to ship than when liquid. Solid oleum can then be converted into liquid at the destination through steam heating or dilution or concentration. This requires some care to prevent overheating and evaporation of sulfur trioxide. To extract it from a tank car requires careful heating using steam conduits within the tank car. Great care must be taken to avoid overheating, as this can increase the internal pressure within the tank car to a value exceeding the limit of the tank's safety valve. (In Richmond, California in 1993 a significant release occurred due to overheating, causing a release of sulfur trioxide that absorbed moisture from the atmosphere, creating a mist of micro meter - sized sulfuric acid particles that formed an inhalation health hazard . This mist produced adverse health effects on residents and workers over a wide area ) .

### **3 . 3 . Organic chemistry**

Oleum is a harsh reagent , and is highly corrosive . One important use of oleum as a reagent is the secondary nitration of nitrobenzene. The first nitration can occur with nitric acid in sulfuric acid, but this deactivates the ring towards further electrophilic substitution. A stronger reagent, oleum, is needed to introduce the second nitro group onto the aromatic ring .

### **3 . 4 . Explosives Manufacture**

Oleum is used in the manufacture of many explosives with the notable exception of nitrocellulose . The chemical requirements for explosives manufacture often call for anhydrous mixtures containing nitric acid and sulfuric acid. Ordinary commercial grade nitric acid consists of the constant boiling azeotrope of nitric acid and water, and contains 68 % nitric acid. Mixtures of ordinary nitric acid in sulfuric acid therefore contain substantial amounts of water and are unsuitable for processes such as occur in the manufacture of trinitrotoluene.

Anhydrous nitric acid, referred to as white fuming nitric acid, can be used to prepare water - free nitration mixtures, and this method is used in laboratory scale operations where the cost of material is not of primary importance. Fuming nitric acid is very hazardous to handle and transport, because it is extremely corrosive and volatile. For industrial use, such strong nitration mixtures are prepared by mixing oleum with ordinary commercial nitric acid so that the free sulfur trioxide in the oleum consumes the water in the nitric acid .

## **4 . Reactions**

Like concentrated sulfuric acid, oleum is such a strong dehydrating agent that if poured onto powdered glucose , or virtually any other sugar, it will draw the elements of water out of the sugar in an exothermic reaction, leaving nearly pure carbon as a solid. This carbon expands outward, hardening as a solid black substance with gas bubbles in it.

