

## OLEUM

### Section: Concentrated Sulfuric Acid

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When heated, the pure 100% acid loses sulfur trioxide gas,  $\text{SO}_3$ , until a constant-boiling solution, or azeotrope, containing about 98.5%  $\text{H}_2\text{SO}_4$  is formed at  $337^\circ\text{C}$ . Concentrated sulfuric acid is a weak acid (see [acids and bases](#)) and a poor [electrolyte](#) because relatively little of it is dissociated into ions at room temperature. When cold it does not react readily with such common metals as iron or copper. When hot it is an oxidizing agent, the sulfur in it being reduced; sulfur dioxide gas may be released. Hot concentrated sulfuric acid reacts with most metals and with several nonmetals, e.g., sulfur and carbon. Because the concentrated acid has a fairly high boiling point, it can be used to release more volatile acids from their salts, e.g., when sodium chloride ( $\text{NaCl}$ ), or common salt, is heated with concentrated sulfuric acid, hydrogen chloride gas,  $\text{HCl}$ , is evolved.

Concentrated sulfuric acid has a very strong affinity for water. It is sometimes used as a drying agent and can be used to dehydrate (chemically remove water from) many compounds, e.g., carbohydrates. It reacts with the sugar sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , removing eleven molecules of water,  $\text{H}_2\text{O}$ , from each molecule of sucrose and leaving a brittle spongy black mass of carbon and diluted sulfuric acid. The acid reacts similarly with skin, cellulose, and other plant and animal matter.

When the concentrated acid mixes with water, large amounts of heat are released; enough heat can be released at once to boil the water and spatter the acid. To dilute the acid, the acid should be added slowly to cold water with constant stirring to limit the buildup of heat. Sulfuric acid reacts with water to form hydrates with distinct properties.

### Section: Dilute Sulfuric Acid

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Dilute sulfuric acid is a strong acid and a good electrolyte; it is highly ionized, much of the heat released in dilution coming from hydration of the hydrogen [ions](#). The dilute acid has most of the properties of common strong acids. It turns blue litmus red. It reacts with many metals (e.g., with zinc), releasing hydrogen gas,  $\text{H}_2$ , and forming the [sulfate](#) of the metal. It reacts with most hydroxides and oxides, with some carbonates and sulfides, and with some salts. Since it is dibasic (i.e., it has two replaceable hydrogen atoms in each molecule), it forms both normal sulfates (with both hydrogens replaced, e.g., sodium sulfate,  $\text{Na}_2\text{SO}_4$ ) and acid sulfates, also called bisulfates or hydrogen sulfates (with only one hydrogen replaced, e.g., sodium bisulfate,  $\text{NaHSO}_4$ ).

### Section: Production of Sulfuric Acid

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There are two major processes (lead chamber and contact) for production of sulfuric acid, and it is available commercially in a number of grades and concentrations. The lead chamber process, the older of the two processes, is

used to produce much of the acid used to make fertilizers; it produces a relatively dilute acid (62%-78%  $\text{H}_2\text{SO}_4$ ). The contact process produces a purer, more concentrated acid but requires purer raw materials and the use of expensive catalysts. In both processes **sulfur dioxide** is oxidized and dissolved in water. The sulfur dioxide is obtained by burning sulfur, by burning pyrites (iron sulfides), by roasting nonferrous sulfide ores preparatory to smelting, or by burning hydrogen sulfide gas. Some sulfuric acid is also made from ferrous sulfate waste solutions from pickling iron and steel and from waste acid sludge from oil refineries.

## Lean Chamber Process

In the lead chamber process hot sulfur dioxide gas enters the bottom of a reactor called a Glover tower where it is washed with nitrous vitriol (sulfuric acid with nitric oxide,  $\text{NO}$ , and nitrogen dioxide,  $\text{NO}_2$ , dissolved in it) and mixed with nitric oxide and nitrogen dioxide gases; some of the sulfur dioxide is oxidized to sulfur trioxide and dissolved in the acid wash to form tower acid or Glover acid (about 78%  $\text{H}_2\text{SO}_4$ ). From the Glover tower a mixture of gases (including sulfur dioxide and trioxide, nitrogen oxides, nitrogen, oxygen, and steam) is transferred to a lead-lined chamber where it is reacted with more water. The chamber may be a large, boxlike room or an enclosure in the form of a truncated cone. Sulfuric acid is formed by a complex series of reactions; it condenses on the walls and collects on the floor of the chamber. There may be from three to twelve chambers in a series; the gases pass through each in succession. The acid produced in the chambers, often called chamber acid or fertilizer acid, contains 62% to 68%  $\text{H}_2\text{SO}_4$ . After the gases have passed through the chambers they are passed into a reactor called the Gay-Lussac tower where they are washed with cooled concentrated acid (from the Glover tower); the nitrogen oxides and unreacted sulfur dioxide dissolve in the acid to form the nitrous vitriol used in the Glover tower. Remaining waste gases are usually discharged into the atmosphere.

## Contact Process

In the contact process, purified sulfur dioxide and air are mixed, heated to about  $450^\circ\text{C}$ , and passed over a catalyst; the sulfur dioxide is oxidized to sulfur trioxide. The catalyst is usually platinum on a silica or asbestos carrier or vanadium pentoxide on a silica carrier. The sulfur trioxide is cooled and passed through two towers. In the first tower it is washed with oleum (fuming sulfuric acid, 100% sulfuric acid with sulfur trioxide dissolved in it). In the second tower it is washed with 97% sulfuric acid; 98% sulfuric acid is usually produced in this tower. Waste gases are usually discharged into the atmosphere. Acid of any desired concentration may be produced by mixing or diluting the products of this process.

## **sulfur dioxide** Track this topic

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chemical compound,  $\text{SO}_2$ , a colorless gas with a pungent, suffocating odor.

It is readily soluble in cold water, sparingly soluble in hot water, and soluble in alcohol, acetic acid, and sulfuric acid. It is corrosive to organic materials and dissolves in water to form sulfurous acid,  $\text{H}_2\text{SO}_3$ . Sulfur dioxide is used in bleaching and in chemical manufacture and as a refrigerant and a food preservative, e.g., for fumigating fruit. It may be produced by reaction of sulfur with oxygen, e.g., by burning sulfur in air, and it is often produced during the roasting of sulfide ores, e.g., in zinc smelting. Sulfur dioxide is a dangerous air pollutant because of its corrosive properties; it irritates the eyes, nose, and lungs. It is produced by combustion of coal, fuel oil, and gasoline, since these fuels contain sulfur. The sulfur content of a fuel can be reduced by refining, so that less sulfur dioxide is emitted when the fuel is burned.

### **Section: History of Sulfuric Acid**

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Although sulfuric acid is now one of the most widely used chemicals, it was probably little known before the 16th cent. It was prepared by Johann Van Helmont (c.1600) by destructive distillation of green vitriol (ferrous sulfate) and by burning sulfur. The first major industrial demand for sulfuric acid was the Leblanc process for making sodium carbonate (developed c.1790). Sulfuric acid was produced at Nordhausen from green vitriol but was expensive. A process for its synthesis by burning sulfur with saltpeter (potassium nitrate) was first used by Johann Glauber in the 17th cent. and developed commercially by Joshua Ward in England c.1740. It was soon superseded by the lead chamber process, invented by John Roebuck in 1746 and since improved by many others. The contact process was originally developed c.1830 by Peregrine Phillips in England; it was little used until a need for concentrated acid arose, particularly for the manufacture of synthetic organic dyes.

### **Section: Uses of Sulfuric Acid**

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Sulfuric acid is one of the most important industrial chemicals. More of it is made each year than is made of any other manufactured chemical; more than 40 million tons of it were produced in the United States in 1990. It has widely varied uses and plays some part in the production of nearly all manufactured goods. The major use of sulfuric acid is in the production of fertilizers, e.g., superphosphate of lime and ammonium sulfate. It is widely used in the manufacture of chemicals, e.g., in making hydrochloric acid, nitric acid, sulfate salts, synthetic detergents, dyes and pigments, explosives, and drugs. It is used in petroleum refining to wash impurities out of gasoline and other refinery products. Sulfuric acid is used in processing metals, e.g., in pickling (cleaning) iron and steel before plating them with tin or zinc. Rayon is made with sulfuric acid. It serves as the electrolyte in the lead-acid storage battery commonly used in motor vehicles (acid for this use,

containing about 33%  $\text{H}_2\text{SO}_4$  and with specific gravity about 1.25, is often called battery acid).