It is prepared on the industrial scale for the manufacture of sulphuric acid, for the preparation of sodium sulphate by the Hargreaves process, and for use as a bleaching-disinfecting agent and as a preservative. When compressed it is also used largely as a refrigerating agent, and in virtue of its property of neither burning nor supporting combustion it is also used as a fire extinctor. The solution of the gas in water is used under the name of sulphurous acid. The free acid has not been isolated, since on evaporation the solution gradually loses sulphur dioxide. This solution possesses re­ducing properties, and gradually oxidizes to sulphuric acid on exposure. When heated in a sealed tube to 180° C. it is transformed into sul­phuric acid, with liberation of sulphur. Numerous salts, termed sulphites, are known. Since the free acid would be dibasic, two series of salts exist, namely, the neutral and acid salts. The neutral alkaline salts are soluble in water and show an alkaline reaction, the other neutral salts being either insoluble or difficultly soluble in water. The acid salts have a neutral or slightly acid reaction. The sulphites are prepared by the action of sulphur dioxide on the oxides, hydroxides or carbonates of the metals, or by processes of precipitation. Sulphurous acid may have either of the constitutions ∕OH C∖ ∕0H

I or q∕≡∖ , or be an equilibrium mixture of these

two substances. Although the correct formula for the acid is not known, sulphites are known of both types. Sodium sulphite is almost certainly of the second and unsymmetrical type. Two ethyl sulphites are known, the first or symmetrical form being derived from sulphuryl chloride and alcohol, and the second and unsym­metrical from sodium sulphite and ethyl iodide; the junction of one ethyl group with a sulphur atom in the second salt follows because it yields ethyl sulphonic acid, also obtainable from ethyl mercaptan, C2H6SH. Two isomeric sodium potassium sulphites are known, and may be obtained by neutralizing acid sodium sulphite with potassium carbonate, and acid potassium sulphite with sodium carbonate; their formulae are : O2SK(ONa) and O2SNa(OK).

There are various haloid derivatives of sulphurous acid. Thionyl fluoride, SOF2, has been obtained as a fuming gas by decomposing arsenic fluoride with thionyl chloride (Moissan and Lebeau, *Compt. rend.,* 1900, 130, p. 1436). It is decomposed by water into hydro­fluoric and sulphurous acids. Thionyl chloride, SOCl2, may be ob­tained by the action of phosphorus pentachloride on sodium sulphite ; by the action of sulphur trioxide on sulphur dichloride at 75—80° C. *(Journ. Chem. Soc.,* 1903, p. 420); and by the action of chlorine monoxide on sulphur at low temperature. It is a colourless, highly refracting liquid, boiling at 78°; it fumes on exposure to moist air. Water decomposes it into hydrochloric and sulphurous acids. On treatment with potassium bromide it yields thionyl bromide, SOBr2, an orange-yellow liquid which boils at 68° C. (40 mm.) (Hartoz and Sims, *Cnetn. News,* 1893, 67, p. 82).

Sulphur trioxide, SO3, mentioned by Basil Valentine in the 15th century, was obtained by N. Lemery in 1675 by distilling green vitriol. It may be prepared by distilling fuming sulphuric acid, or concentrated sulphuric acid over phosphorus pentoxide, or by the direct union of sulphur dioxide with oxygen in the presence of a catalyst, such as platinized asbestos (see Sulphuric Acid). This oxide exists in two forms. The *α* form is readily fusible and melts at 14∙8° C. It corresponds to the simple molecular complex SO≡. The *ß-* variety is infusible, but on heating to 50° C. is transformed into the *α*- form. It corresponds to the molecular complex (SO5)2. When perfectly dry this oxide has no caustic properties; it combines rapidly, however, with water to form sulphuric acid, with the development of much heat. It combines directly with concentrated sulphuric acid to form pyrosulphuric acid, H2S2O7. It reacts most energetically with many organic compounds, removing the elements of water in many cases and leaving a carbonized mass. It com­bines directly with many elements and compounds and frequently acts as energetic oxidizing agent. It finds considerable application in the colour industry.

Sulphuryl fluoride, SO2F2, formed by the action of fluorine on sul­phur dioxide (H. Moissan, *Compt. rend.* 132, p. 374), is an exceedingly stable colourless gas at ordinary temperatures, becoming solid at about —120° C. Sulphuryl chloride, SO2Cl2, first obtained in 1838 by Regnault *(Ann. Mm. phys.,* 1838, (2), 69, p. 170), by the action of chlorine on a mixture of ethylene and sulphur dioxide, may also be obtained by the direct union of sulphur dioxide and chlorine (especially in the presence of a little camphor); and by heating chlorsulphonic acid in the presence of a catalyst, such as mercuric sulphate (Pawlewski, *Ber.,* 1897, 30, p. 765) : 2SO2Cl∙OH =SO2Cl2+ H2SO1. It is a colourless fuming liquid which boils at 69° C. and which is readily decomposed by water into sulphuric and hydrochloric acids. Fluorsulphoric acid, SO2F∙OH, is a mobile liquid obtained by the action of an excess of hydrofluoric acid on well-cooled sulphur trioxide. It boils at 162∙6° and is decomposed violently by water. Chlorsulphonic acid, SO2Cl∙OH, first prepared by A. Williamson (Froc. *Roy. Soc.,* 1856, 7, p. 11) by the direct union of sulphur trioxide with hydrochloric acid gas, may also be obtained by distill­ing concentrated sulphuric acid with phosphorus oxychloride: 2H2SO4+POCl3=2SO2Cl∙OH+HCI4-HPO3. It is a colourless fuming liquid which boils at 152-153° C. When heated under pressure it decomposes, forming sulphuric acid, sulphuryl chloride, &c. (Ruff, *Ber.,* 1901, 34, p. 3509). It is decomposed by water with explosive violence. Disulphuryl chloride, S2O5Cl2, corresponding to pyrosulphuric acid, is obtained by the action of sulphur trioxide on sulphur dichloride, phosphorus oxychloride, sulphuryl chloride or dry sodium chloride : 6SO3 +2POCl3 = P2O5 +3S2O5Cl2; S2Cl2 + 5SO3 = S2O2Cl2 + 5SO2 ; SO, + SO2Cl2 - = S2O5Cl2 ; 2NaCl + 3SO2 = S2O5Cl2+Na2SO4. It may also be obtained by distilling chlor- sulphonic acid with phosphorus pentachloride : 2SO2Cl∙OH+PCl5 = S2O5Cl2 + POCl+2HCl. It is a colourless, oily, fuming liquid which is decomposed by water into sulphuric and hydrochloric acids. An oxychloride of composition S2O3Cl4 has been described.

Sulphur sesquioxide, S2O2, is formed by adding well-dried flowers of sulphur to melted sulphur trioxide at about 12-15° C. The sulphur dissolves in the form of blue drops which sink in the liquid and finally solidify in blue-green crystalline crusts. It is unstable at ordinary temperatures and rapidly decomposes into its generators on warming. It is readily decomposed by water with formation of sulphurous, sulphuric and thiosulphuric acids, with simultaneous liberation of sulphur. Hyposulphurous acid, H2S2O4, was first really obtained by Berthollet in 1789 when he showed that iron left in contact with an aqueous solution of sulphur dioxide dissolved with­out any evolution of gas, whilst C. F. Schönbein subsequently showed the solution possessed reducing properties. P. Schutzenberger *(Compt. rend.,* 1869, 69, p. 169) obtained the sodium salt by the action of zinc on a concentrated solution of sodium bisulphite : Zn + 4NaHSO3 = Na2S2O4 + ZnSO3 + Na2SO4 + 2H2O, the salt being separated from the sulphites formed by fractional precipita­tion. A solution of the free acid may be prepared by adding oxalic acid to the solution of the sodium salt. This solution is yellow in colour, and is very unstable decomposing at ordinary temperature into sulphur and sulphur dioxide. A pure zinc salt has been prepared by Nabl *(Monats.* 1899, 20, p. 679) by acting with zinc on a solution of sulphur dioxide in absolute alcohol, whilst H. Moissan *(Compt. rend.,* 1902, 135, p. 647) has also obtained salts by the action of dry sulphur dioxide on various metallic hydrides. Considerable controversy arose as to the constitution of the salts of this acid, the formula of sodium salt, for example, being written as NaHSO2 and Na2S2O4; but the investigations of C. Bernthsen *(Ann.,* 1881, 208, ρ. 142; 1882, 211, p. 285: *Ber.,* 1900, 33, p. 126) seem to decide definitely in favour of the latter (see also T. S. Price, *Journ. Chem. Soc.* ; also Bucherer and Schwalbe, *Zeil, angew. Chem.,* 1904, 17, p. 1447). Although this acid appears to be derived from an oxide S2O3, it is not certain that the known sesquioxide is its anhydride.

Persulphuric anhydride, S2O7, is a thick viscous liquid obtained by the action of the silent discharge upon a mixture of sulphur trioxide and oxygen. It solidifies at about 0° C. to a mass of long needles, and is very volatile. It is decomposed readily into sulphur trioxide and oxygen when heated. Water decomposes it with forma­tion of sulphuric acid and oxygen : 2S2O7 + 4H3O = 4H2SO4 + O2. Persulphunc acid, HSO4, the acid corresponding to S2O7, has not been obtained in the free state, but its salts were first prepared in 1891 by H. Marshall *(Journ. Chem. Soc.,* 1891, p. 771) by electrolysing solutions of the alkaline bisulphates. The potassium salt, after recrystallization from warm water, separates in large tabular crystals. Its aqueous solution gradually decomposes with evolution of oxygen, behaves as a strong oxidant, and liberates iodine from potassium iodide. Solutions of persulphates in the cold give no precipitate with barium chloride, but when warmed barium sulphate is precipi­tated with simultaneous liberation of chlorine : K2S2O8 + BaCl2 = BaSO4 + K2SO4 + Cl2. The conductivity measurements of G. Bredig point to the salt possessing the double formula.

Thiosulphuric acid, formerly called hyposulphurous acid, H2S2O3, cannot be preserved in the free state, since it gradually decomposes with evolution of sulphur dioxide and liberation of sulphur : H-S1O1 = S+SO2+H2O. The salts of the acid, however, are stable, the sodium salt in particular being largely used for photographic purposes under the name of “ hypo.” This salt may be prepared by digesting flowers of sulphur with sodium sulphite solution or by boiling sulphur with milk of lime. In this latter reaction the deep yellow solution obtained is exposed to air when the calcium polysulphide formed is gradually converted into thiosulphate by oxidation, and the calcium salt thus formed is converted into the sodium salt by sodium carbonate or sulphate. The thiosulphates are readily decomposed by mineral acids with liberation of sulphur dioxide and precipitation of sulphur: Na2SO3 + 2HCl = 2NaCl + S + SO2 + H2O. They form many double salts and give a dark violet coloration with ferric chloride solution, this colour, however, gradually disappearing on standing, sulphur being precipitated. The acid is considered to possess the structure O2S(SH) (OH), since sodium thiosulphate reacts with ethyl bromide to give sodium ethyl thiosulphate, which on treatment with barium chloride gives presumably barium ethyl thiosulphate. This salt, on standing, decomposes into barium dithionate, BaS2O6, and diethyl disulphide, (C2H3)2S2, which points to the presence of the SH group in the molecule.

The *thionic acids* are a group of sulphur-containing acids of general formula H2SnO6, where *n=*2*,* 3, 4, 5 and possibly 6. Dithionic acid, H2S2O6, prepared by J. Gay-Lussac in 1819, is usually obtained