

oxidation to sulphuric acid renders it an unlikely occurrence except in very special cases.

**Preparation.**—Sulphur dioxide is formed when sulphur burns in air or oxygen. Some sulphur trioxide is produced at the same time, as indicated in connection with the chemical properties of sulphur. If air be employed, the sulphur dioxide is of course accompanied by nitrogen from the air. The nitrogen does no harm in some of the technical applications of the gas. Numerous furnaces have been devised for burning sulphur; many of these are provided with automatic feeders, and agitators. These are described by W. Wyld,<sup>3</sup> and others in works devoted to the manufacture of sulphuric acid. The gas is also obtained by roasting many metal sulphides in air. In 1818, T. Hills and U. Haddock obtained a patent in England for producing sulphur dioxide by roasting pyrites for the manufacture of sulphuric acid; but, according to E. Sorel, this was done by a French manufacturer, M. d'Artigues, in 1793. N. Clement also made experiments on the subject in 1810. The burning of pyrites on a large scale is done by heating iron pyrites, copper pyrites, zincblende, etc., in special kilns or burners, so arranged that the heat of oxidation is utilized for maintaining the process without extraneous fuel. As shown by A. Scheurer-Kestner, G. Lunge and F. Salathé, and D. Pierson, some sulphur trioxide is formed in this operation—*vide supra*, the oxidation of sulphur. There are also burners arranged for roasting the spent oxide of gas-works so as to convert the sulphur into sulphur dioxide; hydrogen sulphide may also be burnt to sulphur dioxide in special burners. Some sulphide ores are roasted in heaps in the open air without any regard for the contained sulphur. The ultimate object is the extraction of the metal. The damage to health and vegetation is, however, so great that the nuisance has been stopped by legal enactments. For the same reason, the noxious vapours—mainly sulphur dioxide—in many manufacturing districts have to be treated for the removal of sulphur dioxide and trioxide before the “smoke” is permitted to escape into the atmosphere. The various methods for treating acid-smoke, smelter-fumes, hydrogen sulphide, etc., for the recovery of the sulphur in the gas as sulphur dioxide, are described in special treatises—*e.g.* by C. A. Hering, C. Schnabel, W. Wyld, etc. F. Siemens converted hydrogen sulphide into sulphur dioxide by burning it admixed with air at 280°–320° in contact with a catalyst containing a metal capable of combining with sulphur—*e.g.* copper, nickel, or iron—and an oxygen carrier—*e.g.* vanadium, chromium, or molybdenum. L. H. Diehl devised a process for recovering the 1.5 per cent. of sulphur—chiefly as calcium sulphide—in blast-furnace slag, by blowing hot air through the fused slag as it is tapped from the furnace. The air which escapes at about 950° contains about 10 per cent. of sulphur dioxide by vol. Sulphur dioxide is also formed when other sulphur compounds are heated in air—*e.g.* when carbon disulphide is burnt; and as U. Collan and others have shown, when coal gas is burnt.

Sulphur dioxide is also produced when the oxides of many metals—manganese, zinc, lead, mercury, etc., are heated with sulphur, or with sulphur compounds of the same metals. Thus, P. Berthier used pyrolusite,  $\text{MnO}_2 + 2\text{S} = \text{MnS} + \text{SO}_2$ ; or  $2\text{MnO}_2 + \text{S} = \text{SO}_2 + 2\text{MnO}$ ; and R. F. Marchand, a mixture of copper oxide and sulphur:  $2\text{CuO} + 2\text{S} = \text{Cu}_2\text{S} + \text{SO}_2$ . F. Stolba heated sulphur with ferrous sulphate,  $\text{FeSO}_4 + 2\text{S} = \text{FeS} + 2\text{SO}_2$ , and, as a by-product, obtained ferrous sulphide for the manufacture of hydrogen sulphide; T. Terrell utilized the reaction:  $2\text{FeSO}_4 + 2\text{S} + 3\text{O} = \text{Fe}_2\text{O}_3 + 4\text{SO}_2$ , and employed the ferric oxide as a pigment; the reaction of sulphur with cupric sulphate was stated by H. Schiff to proceed more easily than with ferrous sulphate. C. Brückner made a special study of the action of sulphur on the sulphates. F. Martin and O. Fuchs found that the alkaline earth sulphates are reduced to sulphides when heated with iron, and the reduction occurs at a lower temp. than when coal is substituted for the iron. The reduction is complete in half an hour at 750° for calcium sulphate; at 850° for strontium sulphate; and at about 950° for barium sulphate. In the presence of insufficient iron and at about 150° higher, a rapid evolution of sulphur dioxide takes place.

The best conditions for this are, for calcium sulphate the mixture  $16\text{CaSO}_4 + 15\text{Fe}$ , giving 80 per cent. of the theoretical yield of sulphur dioxide; for strontium sulphate the mixture  $9\text{SrSO}_4 + 8\text{Fe}$ , giving an 88.9 per cent. yield. These reactions lead to the formation of well defined ferrites,  $3\text{CaO}, 2\text{Fe}_2\text{O}_3 = \text{Ca}_3\text{Fe}_4\text{O}_9$ ;  $2\text{SrO}, \text{Fe}_2\text{O}_3 = \text{Sr}_2\text{Fe}_2\text{O}_5$ ; and  $\text{BaO}, \text{Fe}_2\text{O}_3 = \text{BaFe}_2\text{O}_4$ . Too little iron leads to the formation of alkaline-earth sulphide, too much iron gives also iron sulphide. Sulphur dioxide is also evolved by heating the alkaline-earth sulphates with iron sulphide; this can be carried out commercially by using pyrites to which has been added a little iron oxide. L. Moser purified the gas by the fractional distillation of the liquefied gas.

Sulphur dioxide is produced in the thermal decomposition of conc. sulphuric acid, as when the acid is dropped into a red-hot platinum flask packed with pumice-stone. Sulphur dioxide is also formed when many sulphates are heated, for the sulphur trioxide first given off breaks up into oxygen and the gas in question. The Verein Chemischer Fabriken Mannheim used iron oxide as catalyst at about  $900^\circ$ —*vide supra*, sulphur. H. S. Elworthy obtained it by heating a mixture of sodium sulphide with calcium or sodium sulphate in a converter furnace in air, when all the sulphur is given off as sulphur dioxide; and L. P. Basset heated a mixture of calcium sulphate with alumina and powdered coal. Sulphur dioxide is also formed when sulphuric acid is heated with sulphur:  $2\text{H}_2\text{SO}_4 + \text{S} = 3\text{SO}_2 + 2\text{H}_2\text{O}$ , as shown by J. B. A. Dumas, and C. F. Anthon. H. L. F. Melsens found it to be an advantage to mix the acid and sulphur with pumice-stone. E. Hart recommended warming sulphur with fuming sulphuric acid, containing 30 per cent.  $\text{SO}_3$ , when the blue soln. so formed is heated, sulphur dioxide mixed with some trioxide is given off. The evolution of the dioxide ceases when all the trioxide has been acted upon, and the sulphur melts. J. Knezaurek obtained sulphur dioxide by heating sulphuric acid with charcoal:  $2\text{H}_2\text{SO}_4 + \text{C} = 2\text{H}_2\text{O} + 2\text{SO}_2 + \text{CO}_2$ , for purposes where the admixed carbon monoxide and dioxide will do no harm. W. L. Scott recommended using acid of sp. gr. 1.824 containing 74 per cent.  $\text{SO}_3$ . If a more conc. acid is used, a portion is reduced to sulphur; and if a more dil. acid is employed, some hydrogen sulphide is formed. The washing liquid should be mixed with lead sulphate or coarsely powdered charcoal. One of the commonest methods of preparing small quantities of sulphur dioxide is to heat conc. sulphuric acid with copper:  $\text{Cu} + 2\text{H}_2\text{SO}_4 = \text{SO}_2 + 2\text{H}_2\text{O} + \text{CuSO}_4$ —*vide* 3, 21, 6. According to G. J. Warner, sulphuric acid is reduced to sulphur dioxide at  $160^\circ$ , and S. Cooke showed that the reaction is accelerated by the presence of platinum. C. Bollé heated nitre-cake, acid sodium sulphate with wood-shavings and coke; J. S. and A. A. Blowski, with petroleum sludge; G. Schildhaus and C. Condeira, with acid-tar or sludge; and I. P. Llewellyn and P. Spence, and P. Hart with pyrites in order to obtain sulphur dioxide. Sulphur dioxide is formed by the action of conc. mineral acids on sulphites, on thiosulphates, and on all polythionic acids. L. G. Wesson found that solid metahydrosulphite alone or mixed with a dry solid pyrosulphate is hygroscopic in moist air, and gives off sulphur dioxide. G. Neumann obtained sulphur dioxide from a Kipp's apparatus by using cubes made of calcium sulphite and plaster of Paris, and conc. sulphuric acid. E. Geisel, and F. W. Küster and F. Abegg devised an apparatus for preparing the gas from conc. sulphuric acid and soln. of hydrosulphites. W. Garroway decomposed a soln. of sodium hydrosulphite by sodium hydrosulphate or sulphuric acid. Most of the sulphur dioxide is driven out in the cold, the remainder by the injection of steam. L. Monnet fused a mixture of alkali hydrosulphite and sodium thiosulphate, and found sulphur dioxide is given off when the granulated mass comes in contact with water. P. Pierron obtained sulphur dioxide at the anode during the electrolysis of ammonium thiosulphate. F. Clausnizer observed that sulphur dioxide is formed by the action of phosphorus pentabromide on sulphuric acid; E. Divers and T. Haga, by the action of alkali metals on nitrosulphates; and H. Beckurts and R. Otto, by heating chlorosulphonic acid to  $170^\circ$ – $180^\circ$ . E. Cardoso discussed the preparation and purification of the gas.

According to A. Gautier, water vapour attacks sulphides of the heavy metals—FeS, PbS, etc.—at an incipient red-heat, forming hydrogen sulphide, hydrogen, and sulphur dioxide. In some cases, the sulphide is reduced to metal—e.g.  $\text{Cu}_2\text{S} + 2\text{H}_2\text{O} = 2\text{Cu} + \text{SO}_2 + 2\text{H}_2$ . The sulphur of hydrogen sulphide may be oxidized by the oxygen of water-vapour at a red-heat giving sulphur dioxide, hydrogen, and traces of sulphur, sulphuric acid, and thionic acids. Hence, the presence of oxygen is not necessary to account for sulphur dioxide in volcanic gases.

Sulphur dioxide for liquefaction is made by a process which gives a product of a higher degree of purity than is needed for some operations. If the sulphur dioxide is diluted with much inert gas, it requires concentration. This subject is discussed in a special monograph by A. Harpf, and E. Schütz. In some cases, the burner gases are scrubbed with water, cooled with water, and the resulting liquid heated in order to recover the absorbed sulphur dioxide—e.g. R. Pictet, F. R. Carpenter, H. Hegeler and N. L. Heinz, Compagnie Industrielle des Alcools de l'Ardeche, E. Schroeder and M. Haenisch, A. H. Eustis, etc. Other liquids have been recommended in place of water—e.g. E. Bergmann and T. Berliner used a soln. of calcium hydrophosphate; F. E. Coombs, milk of lime or sodium carbonate; H. K. Moore and R. B. Wolf, calcium chloride; J. L. Babé and H. Pape, a soln. of an indifferent salt; F. Kuhlmann, heavy coal-tar oil; P. Pascal, carbolic oil; etc. F. W. Andrews discussed the purification of commercial sulphur dioxide by fractional volatilization of the liquid.

**The physical properties of sulphur dioxide.**—At ordinary temp. and press., sulphur dioxide is a colourless gas of suffocating smell. It can be condensed to a colourless liquid, and frozen to a colourless, transparent, crystalline solid. The **relative density** of the gas, air unity, was found by H. Davy<sup>4</sup> to be 2.193; T. Thomson gave 2.2222; R. F. Marchand, 2.0412; H. V. Regnault, 2.221; J. Buff, 2.2277; J. J. Berzelius, 2.247; J. L. Gay Lussac, 2.255; L. Bleekrode, 2.234 at 15°; A. Leduc, 2.2639 ± 0.0001; G. Bauer, 2.881 at 716 mm., and 2.910 at 724 mm. D. Berthelot gave 2.04835 (oxygen unity) at 0° and 1 atm. press. E. Mathias found the density, *D*, of the sat. vapour of sulphur dioxide can be represented by  $D = 1.4328\{1 - m - 1.140(1 - m)^{\frac{1}{2}} + 0.5792\}$ , where *m* represents temp. referred to the critical temp. as unit,  $m = T/T_c$ ; or  $D = 1.0019 - 0.00334\theta - 0.07887(156 - \theta)^{\frac{1}{2}}$ . L. P. Cailletet and E. Mathias found the density of the sat. vapour of sulphur dioxide, referred to water at 4°, to be :

	7.3°	24.7°	58.2°	78.7°	100.6°	123.0°	144.0°	154.9°
Density .	0.00624	0.0112	0.0310	0.0464	0.0786	0.1340	0.2495	0.4017

Towards the critical temp. 156°, the density of liquid and gas approach the limiting value 0.52. C. von Linde gave 0.002861 for the density of the gas at 0°—water unity; and G. Bauer, 0.00286 at -10° and atm. press.

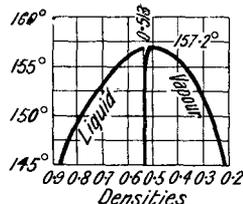


FIG. 44.—Law of Rectilinear Diameter for Liquid and Gaseous Sulphur Dioxide.

E. Exner made some observations on this subject. The **weight of a normal litre** of sulphur dioxide was found by A. Leduc to be 2.9267 grms. and for the weight *W* of gas at normal press. when the weight is  $W_p$  at a press., *p*, between 0.5 and 1.0 atm., is  $W = W_p 760\{1 + 0.0000323(760 - p)\}/p$ , A. Jaquero and A. Pintza found 2.92664 ± 0.0001 grms. when the value for oxygen was 1.4292 grms. The weight of a litre of the gas at 0° was 2.18172 grms. at 570 mm. press., and 1.44572 grms. at 380 mm. press. G. Baume gave 2.9266 grms. for the weight of the normal litre, and the coeff. representing the deviation from Boyle's law is 0.02380 between 0 and 1 atm. press. M. S. Blanchard and S. F. Pickering reviewed the literature on this subject. M. Faraday gave 1.42 for the **specific gravity** of liquid sulphur dioxide; A. Bussy, 1.45; L. Dufour, 1.49 at -20°; J. I. Pierre, 1.4911 at