solution. The filtrate is allowed to stand in a tightly sealed flask at room temperature or on ice until crystallization occurs. After several hours, yellow needles of $(NH_4)_2S_5$ are formed. These are stable for a fairly long time if submerged in the mother liquor in the absence of air, but they decompose very rapidly when dry to form NH_3, H_2S and S. The product is isolated by rapid suction-filtration through filter paper, removal of adhering mother liquor by pressing between filter papers, and consecutive washing with ether-methanol (5 : 1), absolute ether and anhydrous chloroform. The still moist product is allowed to stand in a vacuum desiccator over CaO which has been wetted with some concentrated ammonium hydroxide. However, because of decomposition, it contains about 10% of elemental sulfur after five hours. Freshly prepared $(NH_4)_2S_5$ should give a clear solution in 5% ammonium hydroxide.

SYNONYM:

Diammonium pentasulfane.

PROPERTIES:

Yellow to orange-yellow crystals; very easily decomposed to NH_3, H_2S and S. Melts in a sealed tube at 95°C to form a red liquid; decomposes on heating in an open tube. Rapidly precipitates S with water; soluble in ammonium hydroxide (see above).

REFERENCE:

H. Mills and P. L. Robinson, J. Chem. Soc. (London) 1928, 2326.

Dichloromonosulfane

SCl_2

I.

$$\underset{32.07}{S} + \underset{70.91}{Cl_2} = \underset{102.98}{SCl_2}$$

Coarsely ground roll sulfur (200 g.) is placed in a one-liter, round-bottom, ground glass flask equipped with a side arm serving as gas inlet. A reflux condenser is set in the ground joint and a thermometer is fastened in such a way that it protrudes from the flask into the lower part of the condenser. From the upper end of the condenser an outlet tube leads to the hood through a wash bottle containing H_2SO_4. A fast stream of carefully dried Cl_2 gas is passed through the S until the contents of the flask have completely liquefied, forming crude S_2Cl_2 (heat is evolved). Then a spatula tip (about 0.1 g.) of Fe powder or anhydrous $FeCl_2$ or $FeCl_3$ is added and the gas flow is continued for another 0.5 hour; during this time the reaction mixture is gradually cooled to 20°C by immersing the flask in water. The dark red liquid which forms, and which contains S_2Cl_2 and Cl_2 in addition to the SCl_2, is left to stand for about one hour. Then 2 ml. of PCl_3 is added and the solution is distilled through a small fractionating column. The middle fraction boiling between 55 and 62°C is collected in a receiver containing a few drops of PCl_3 and is again fractionated. A very pure product with a constant boiling point of 60°C is obtained. The yield is about 70%.

The substance is stable for a few days when stored in glass vessels in the presence of a few drops of PCl_3. Pure SCl_2 can always be recovered from the mixtures with S_2Cl_2 and Cl_2 that form on prolonged standing by distillation with PCl_3.

II.

$$\underset{135.04}{S_2Cl_2} + \underset{70.91}{Cl_2} = \underset{205.95}{2\,SCl_2}$$

The substance can also be prepared starting directly with S_2Cl_2. Otherwise, the procedure is the same as in method I.

SYNONYM:

Sulfur dichloride.

PROPERTIES:

Dark-red liquid with a pungent, chlorinelike odor; it decomposes readily, reversing reaction II, to form S_2Cl_2 and Cl_2; sensitive to atmospheric moisture. M.p. −121°C, b.p. +59.6°C; d (20°C) 1.621.

Reacts with water with precipitation of sulfur and formation of $H_2S_2O_3$, $H_2S_nO_6$ and H_2SO_4; soluble in n-hexane without decomposition.

REFERENCES:

H. Jonas and H. Stöhr, unpublished, private communication.
See also Naturforschung und Medizin in Deutschland 1939-1946 (FIAT-Review), 23, 191.

Dichlorodisulfane

S_2Cl_2

$$\underset{64.13}{2\,S} + \underset{70.91}{Cl_2} = \underset{135.04}{S_2Cl_2}$$

Sulfur is melted in a flask equipped with a side arm and a neck elongated into a gradually narrowing tube. By tilting the flask, the walls are coated with a uniform layer of sulfur melt. After cooling, the flask is mounted vertically in such a way that the tube end passes through a rubber stopper into another flask below. From the latter, a gas outlet tube passes through a drying tube directly to the hood. A moderately rapid stream of carefully dried Cl_2 is introduced through the side arm of the top flask and the walls of that flask are simultaneously heated to 50-80°C by fanning with a flame. Once the reaction is in progress, the S_2Cl_2 product flows into the lower flask in a rapid succession of drops. The orange-red substance is still contaminated by dissolved starting materials. Some sulfur is added and it is distilled at atmospheric pressure. The portion which distills above 137°C is refractionated over sulfur at about 12 mm. in an apparatus with ground glass joints; b.p. of the pure product is 29-30°C at this pressure.

This material is used on a large scale in industry as a solvent for sulfur in the vulcanization of rubber.

SYNONYMS:

Disulfur dichloride; older designations "sulfurous chloride" and "sulfur monochloride."

PROPERTIES:

Golden yellow, oily liquid; when less pure, orange to reddish because of SCl_2 impurities; fumes in moist air, unpleasant pungent odor. M.p. −77°C, b.p. (760 mm.) +138°C; d (20°C) 1.6773.

Hydrolyzes with water to form HCl, SO_2 and H_2S; these then convert to S, $H_2S_2O_3$ and $H_2S_nO_6$. Readily soluble in CS_2.

REFERENCE:

Abegg, Handbuch der anorganischen Chemie, Vol. IV, 1, p. 287.

Dichlorotri-, -tetra-, -tenta-, -hexa-, -hepta- and -octasulfane

S_3Cl_2, S_4Cl_2, S_5Cl_2, S_6Cl_2, S_7Cl_2, S_8Cl_2

If the ratios of the reactants are reversed, then the general synthetic method used in the preparation of the sulfanes (p. 353) can also be used for the preparation of the chlorosulfanes. The sulfane component is added to an excess of chlorosulfane at low temperature and after the reaction

$$(a-2)\,Cl_2S_n + Cl{-}S_n{-}\boxed{Cl + H}{-}S_m{-}\boxed{H + Cl}{-}S_n{-}Cl$$
$$= Cl_2S_{2n+m} + 2\,HCl + (a-2)\,Cl_2S_n$$
$$(n = 1, 2;\ m = 1, 2, 3, 4, 5, 6).$$

is complete, excess chlorosulfane $(a - 2)Cl_2S_n$ is distilled off.

With suitable choice of reactants and careful following of element. With the nonmetallic elements, the halogen compound is likely to be a low-melting solid or liquid with few of the characteristics of a salt; they are decomposed by water, undergoing extensive or complete hydrolysis. As a consequence, they fume strongly in moist air. The liquid representatives of the class usually have a high density and refractive index. The easily volatile haloids can be prepared by conducting a stream of the gaseous halogen element over the other element, and as a rule very little heating is required to bring about this action. The halogen compounds of carbon are exceptional in their chemical stability.

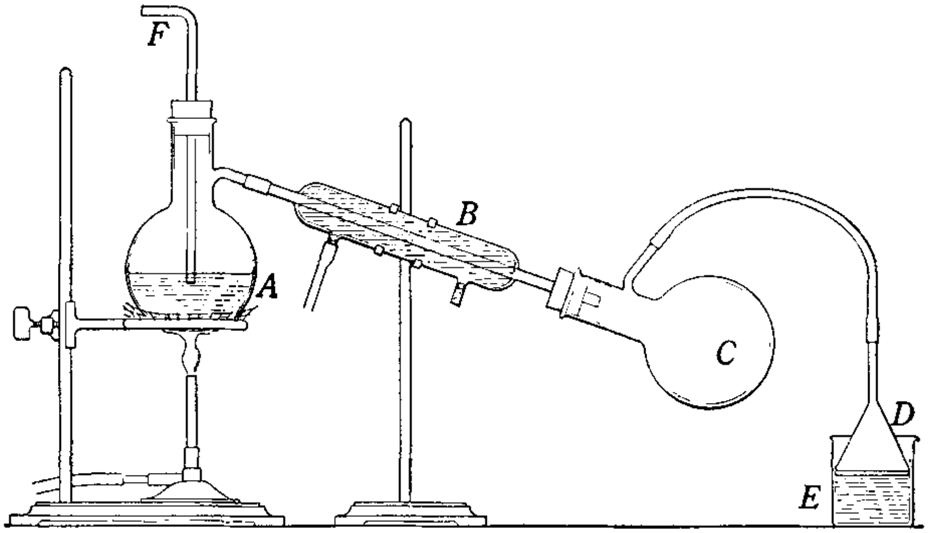

FIG. 12.—Preparation of volatile chlorides.

EXERCISE 26. SULFUR MONOCHLORIDE, S_2Cl_2; PHOSPHORUS TRICHLORIDE, PCl_3; STANNIC CHLORIDE, $SnCl_4$

The following directions will serve for the preparation of the chloride of sulfur (S_2Cl_2), phosphorus (PCl_3); or tin ($SnCl_4$). All of the apparatus used must be entirely dry. Place about 25 g. of sulfur, phosphorus, or mossy tin in a 200-cc. distilling flask *A* (Fig. 12), connected with a good condenser *B*. Fit another distilling flask *C* to the condenser to act as a receiver, making a tight connection with a cork. To absorb the excess of chlorine, connect a funnel *D* of about 8 cm. diameter by its stem to the exit tube of the second distilling flask and dip the rim of the funnel *just under* the surface of the concentrated solution of sodium hydroxide contained in a good-sized beaker *E*. This arrangement avoids back pressure and provides good absorption. It is better than a wash bottle. If phosphorus is used, the white modification should be cut into pieces small enough to slip down the neck of the flask easily. The cutting should be done under water in a roomy evaporating dish, each piece being picked up with tongs, dried with filter paper, and dropped into the flask *A*, the greatest care being exercised not to touch the phosphorus while it is out of the water. Provide a well-fitting stopper for the distilling flask, arranging a right-angled tube *F* to pass through the stopper and reach to just above the material in the flask. Pass *dry* chlorine into the flask through this tube, at the same time heating the sulfur to a point somewhat above its melting point but applying no heat to the phosphorus or tin. Keep the end of the tube *F* just above the surface of the material in the flask. Most of the sulfur monochloride will distill over into the receiver as it is formed, while the phosphorus chloride and the tin tetrachloride will to a large extent remain in the flask. When the reaction is complete, heat the flask and distill the liquid into the receiving flask *C*. Clean and dry the flask *A*, reverse the position of flasks *A* and *C*, and redistill, saving the portion which comes within 5° of the proper boiling point. The product should be poured into a dry bottle, and the stopper sealed with sealing wax.

The dry chlorine used in these preparations may be obtained in either of several ways: (1) It may be drawn directly from a tank of liquid chlorine. (2) Carefully place about 500 g. of rather coarse pyrolusite in a round-bottomed flask of about 1,500 cc. capacity and pour on it a liter of commercial (concentrated) hydrochloric acid. Provide the flask with a safety thistle tube, dipping into the liquid. Place the flask on a sand bath, taking care first to rotate the flask until all of the pyrolusite has become wet with the acid. Fill a gas-washing flask half full of sulfuric acid and pass the chlorine through the acid and then into the distilling flask containing the sulfur. Regulate the evolution of chlorine by a very small flame placed under the sand bath. (3) Instead of the pyrolusite, solid potassium permanganate (200 g.) may be placed in the flask, and the hydrochloric acid may be added drop by drop from a dropping funnel used instead of the thistle tube. This costs a little more but is under much better control.

References: (S_2Cl_2) Friend, VII (II), 76; Mellor, X, 633; Mann, Pope, and Vernon, *J. Chem. Soc.*, **119**, 636 (1921). (PCl_3) Mellor, VIII, 999; ($SnCl_4$) Friend, V, 346; Mellor, VII, 436; Lorenz, *Z. anorg. Chem.*, **10**, 44 (1895).

Additional Exercises: Phosphorus bromide, PBr_3; antimony chloride, $SbCl_3$.

2. Double Decomposition.—Many binary compounds may be regarded as salts of definite binary acids as well as compounds formed by the union of two elements. Among such compounds are the metallic halides, sulfides, selenides, tellurides, and peroxides. Many salts of these acids may be made by neutralizing a soluble base with the appropriate acid; a much larger number may be made by the method of double decomposition (Exercise 15).

EXERCISE 27. STANNOUS SULFIDE, SnS

The method is based upon the precipitation of a solution of a stannous salt by hydrogen sulfide. The most available stannous salt is the chloride, which may existence of *sulphur subchlorides*, probably S_4Cl_2 and S_3Cl_2. When a mixture of sulphur and sulphur monochloride is dissolved in bromoform, the lowering of the freezing-point is less than the sum of the depressions produced by the two solutes separately.[1] This is apparently due to the presence of sulphur subchlorides in equilibrium with their components. Moreover, the composition of a saturated solution of sulphur in sulphur monochloride corresponds approximately with the formula S_4Cl_2, and a study of the boiling-points of solutions containing increasing concentrations of sulphur in the monochloride suggests that such reactions as the following may occur:[2]

$$S_8+8S_2Cl_2 \rightleftharpoons 8S_3Cl_2,$$

and

$$S_8+4S_2Cl_2 \rightleftharpoons 4S_4Cl_2,$$

the latter reaction predominating when the sulphur concentration is high. The solubility of the sulphur at any given temperature is increased by previously heating the solution to a higher temperature, the increase being greater the higher the temperature of preheating.[3]

Sulphur Monochloride or **Disulphur Dichloride, S_2Cl_2,** the initial product of the combination of sulphur and chlorine, was first thoroughly studied in 1810 by Davy and Buchholz, independently.

Preparation.—Sulphur and chlorine interact slowly at the ordinary temperature but much more readily on warming. The customary procedure is to pass dried chlorine into fused sulphur or over dry "flowers of sulphur" until most of the sulphur has disappeared. The resulting monochloride contains considerable amounts of higher sulphur chlorides in solution, but if the mixture is heated for some time under a reflux condenser the pure monochloride can subsequently be distilled over.

Industrially, much sulphur monochloride is obtained as a by-product in the manufacture of carbon tetrachloride by the action of chlorine on carbon disulphide in the presence of a suitable catalyst, *e.g.* iodine:[4]

$$CS_2+3Cl_2=CCl_4+S_2Cl_2.$$

Various other processes can be made to yield sulphur monochloride. The distillation of sulphur with stannous chloride or mercuric chloride yields sulphur monochloride and, indeed, may be regarded as a modification of the method first given. The action of phosphorus pentachloride on sulphur or on metallic sulphides and the action of chlorine on metallic sulphides form closely analogous processes, especially in view of the formation of chlorine as a dissociation product from phosphorus pentachloride. With phosphorus pentachloride the phosphorus is found finally as sulphochloride. Of other methods there may be mentioned the interaction of sulphur or of phosphorus sulphide with thionyl chloride,[5] and the action of dry chlorine on a hot or boiling solution of

[1] Bruni and Amadori, *Atti R. Accad. Lincei*, 1919, [v.], 28, i., 217.

[2] Ruff and Golla, *Zeitsch. anorg. Chem.*, 1924, 138, 33. See also Bruni, *ibid.*, 1925, 149, 387; Trautz and others, *Zeitsch. Elektrochem.*, 1929, 35, 110.

[3] Hammick and Zvegintzov, *J. Chem. Soc.*, 1928, p. 1785; Aten, *Zeitsch. physikal. Chem.*, 1913, 81, 257.

[4] Weber, *Ann. Phys. Chem.*, 1866, [ii.], 128, 559.

[5] Carius, *Annalen*, 1858, 106, 331.

sulphur in sulphur dichloride [1] or on a strongly heated mixture of barium sulphate with coal, coke or hydrocarbons of high carbon content.[2]

The monochloride may be obtained in a highly purified condition by mixing a high-grade commercial sample with 1 per cent. by weight of a mixture of highly absorbent charcoal and sulphur, distilling in glass apparatus and collecting the fraction distilling above 137° C. This fraction, after addition of more charcoal and sulphur, is redistilled in a vacuum under a pressure of 28 mm., pure sulphur monochloride distilling at 41° C.[3]

Physical Properties.—Sulphur monochloride is a golden-yellow liquid which fumes in moist air; it has an unpleasant pungent odour and a hot, bitter taste. At 25° C. the density of the liquid is 1·67328; [4] the surface tension, measured at 22° C. by the capillary rise method, is 40·78; the relative viscosity at 18° C. is 1·908, and the specific heat at 22° C. is 0·22 (±2·8 per cent.).[5] The boiling-point is 138° C. and the melting-point −76° to −75° C.[6] The vapour pressure through the temperature range 0° to 138° C. is given in the following table: [7]

° C.	Vapour Pressure in mm. (P.).	° C.	Vapour Pressure in mm. (P.).	° C.	Vapour Pressure in mm. (P.).
0	3·7	50	43·0	100	257·0
10	6·4	59	60·0	110	351·5
20	10·7	70	93·0	120	469·7
31	18·6	80	135·0	130	615·2
40	28·0	90	186·4	138	760·0

The equation for the corresponding curve is:

$$\log_{10}P = 7\cdot4550 - 1880\cdot1/T \quad (T = \text{abs. temp.}),$$

from which the latent heat of evaporation is calculated to be 63·9 cals./gm. or 8626·5 cals./mol., and the molecular boiling-point elevation constant is 52·9.[8] Under the foregoing conditions sulphur monochloride is a stable, well-defined compound.

The monochloride exhibits a slight tendency to molecular dissociation,[9] but the effect is so small that both in the dissolved and in the gaseous condition the molecular weight agrees with the formula S_2Cl_2. As it does not combine with bromine, ebullioscopic determinations of

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[1] Terlinck, *French Patent*, 611141 (1925); *Chem. Zeit.*, 1927, 51, 861.

[2] *Chem. Fabr. Griesheim-Elektron*, Assees. of K. L. Gonder, *German Patent*, 417853 (1922).

[3] Harvey and Schuette, *J. Amer. Chem. Soc.*, 1926, 48, 2065.

[4] Harvey and Schuette, *loc. cit.*: Fawsitt (*J. Soc. Chem. Ind.*, 1886, 5, 638) gives the density at 0° C. as 1·706, and at 15° C. as 1·683: Kretov (*J. Chem. Ind. Moscow*, 1928, 5, 1268) gives $d_{20}^{20} = 1\cdot6824$.

[5] Trautz and others, *Zeitsch. Elektrochem.*, 1929, 35, 110.

[6] Beckmann, *Zeitsch. physikal. Chem.*, 1909, 65, 289; Frank and Marckwald, *Gummi. Zeit.*, 1914, 28, 1580; Roozeboom, *Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 63; Aten, *Zeitsch. physikal. Chem.*, 1905, 54, 55.

[7] Harvey and Schuette, *loc. cit.*; *cf.* Trautz and others, *loc. cit.*

[8] *Cf.* Orndorff and Terrasse, *Amer. Chem. J.*, 1896, 18, 173; Beckmann, *loc. cit.*

[9] Besson and Fournier, *Compt. rend.*, 1910, 150, 1752.

the molecular weight have been made in this solvent, and also even in liquid chlorine (see p. 81).

The compound is exothermic:[1]

$$S_2(\text{rhombic}) + Cl_2(\text{gas}) = S_2Cl_2(\text{liquid}) + 14{,}260 \text{ calories.}$$

Sulphur monochloride is soluble in many organic solvents, *e.g.* carbon disulphide, benzene, carbon tetrachloride and light petroleum; it also possesses solvent properties, dissolving sulphur very readily on warming and slowly depositing much of the solid on cooling; the molecular heat of solution of sulphur in sulphur monochloride is from −1300 to −3000 calories (see p. 76).[2] Chlorine, bromine and iodine are also dissolved, the two latter without chemical change; with chlorine, however, combination occurs readily at the ordinary temperature, although at the boiling-point of liquid chlorine simple solution occurs primarily (see before and p. 81). The heat of solution of chlorine in sulphur monochloride is shown in the following equations:[3]

$$S_2Cl_2(\text{liq.}) + Cl_2(\text{gas}) = 2SCl_2(\text{dissolved in } S_2Cl_2) + 9800 \pm 400 \text{ calories,}$$

and

$$S_2Cl_2(\text{liq.}) + 3Cl_2(\text{gas}) = 2SCl_4(\text{dissolved in mixture of } S_2Cl_2 \text{ and } SCl_2) + 12{,}000 \text{ to } 14{,}000 \text{ calories.}$$

Chemical Properties.—Sulphur monochloride will not burn under ordinary conditions in the air, but when passed through a red-hot tube in the vapour condition and mixed with air or oxygen, combustion occurs, accompanied by a greenish-blue flame and the formation of sulphur dioxide and trioxide, together with chlorine. In contact with water the monochloride undergoes decomposition according to the equation:[4]

$$S_2Cl_2 + 2H_2O = H_2S + 2HCl + SO_2.$$

Even in the presence of a large excess of water decomposition only proceeds to the extent of 93·68 per cent., being partly restrained by the presence of the hydrogen chloride formed. The other factor which influences the extent of the action is the sulphur formed by subsequent reaction between the hydrogen sulphide and the sulphur dioxide. Polythionic acids are formed in solution and the sulphur which separates encloses undecomposed chloride and may also dissolve in it.[5]

With phosphorus the reaction products vary according to the conditions. In the presence of an excess of monochloride, phosphorus sulphochloride and free sulphur are obtained, whereas if the monochloride is introduced into an excess of molten phosphorus, the products are the trichloride and sulphide of phosphorus, some red phosphorus also being formed.[6]

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[1] Thomsen, *Thermochemische Untersuchungen*, 1906, p. 188; Ogier, *Compt. rend.*, 1881, 92, 922. Trautz and his coworkers (*loc. cit.*) give 14·5±0·4 Cals.

[2] See also Beckmann, *Zeitsch. physikal. Chem.*, 1909, 65, 289.

[3] Trautz and others, *loc. cit.*

[4] Carius, *Annalen*, 1858, 106, 291; Olin, *J. Amer. Chem. Soc.*, 1926, 48, 167.

[5] Neumann and Fuchs, *Zeitsch. angew Chem.*, 1925, 38, 277; Noack, *Zeitsch. anorg. Chem.*, 1925, 146, 239.

[6] de Claubry, *Ann. Chim. Phys.*, 1843, [iii.], 7, 213; Wohler, *Annalen*, 1855, 93, 274; *Ann. Chim. Phys.*, 1855, [iii.], 44, 56; Chevrier, *Compt. rend.*, 1867, 64, 302; Michaelis, *Bull. Soc. chim.*, 1871, 15, 185.

With regard to the general reaction of sulphur monochloride with metals, Domanicki[1] has stated that univalent metals do not react, and bivalent metals, with the exception of mercury, if they react at all, do so with much greater difficulty than ter- or quadri-valent metals. There are other important exceptions to this rule, however; silver is slightly attacked by the monochloride, whilst copper and manganese are very considerably attacked. On the other hand, cobalt and chromium are unaffected, and it has been suggested that drums made of alloy or plated steel provide suitable containers for sulphur monochloride.[2] The corrosive action is greatly accelerated by the presence of dry ether, with which the metallic chlorides form complexes, thus enhancing the thermal effect of the action.

Many metallic oxides, especially those yielding volatile chlorides, are attacked by the vapour of sulphur monochloride, and the reaction forms a useful method for the conversion of such oxides into the corresponding anhydrous chlorides.[3] Assuming a bivalent metal M, the change is:

$$2MO+2S_2Cl_2=2MCl_2+SO_2+3S.$$

Such treatment can be extended to mineral substances, some of which at 800° C. under the action of sulphur monochloride vapour are easily convertible into the corresponding metallic chlorides.[4]

Sulphur trioxide and sulphur monochloride react to give pyrosulphuryl chloride, $S_2O_5Cl_2$, whilst sulphates when heated in the monochloride vapour are converted into chlorides[5] in the following manner:

$$Na_2SO_4+2S_2Cl_2=SO_2Cl_2+2NaCl+SO_2+3S.$$

Under the influence of the silent discharge sulphur monochloride vapour is reduced by hydrogen to hydrogen chloride and sulphur or hydrogen sulphide.[6] Hydriodic acid effects a similar reduction[7] at the ordinary temperature, the products being hydrochloric acid, sulphur and hydrogen sulphide, together with iodine.

Phosphorus trichloride reacts with sulphur monochloride, iodine acting as a catalyst; the products are phosphorus pentachloride and phosphorus sulphochloride:[8]

$$3PCl_3+S_2Cl_2=PCl_5+2PSCl_3.$$

Antimony pentachloride reacts to form the compound $SbCl_5.SCl_4$, which may be obtained as amber-coloured crystals.[9]

When an ice-cold solution of ammonia in chloroform is added to

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[1] Domanicki, *J. Russ. Phys. Chem. Soc.*, 1916, 48, 1724.

[2] Harvey, *Chem. Met. Eng.*, 1928, 35, 684.

[3] Bourion, *Ann. Chim. Phys.*, 1910, [viii.], 21, 56; *Compt. rend.*, 1907, 145, 62; 1909, 148, 170; Hicks, *J. Amer. Chem. Soc.*, 1911, 35, 1492.

[4] E. F. Smith, *J. Amer. Chem. Soc.*, 1898, 20, 289; Hall, *ibid.*, 1904, 26, 1243; Hicks, *ibid.*, 1911, 33, 1492; Lukens, *ibid.*, 1913, 35, 1464; Serra, *Gazzetta*, 1899, 29, 355; Oddo and Giachery, *ibid.*, 1923, 53, i., 63; Bourion, *Ann. Chim. Phys.*, 1910, 20, 547; Budnikov and Schilov, *Chem. Zentr.*, 1925, ii., 388.

[5] Carius, *Annalen*, 1858, 106, 291.

[6] Besson and Fournier, *loc. cit.*

[7] [illegible]

a solution of sulphur monochloride in the same solvent, sulphides of nitrogen are formed, the primary reaction being :[1]

$$6S_2Cl_2+16NH_3=N_4S_4+12NH_4Cl+8S.$$

The tetrasulphide may be precipitated by the addition of alcohol, and by concentration of the mother-liquor the pentasulphide, N_2S_5, and the hexasulphamide, S_6NH_2, may be obtained.

Sulphur monochloride reacts vigorously with many organic compounds, generally exerting a chlorinating or a sulphurating action.[2] Thus it converts ethyl alcohol into ethyl chloride,[3] aniline into dithiophenylamine,[4] and anthracene into 9-anthryldithiochloride, $C_{14}H_9S_2Cl$.[5] Even ether is slowly decomposed by sulphur monochloride.[6] The sodium salts of the fatty acids are converted into their corresponding acid chlorides.[7]

The purity of a sample of sulphur monochloride may be determined by heating with aqueous sodium hydroxide (2*N*) for four hours in a long-necked flask on a water-bath and, after cooling, adding a few c.c. of 30 per cent. hydrogen peroxide. The mixture is then reheated for not more than half an hour, slightly acidified with nitric acid, and diluted to a known volume. The chlorine may then be estimated volumetrically and the sulphur gravimetrically in aliquot portions.[8]

Sulphur monochloride is extensively used in the vulcanisation of caoutchouc at the ordinary temperature by a process discovered by Parkes ;[9] the chemical reaction appears to involve merely the addition of sulphur chloride to an unsaturated hydrocarbon.[10] A similar reaction is involved in the manufacture of "mustard gas," dichlorodiethylsulphide, from ethylene and sulphur monochloride :

$$2C_2H_4+S_2Cl_2=S(C_2H_4Cl)_2+S.$$

The monochloride is also employed in the manufacture of carbon tetrachloride and certain anhydrous inorganic chlorides. Its use has also been suggested in the refining of sugar.

Constitution.—Although the structure $S : SCl_2$ is possible for sulphur monochloride,[11] there appears to be little real evidence[12] in confirmation

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[1] Macbeth and Graham, *Proc. Roy. Irish Acad.*, 1923, 36, 31.

[2] Carius, *loc. cit.* ; Guthrie, *Annalen*, 1859, 113, 266 ; Bottger, *ibid.*, 1884, 223, 346 ; Holmberg, *ibid.*, 1909, 359, 181 ; Klason, *Ber.*, 1887, 20, 2376 ; Edinger and Goldberg, *ibid.*, 1900, 33, 2875, 2883 ; Ferrario, *Bull. Soc. chim.*, 1910, [iv.], 7, 518 ; Silberrad, Silberrad and Parke, *Trans. Chem. Soc.*, 1925, 127, 1724. For the action of sulphur monochloride on aromatic amines, see Cassella & Co., *German Patent*, 370854 (1923) ; *Chem. Zentr.*, 1923, iv., 538 ; on acid amides, see Naik and Patel, *J. Indian Chem. Soc.*, 1924, 1, 27 ; Naik and Bhat, *ibid.*, 1927, 4, 525 ; Naik, *Trans. Chem. Soc.*, 1921, 119, 1166 ; on mercaptans and thioamides, see Chakravarti, *ibid.*, 1923, 123, 964 ; Ishikawa, *Sci. Papers Inst. Phys. Chem. Res.*, 1925, 3, 147 ; on hydrocarbons, see Lorand, *Ind. Eng. Chem.*, 1927, 19, 733.

[3] Carius, *loc. cit.* ; Ebelmen and Bouguet, *Ann. Chim. Phys.*, 1846, [3], 17, 65.

[4] Coffey, *Rec. Trav. chim.*, 1921, 40, 747.

[5] Friedlander and Simon, *Ber.*, 1922, 55, [B], 3969.

[6] Dumas, *Ann. Chim. Phys.*, 1825, [2], 49, 204.

[7] Denham and Woodhouse, *Trans. Chem. Soc.*, 1909, 95, 1235 ; 1913, 103, 1861 ; Hewitt and Lumsden, *J. Soc. Chem. Ind.*, 1916, 35, 210.

[8] Kretov, *J. Chem. Ind. Moscow*, 1928, 5, 1268.

[9] Parkes, *British Patent*, 11147 (1846).

[10] Guthrie, *Annalen*, 1860, 113, 270.

[11] Henriques, *Ber.*, 1894, 27, 2993 ; Lippmann and Pollak, *ibid.*, 1901, 34, 2767.

[12] The reactions of the double compound $AlCl_3.2S_2Cl_2$ appear to favour the unsymmetrical formula ; see Ruff and Golla, *Zeitsch. anorg. Chem.*, 1924, 138, 17.

of such an analogy with thionyl chloride, $O : SCl_2$. The relation of sulphur monochloride to the other chlorides of sulphur, and the fact that in its interaction with organo-magnesium compounds products are obtainable which are known definitely to have the constitution R·S·S·R,[1] where R represents an organic radical, are entirely in support of a structure Cl·S·S·Cl, analogous to the probable structure of hydrogen disulphide.

Trisulphur Tetrachloride, S_3Cl_4.—That this chloride is capable of existence has recently been demonstrated (see p. 74).

Sulphur Dichloride, SCl_2.—As explained already, the existence of this substance has been the subject of much controversy, the view held by some chemists [2] being that the liquid described by others [3] as sulphur dichloride is in reality a mixture of the monochloride with the tetrachloride or with chlorine. A difficulty encountered in the characterisation of such a substance is that molecular weight determinations with the gaseous or dissolved substance do not distinguish between SCl_2 molecules and a mixture of S_2Cl_2 and Cl_2 molecules in equal numbers [4] (see the following, however).

The freezing-point curves [5] for mixtures of sulphur monochloride and chlorine containing up to 92 per cent. of total chlorine, as obtained by earlier workers, supplied no evidence of the existence of sulphur dichloride, the only maxima on the curve being found at $-80°$ C. for a composition corresponding with sulphur monochloride, S_2Cl_2, and at $-30{\cdot}5°$ C. for the composition of sulphur tetrachloride, SCl_4; some indication of a more highly chlorinated derivative such as SCl_{11} was observable, but there was no suggestion of the existence of SCl_2. This result, of course, did not exclude the possibility of the existence of a compound SCl_2, or its formation from sulphur monochloride and sulphur at higher temperatures.

Beckmann in 1906, however, by the artifice of employing liquid chlorine as an ebullioscopic solvent,[6] found indication of the existence of SCl_2 molecules; with this solvent a mixture of S_2Cl_2 and Cl_2 molecules will not produce the same effect as simple SCl_2 molecules.

In 1927, Lowry succeeded in freezing out some sulphur dichloride from an over-chlorinated equilibrium mixture having its composition adjusted to that of SCl_2 by addition of the monochloride. The product was recrystallised from light petroleum, and upon analysis yielded the empirical formula SCl_2.

An equilibrium mixture of composition corresponding to SCl_2 is most easily prepared by allowing a solution of sulphur monochloride in liquid chlorine to warm to the ordinary temperature; [7] a modification

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[1] Strecker, *Ber.*, 1910, 43, 1131; Boeseken, *Rec. Trav. chim.*, 1911, 30, 116; 1905, 24, 209.

[2] Carius, *Annalen*, 1858, 106, 291; 1859, 110, 209; Chevrier, *Compt. rend.*, 1866, 63, 1003; 1867, 64, 302; Rose, *Ann. Phys. Chem.*, 1837, [ii.], 42, 517; Isambert, *Compt. rend.*, 1878, 86, 664.

[3] Costa, *Atti R. Accad. Lincei*, 1890, 6, 408; Dalziel and Thorpe, *Chem. News*, 1871, 24, 159; Michaelis and Schifferdecker, *Annalen*, 1873, 170, 1; Hubner and Guéroult, *Zeitsch. Chem.*, 1870, [ii.], 6, 455.

[4] Hubner and Guéroult, *loc. cit.*; Costa, *loc. cit.*: Oddo, *Gazzetta*, 1901, [ii.], 31, 222.

[5] Ruff and Fischer, *Ber.*, 1903, 36, 418; Ruff, *ibid.*, 1904, 37, 4513.

[6] Beckmann, *Zeitsch. anorg. Chem.*, 1906, 51, 96. *Zeitsch. physikal. Chem.*, 1909, 65, 289; *Sitzungsber. K. Akad. Wiss. Berlin*, 1913, p. 886. See also Bergmann and Bloch, *Ber.*, 1920, 53, [B], 977.

[7] Aten, *Zeitsch. physikal. Chem.*, 1905, 54, 55.

of this process is to saturate the monochloride, cooled in a freezing mixture, with chlorine and subsequently remove excess of the latter gas by a stream of carbon dioxide. Powdered absorbent charcoal acts catalytically in facilitating the action.[1] As prepared in this way, the mixture is a deep, reddish-brown liquid, of density 1·622 at 15° C.[2] It boils at 59° C. under atmospheric pressure, and at −24° C. under 4 mm., but on account of the very considerable dissociation into monochloride and chlorine, the boiling-point is not constant. When cooled, it solidifies near −88° C. and remelts at −78° C.[3]

Sulphur dichloride is decomposed by water, giving hydrochloric and thiosulphuric acids, the latter gradually yielding sulphurous acid and sulphur. This recalls the corresponding behaviour of the monochloride, and, probably on account of the considerable dissociation, even in the liquid condition, the chemical properties of the "dichloride" are generally similar to those of the monochloride.

Sulphur Tetrachloride, SCl_4.—When a mixture of sulphur monochloride with liquid chlorine is kept in a sealed tube, slow combination ensues, with formation of sulphur tetrachloride. At ordinary temperatures the rate of combination is very slow, but it is hastened by a moderate rise in temperature.[4]

The product is a brownish-red liquid at ordinary temperatures; when cooled it exhibits in a marked manner the phenomenon of "suspended transformation," and generally does not solidify above −70° C., the yellowish-white solid obtained below this temperature melting at −30·5° C. A few degrees above the melting-point the dissociation pressure reaches one atmosphere, so that dissociation into sulphur monochloride and chlorine, probably with the production of sulphur dichloride as an intermediate stage, occurs exceedingly readily, and at the ordinary temperature the liquid contains only a small proportion of the tetrachloride, the dissociation products[5] preponderating (see the following).

Water causes immediate and almost quantitative decomposition of sulphur tetrachloride, with formation of hydrochloric and sulphurous acids, the latter standing in the same relation to sulphur tetrachloride as carbonic acid to carbon tetrachloride and silicic acid to silicon tetrachloride:

$$SCl_4+3H_2O=H_2SO_3+4HCl.$$

With anhydrous ammonia the tetrachloride reacts to form nitrogen sulphide:[6]

$$12SCl_4+16NH_3=3N_4S_4+48HCl+2N_2.$$

With an equimolecular proportion of sulphur trioxide, interaction occurs forming thionyl chloride, sulphur dioxide and chlorine:

$$SCl_4+SO_3=SOCl_2+SO_2+Cl_2,$$

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[1] Pope and Heycock, *British Patent*, 142879 (1918).

[2] Kretov (*J. Chem. Ind. Moscow*, 1928, 5, 1268) gives d_{20}^{20} 1·6222.

[3] Beckmann, *Zeitsch. physikal. Chem.*, 1909, 65, 289.

[4] Michaelis and Schifferdecker, *Ber.*, 1872, 5, 924; 1873, 6, 996; Roozeboom and Aten, *Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 599; Aten, *Zeitsch. physikal. Chem.*, 1905, 54, 55; Beckmann, *ibid.*, 1909, 65, 289; Ruff, *Ber.*, 1904, 37, 4513; Ruff and Fischer, *ibid.*, 1903, 36, 418.

[5] Beckmann, *loc. cit.*; Ruff, *loc. cit.*

[6] Ruff and Geisel, *Ber.*, 1904, 37, 1573.