CCCXLV.—*Arsenic Trichloride and Sulphur Chloride.*

By James Riddick Partington.

By the action of chlorine on arsenic trisulphide, Rose (*Pogg. Ann.*, 1837, **42**, 517) obtained a brown liquid in which the chlorine and sulphur were determined by precipitation as silver chloride and barium sulphate, respectively, from the solution in dilute nitric acid, the arsenic being obtained by difference. The results (As, 22·92; S, 13·98; Cl, 63·10%) were regarded as leading to the formula $2AsCl_3,3SCl_2$, although this seems to have been deduced from the method of preparation, thus, $As_2S_3 + 6Cl_2 = 2AsCl_3,3SCl_2$. Rose states that he was unable to prepare the substance SCl_2 itself by the method described by Dumas (*Ann. Chim. Phys.*, 1825, **49**, 204), but the supposed compound obtained by Rose has been quoted (*e.g.*, Roscoe and Schorlemmer, " A Treatise on Chemistry," Vol. 1, 1905, p. 396) as evidence of the existence of sulphur dichloride. Another supposed additive compound of sulphur dichloride, *viz.*, that with ethylene (Guthrie, *Annalen*, 1859, **113**, 266), has been shown (Gibson and Pope, J., 1920, **117**, 271) to be quite a different substance, *viz.*, ββ-dichlorodiethyl sulphide, $(CH_2Cl{\cdot}CH_2)_2S$, and the substance formed with amylene, C_5H_{10},SCl_2, probably has a similar composition, although it was described by Guthrie (*loc. cit.*) as an additive compound.

EXPERIMENTAL.

When arsenic chloride was mixed with chlorinated sulphur chloride in various proportions there was no evolution of heat, no solid separated, and the colours of the mixtures were intermediate between those of the constituents. The same result was found with sulphur monochloride. In the first case, the product was still liquid at − 20° ($AsCl_3$ solidifies at − 18°), but partly solidified at − 50°, a little orange-red liquid being still present. The mass gradually liquefied with rise of temperature, the characteristic pearly crystals of arsenic chloride being clearly visible, until at − 28° all was liquid. The product appears to be merely a mixture of the two liquids.

The arsenic chloride was prepared by a modification of the method described by Oddo and Serra (*Gazzetta*, 1899, **29**, ii, 355), who heated together arsenious oxide and sulphur chloride, in the proportion required for the reaction $2As_2O_3 + 6S_2Cl_2 = 4AsCl_3 + 3SO_2 + 9S$, under reflux and decanted the arsenic chloride from the separated sulphur. This reaction was found to proceed as described, with a good yield. It is more convenient, however, to prevent deposition of sulphur, which causes some loss of arsenic chloride in decantation, by modifying the process as follows. A larger proportion of arsenious oxide is used and a current of chlorine is passed through the mixture boiling under an effective reflux condenser, so that the separated sulphur is reconverted into chloride and afterwards eliminated as sulphur dioxide during the reaction, which may be summarised as follows: $4As_2O_3 + 3S_2Cl_2 + 9Cl_2 = 8AsCl_3 + 6SO_2$. If this proportion of arsenious oxide and sulphur chloride is taken initially, the reaction is rather violent and there is a tendency for a crust to form on the flask, leading to fracture. Two-thirds of the arsenious oxide are added first, and when the reaction has proceeded the further third is added, the current of chlorine being maintained. The whole of the sulphur disappears, and the arsenious oxide is converted into arsenic chloride, which may be distilled off directly and does not require purification.

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