LIV.—*On the Preparation of Metallic Chlorides.*

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THE two principal processes for the preparation of chlorides in the dry way consist in (1), passing chlorine over the heated metal; and (2), passing chlorine over a mixture of the oxide with charcoal. The first is usually troublesome, on account of the difficulty attending the preparation of many of the metals; and the second, on account of the fine state of division to which it is necessary to reduce the oxide, if it is desired to obtain any considerable portion of the metal in the state of chloride. This being the case, it appeared advisable to find some more convenient process, and carbon tetrachloride seemed likely to afford a means for the preparation of metallic chlorides, and more especially of the higher chlorides.

The first experiment tried was with stannic oxide. The anhydrous oxide was placed in a long porcelain tube, connected at one end with a small retort, in which the carbon tetrachloride was kept in a state of gentle ebullition, and at the other with a cooled receiver. When the tube was heated to bright redness, and the vapour of carbon tetrachloride passed slowly over the oxide of tin, a liquid soon began to collect in the receiver, accompanied by a small quantity of a yellowish solid, either oxychloride or hydrated chloride of tin. Carbonic acid and chlorine escaped from the receiver (the chlorine being derived from the decomposition of some of the carbon tetrachloride), and a small quantity of stannous chloride was deposited in the cooler parts of the tube.

When the contents of the receiver were fractionally distilled, a small

portion came over at about 80° , consisting for the most part of carbon tetrachloride, and the principal portion of the liquid distilled over at 118 — 120° , the boiling-point of stannic chloride; it fumed strongly in the air, and united violently with water, forming a solution of stannic chloride. The product amounted to about 40 per cent. of the tetrachloride used. A small quantity of solid product was left in the distillation flask, subliming in white needles, and consisting of carbon monochloride, C_2Cl_2 .

The next oxide used was titanitic acid, the experiment being conducted in precisely the same way as with stannic oxide. The titanitic acid was introduced into the tube in lumps, about the size of buck-shot. The product amounted to about 50 per cent. of the tetrachloride used; it was accompanied by a small quantity of ferric chloride. The residue in the tube consisted of unaltered titanitic acid, and of skeletons of the lumps of titanitic acid, consisting probably of silica. Similar experiments were tried with silica, both precipitated (from SiF_4) and well-burnt black flint. The tube, about 30 inches long, was heated nearly to whiteness, but in both cases only the merest traces of silicon chloride were obtained, even with the most efficient condensing arrangement.

Tungstic acid and carbon tetrachloride gave a mixture of WCl_4O , and WCl_2O_2 , the principal reaction being probably expressed by the equation—

A similar experiment with chloroform and titanitic acid gave a quantity of titanitic chloride, equal to about 30 per cent. of the chloroform used. A large quantity of secondary product was obtained, consisting of titanium oxychloride, chlorides of carbon, &c.; a notable proportion of the titanitic chloride was also carried off by the gases, hydrochloric and carbonic acids, produced in the reaction. The formation of titanous chloride was not noticed.

Carbon tetrachloride being somewhat expensive, and a notable proportion being always lost, a mixture, in equal volumes, of carbonic oxide and chlorine was tried as a means of producing these chlorides. With titanitic acid a very good result was obtained, although some quantity of the titanitic chloride was carried off by the carbonic acid produced, which has double the volume produced with carbon tetrachloride: $TiO_2 + 2CO + 2Cl_2 = TiCl_4 + 2CO_2$. Silica again was hardly acted on. Tungstic acid gave a mixture of the two oxychlorides, but when a larger proportion of carbonic oxide was used, a small quantity of nearly black crystalline chloride (WCl_6 or WCl_5) was obtained. 5 grams of tungstic acid placed in a small porcelain tube and heated to full redness, was entirely volatilised as oxychloride after

about 3 litres of gas had been passed over it. Amorphous chromic oxide was acted on with great readiness, the crystalline oxide not quite so easily; in both cases, however, an abundant production of chromic chloride resulted, which, when the tube was heated a few inches beyond the oxide, was non-deliquescent, and completely insoluble in water, showing the absence of any chromous chloride.

Red oxide of manganese, Mn_2O_3 , free from iron, was acted on very easily, but the chloride being non-volatile, it could not be perfectly separated from the unaltered oxide. A very small quantity of apparently colourless crystals, containing manganese and chlorine, sublimed to the mouth of the tube at the beginning of the experiment, but the amount was too small for further examination.

A similar experiment was tried with bromine, carbonic oxide, and stannic oxide. The dry carbonic oxide was bubbled through bromine kept warm in a small retort, and covered with strong sulphuric acid to prevent surface evaporation. Stannic bromide volatilised into the receiver, and some stannous bromide was left in the tube.

In all these experiments the carbonic oxide was previously prepared, and stored in a gasometer. Experiments were made in which a mixture of 1 vol. carbonic acid with 2 vols. chlorine, was passed through a tube, three parts filled with carbon, and the rest with oxide, separated from one another by a plug of asbestos. Both wood-charcoal and coke were found very wasteful of chlorine, on account of the hydrogen they contain; and with gas-carbon, although carbonic acid alone was easily converted into carbonic oxide, the mixture of chlorine and carbonic acid passed through almost unchanged.

These experiments were made in the Laboratory of University College. The authors intend pursuing the subject, more especially with regard to the higher chlorides.